

# MOLE-CONCEPT

## 1. The Mole

In 1971, the General conference on weights and measures, adopted mole as the seventh basic SI unit of the amount of a substance.

The term 'mole' is a Latin word which means heap or pile. A mole of atom is a collection of atoms whose total weight is equal to the gram atomic weight. As equal number of moles of different elements contain equal number of atoms, it is very easy to express the amount of a substance in terms of moles. Just as a dozen means twelve objects, in the similar fashion, a mole is a collection of a 'definite number' of particles, viz., atoms, molecules, ions or electrons. This 'definite number' is called Avogadro number which is equal to  $6.023 \times 10^{23}$ . Thus, a mole can be defined as, "the amount of a substance containing as many atoms, molecules, ions, electrons or other elementary entities as there are carbon atoms in exactly 12g of C-12".

Now-a-days, *gram-molecules and gram-atom are termed as a mole of molecules and a mole of atoms respectively, e.g., 1 gram-molecule of chlorine and 1 gram atom of chlorine are expressed as 1 mole of  $Cl_2$  and 1 mole of Cl respectively.*

The number of moles can be calculated by a number of formulae depending upon the data given :

$$\begin{aligned} \text{No. of moles of molecules} &= \frac{\text{Wt. of substance in g}}{\text{Mol. wt. of substance}} \\ \text{No. of moles of atoms} &= \frac{\text{Wt. of element in g}}{\text{At. wt. of the element}} \\ \text{No. of moles of gas} &= \frac{\text{Volume of the gas at STP}}{\text{Standard molar volume (i.e. 22.4L)}} \end{aligned}$$

### Illustration 1.

**How many years it would take to spend Avogadro's number of rupees at the rate of 10 lac rupees per second?**

### Solution :

$$\begin{aligned} \text{Total rupees to be expended} &= 6.023 \times 10^{23} \\ \text{Rupees spent per second} &= 10^6 \\ \text{Rupees spent per year} &= 10^6 \times 60 \times 60 \times 24 \times 365 \\ \square \quad 10^6 \times 60 \times 60 \times 24 \times 365 \text{ Rupees are spent in 1 year} \\ \therefore 6.023 \times 10^{23} \quad \text{“} \quad \text{“} &= \frac{6.023 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365} \\ &= 1.9099 \times 10^{10} \text{ year} \end{aligned}$$

### Illustration 2.

From 200 mg of  $\text{CO}_2$ ,  $10^{21}$  molecules are removed. How many g and mole of  $\text{CO}_2$  are left?

**Solution :**

$$\square \quad 6.023 \times 10^{23} \text{ molecules of } \text{CO}_2 = 44 \text{ g}$$

$$10^{21} \text{ molecules of } \text{CO}_2 = \frac{44 \times 10^{21}}{6.023 \times 10^{23}} = 7.31 \times 10^{-2} \text{ g} = 73.1 \text{ mg}$$

$$\therefore \text{CO}_2 \text{ left} = 200 - 73.1 = \mathbf{126.9 \text{ mg}}$$

$$\text{Also mole of } \text{CO}_2 \text{ left} = \frac{\text{wt.}}{\text{m.wt.}} = \frac{126.9 \times 10^{-3}}{44} = \mathbf{2.88 \times 10^{-3}}$$

## 2. Oxidation Number or Oxidation State

Oxidation state of an element in a particular species (atoms, molecules or ions) is the number of electrons gained or lost by that element during its change from free state into that species. For example, the oxidation state of Na in NaCl is +1, of calcium in  $\text{Ca}_3(\text{PO}_4)_2$  is +2, of chlorine in  $\text{Cl}_2$  is zero.

- (1) Oxidation no. is given positive sign if electrons are lost. oxidation no. is given negative sign if electrons are gained.
- (2) Oxidation no. represents real charge in case of ionic compounds. However, in covalent compounds it represents imaginary charge.

## Rules For Calculation Of Oxidation Number

Following rules have been arbitrarily adopted to decide oxidation no. of elements on the basis of their periodic properties.

1. In uncombined state or free state, oxidation number of an element is zero.
2. In combined state oxidation no. of
  - (a) F is always -1.
  - (b) O is -2. In peroxides it is -1, in superoxides it is -1/2. However in  $\text{F}_2\text{O}$  it is +2.
  - (c) H is +1. In ionic hydrides it is -1 (i.e., IA, IIA and IIIA metals).
  - (d) halogens as halide is always -1.
  - (e) sulphur as sulphide is always -2.
  - (f) metals is always +ve.
  - (g) alkali metals (i.e., I A group — Li, Na, K, Rb, Cs, Fr) is always +1.
  - (h) alkaline earth metals (i.e., II A group—Be, Mg, Ca, Sr, Ba, Ra) is always +2.
3. The algebraic sum of the oxidation no. of all the atoms in a compound is equal to zero, e.g.  $\text{KMnO}_4$ .  

$$\text{Oxidation no. of K} + \text{Ox. no. of Mn} + (\text{Ox. no. of O}) \times 4 = 0$$

$$(+1) + (+7) + 4 \times (-2) = 0$$
4. The algebraic sum of all the oxidation no. of elements in a radical is equal to the net charge on the radical, e.g.,  $\text{CO}_3^{-2}$ .  

$$\text{Oxidation no. of C} + 3 \times (\text{Oxidation no. of O}) = -2$$

$$(+4) + 3 \times (-2) = -2$$
5. Oxidation number can be zero, +ve, -ve (integer or fraction)
6. Maximum oxidation no. of an element is = Group number (Except O and F)  
 Minimum oxidation no. of an element is = Group number - 8 (Except metals)

### Illustration 3 :

Find the oxidation number of

(a) S in  $\text{SO}_4^{2-}$  ion

(b) S in  $\text{HSO}_3^-$  ion

(c) Pt in  $(\text{PtCl}_6)^{2-}$

(d) Mn in  $(\text{MnO}_4)^-$  ion

### Solution :

(a) Let the oxidation number of S be x.

We know that Ox. no. of O = -2

So Ox. no S + 4 (Ox. no. O) = -2  $\Rightarrow x + 4(-2) = -2$

or  $x - 8 = -2 \Rightarrow x = +8 - 2 = +6$

The oxidation number of S in  $\text{SO}_4^{2-}$  ion is +6.

(b) Let the oxidation number of S be x in  $\text{HSO}_3^-$  ion.

We know that Ox. no. of H = +1

Oxidation number of O = -2

So Ox. no. H + Ox. no. S + 3 (Ox. no. O) = -1

$+1 + x + 3(-2) = -1 \Rightarrow +1 + x - 6 = -1 \Rightarrow x - 5 = -1$

or  $x = +5 - 1 = +4 \Rightarrow$  The oxidation number of S in  $\text{HSO}_3^-$  ion is +4.

(c) Let oxidation number of Pt be x. We know that Ox. no. of Cl = -1

So Ox. no. Pt + 6 (Ox. no. Cl) = -2  $\Rightarrow x + 6(-1) = -2$

or  $x - 6 = -2 \Rightarrow$  The oxidation number of Pt in  $(\text{PtCl}_6)^{2-}$  ion is +4.

(d) Let oxidation number of Mn be x. We know that Ox. no. of O = -2

So Ox. no. Mn + 4 (Ox. no. O) = -1  $\Rightarrow x + 4(-2) = -1 \Rightarrow x - 8 = -1$

or  $x = +8 - 1 = +7$ . The oxidation number of Mn in  $(\text{MnO}_4)^-$  ion is +7.

## 1. Daily Practice Problem Sheet

1. Determine the average oxidation no. of following elements given in bold letters :

(a)  $\text{H}_2\text{S}_2\text{O}_8$

(b)  $\text{K}_4\text{Fe}(\text{CN})_6$

(c)  $\text{OsO}_4$

(d)  $\text{HNC}$

(e)  $\text{Fe}_{0.94}\text{O}$

(f)  $\text{Fe}_3\text{O}_4$

(g)  $\text{NH}_2\cdot\text{NH}_2$

(h)  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

(i)  $\text{NOClO}_4$

(j)  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$

(k)  $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$

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

(m)  $(\text{CH}_3)_2\text{SO}$

(n)  $\text{Na}_2\text{S}_2$

2. Determine the oxidation number of the following elements given in bold letters :

(a)  $\text{Ba}_2\text{XeO}_6$

(b)  $\text{C}_3\text{O}_2$

(c)  $\text{V}(\text{BrO}_2)_2$

(d)  $\text{Cs}_4\text{Na}(\text{HV}_{10}\text{O}_{28})$

(e)  $\text{K}[\text{Co}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_3)_2]$

(f)  $[\text{Ni}(\text{CN})_4]^{2-}$

3. Find the oxidation number of bold lettered atoms :

(a) **Mn** in  $\text{K}_2\text{MnO}_4$ ,  $\text{K}_2\text{MnO}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnSO}_4$ ,  $\text{K}_3\text{MnF}_6$ ,  $\text{MnO}_2$

(b) **C** in  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{CO}_2$

(c) **S** in  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{S}_4$ ,  $\text{S}_8$ ,  $\text{Na}_2\text{S}_2\text{O}_7$

(d) **N** in  $\text{NH}_3$ ,  $\text{NH}_2\text{OH}$ ,  $\text{NaN}_3$ ,  $\text{NH}_4\text{NO}_2$

(e) **Cl** in  $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$ ,  $\text{KClO}_3$ ,  $\text{Cl}_2\text{O}_7$

4. Determine the oxidation number of bold lettered atoms in the following :

(a)  $8\text{KClO}_3 + 24\text{HCl} \longrightarrow 8\text{KCl} + 12\text{H}_2\text{O} + 9\text{Cl}_2 + 6\text{ClO}_2$

(b)  $3\text{I}_2 + 6\text{NaOH} \longrightarrow \text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$

5. Find the oxidation number of bold lettered atoms :

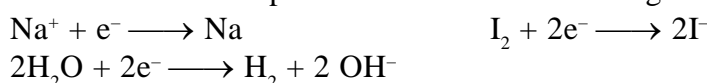
- |                                     |                                 |                                     |  |
|-------------------------------------|---------------------------------|-------------------------------------|--|
| (a) $\text{SnS}_3^{-2}$             | (b) $\text{S}_2\text{O}_3^{-2}$ | (c) $\text{S}_2\text{O}_7^{-2}$     | (d) $\text{NH}_4^+$                              |
| (e) $\text{ClO}_2^-$                | (f) $\text{P}_2\text{O}_7^{-4}$ | (g) $\text{O}_2^{-2}$               | (h) $\text{C}_2\text{O}_4^{-2}$                  |
| (i) $\text{Cr}_2\text{O}_7^{-2}$    | (j) $\text{MnO}_4^-$            | (k) $\text{Be}_3\text{N}_2$         | (l) $\text{Na}_3\text{Fe}(\text{CN})_5\text{NO}$ |
| (m) $\text{KCrO}_3 \cdot \text{Cl}$ | (n) $\text{F}_2\text{H}_2$      | (o) $\text{Co}(\text{NH}_3)_6^{+3}$ | (p) $\text{CuH}$                                 |
| (q) $\text{O}_2\text{F}_2$          |                                 |                                     |  |

### 3. Redox Reaction

**Oxidation :** It is a process in which electrons are lost by an atom, ion or molecule.



**Reduction :** Reduction is a process in which electrons are gained by an atom, ion or molecule.



**Redox Reactions :** Those reactions in which electrons are transferred from one substance to another are called Redox Reactions.



### 4. Oxidising Agents and Reducing Agents (oxidants and Reductants)

Those species (atoms, molecules and ions) which have tendency to accept the electrons are known as oxidizing agents or oxidants, whereas those species (atoms, molecules or ions) which releases the electrons are called reducing agents or reductants. In other words, oxidizing agents are reduced and reducing agents are oxidized.

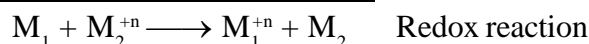
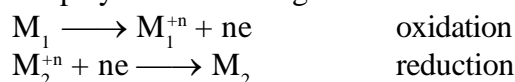
(1) Oxidants are substances which :

- oxidize other
- are reduced themselves
- show electronation.
- show a decrease in oxidation number during a redox change
- has higher oxidation no. in a conjugate pair of redox.

(2) Reductant are substances which :

- reduce other
- are oxidized themselves.
- show de-electronation
- show an increase in oxidation no. during a redox change
- has lower oxidation no. in a conjugate pair of redox.

(3) A redox change is one in which a reductant is oxidized to liberate electrons, which are then used up by an oxidant to get itself reduced.

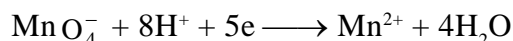


- (4) A redox change occurs simultaneously. For example,  

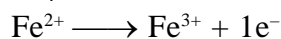
$$2\text{KMnO}_4 + 10\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$$

Oxidant
Reductant

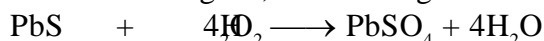
One can see the above equation in the ionic form,



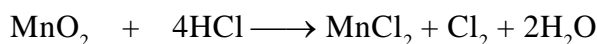
(As  $\text{MnO}_4^-$  is accepting  $5\text{e}^-$ , so it is being reduced and hence it is an oxidant.)



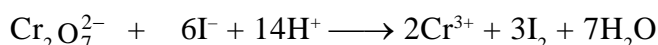
As  $\text{Fe}^{2+}$  is losing  $1\text{e}^-$ , so it is being oxidized and hence it is a reducing agent. Similarly,



Reductant      Oxidant



Oxidant      Reductant



Oxidant      Reductant

### Guidelines for the Identification of Oxidizing and Reducing Agent

1. If an element is in its highest possible oxidation state in a compound, it can function as an oxidizing agent, e.g.  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  etc.
2. If an element is in its lowest possible oxidation state in a compound, it can function as a reducing agent, e.g.  $\text{H}_2\text{S}$ ,  $\text{FeSO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{SnCl}_2$  etc.
3. If an element is in its intermediate oxidation state in a compound, it can function both as an oxidizing agent as well as reducing agent, e.g.  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HNO}_2$ ,  $\text{SO}_2$  etc.
4. If highly electronegative element is in its higher oxidation state in a compound, that compound can function as a powerful oxidizing agent, e.g.  $\text{KClO}_4$ ,  $\text{KClO}_3$ ,  $\text{KIO}_3$  etc.
5. If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent, e.g.  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{N}^{3-}$  etc.

### Common Oxidising and Reducing Agents

Oxidising agent	Effective Change	Decrease in Oxidation Number
$\text{KMnO}_4$ in acid solution	$\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$	5
$\text{KMnO}_4$ in neutral solution	$\text{MnO}_4^- \longrightarrow \text{MnO}_2$	3
$\text{K}_2\text{Cr}_2\text{O}_7$ in acid solution	$\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$	3
dilute $\text{HNO}_3$	$\text{NO}_3^- \longrightarrow \text{NO}$	3
concentrated $\text{HNO}_3$	$\text{NO}_3^- \longrightarrow \text{NO}_2$	1
concentrated $\text{H}_2\text{SO}_4$	$\text{SO}_4^{2-} \longrightarrow \text{SO}_2$	2
manganese (IV) oxide	$\text{MnO}_2 \longrightarrow \text{Mn}^{2+}$	2
Chlorine	$\text{Cl}_2 \longrightarrow \text{Cl}^-$	1
Chloric (I) acid	$\text{ClO}^- \longrightarrow \text{Cl}^-$	2
$\text{KIO}_3$ in dilute acid	$\text{IO}_3^- \longrightarrow \text{I}_2$	5

Oxidising agent	Effective Change	Decrease in Oxidation Number
KIO <sub>3</sub> in concentrated acid	IO <sub>3</sub> <sup>-</sup> → I <sup>+</sup>	4
iron (II) salts (acid)	Fe <sup>2+</sup> → Fe <sup>3+</sup>	1
tin (II) salts (acid)	Sn <sup>2+</sup> → Sn <sup>4+</sup>	2
oxalate (acid)	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → CO <sub>2</sub>	1
sulphites (acid)	SO <sub>3</sub> <sup>2-</sup> → SO <sub>4</sub> <sup>2-</sup>	2
sulphide	S <sup>2-</sup> → S	2
iodides (dilute acid)	I <sup>-</sup> → I <sub>2</sub>	1
iodides (concentrated acid)	I <sup>-</sup> → I <sup>+</sup>	2
metals, e.g. Zn	Zn → Zn <sup>2+</sup>	2
hydrogen	H <sub>2</sub> → H <sup>+</sup>	1

## 2. Daily Practice Problem Sheet

1. Identify the reactants, if any, oxidized or reduced .

- NaH + H<sub>2</sub>O → NaOH + H<sub>2</sub>
- 2FeCl<sub>3</sub> + H<sub>2</sub>S → 2FeCl<sub>2</sub> + S + 2HCl
- 3Mg + N<sub>2</sub> → Mg<sub>3</sub>N<sub>2</sub>
- AgCN + CN<sup>-</sup> → Ag(CN)<sub>2</sub><sup>-</sup>
- SnCl<sub>2</sub> + Br<sub>2</sub> → SnCl<sub>2</sub>.Br<sub>2</sub>
- AlCl<sub>3</sub> + K → Al + 3KCl
- 2CuSO<sub>4</sub> + 4KI → Cu<sub>2</sub>I<sub>2</sub> + K<sub>2</sub>SO<sub>4</sub> + I<sub>2</sub>
- NH<sub>4</sub>NO<sub>2</sub> → N<sub>2</sub> + 2H<sub>2</sub>O
- CaC<sub>2</sub> + 2H<sub>2</sub>O → Ca(OH)<sub>2</sub> + C<sub>2</sub>H<sub>2</sub>
- SnS<sub>2</sub> + S<sup>-2</sup> → SnS<sub>3</sub><sup>-2</sup>
- 3O<sub>2</sub> → 2O<sub>3</sub>

2. Select the oxidants and reductants in the given reactions .

- Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> + 2H<sup>+</sup> → Ag<sup>+</sup> + 2NH<sub>4</sub><sup>+</sup>
- KIO<sub>3</sub> + 5KI + 6HCl → 3I<sub>2</sub> + 6KCl + 3H<sub>2</sub>O
- 2CuSO<sub>4</sub> + SO<sub>2</sub> + 2KBr + 2H<sub>2</sub>O → 2CuBr + 2H<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub>
- C<sub>2</sub>H<sub>4</sub> + Br<sub>2</sub> → C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>
- 2I<sup>-</sup> + H<sub>2</sub>O<sub>2</sub> → 2OH<sup>-</sup> + I<sub>2</sub>
- Si + 2KOH + H<sub>2</sub>O → K<sub>2</sub>SiO<sub>3</sub> + 2H<sub>2</sub>
- 2Cu<sup>+2</sup> + 4I<sup>-</sup> → Cu<sub>2</sub>I<sub>2</sub> + I<sub>2</sub>

## 5. Balancing of Redox Equations

Redox reactions involve oxidation and reduction both. Oxidation means loss of electrons and reduction means gain of electrons. Thus redox reactions involve electron transfer and the number of electrons lost are same as the number of electrons gained during the reaction. This aspect of redox reaction can serve as the basis of a pattern for balancing redox reactions. Two methods are commonly used for this purpose.

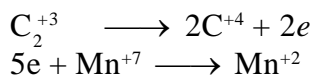
### (A) Ion electron method

It involves three sets of rules depending upon the nature of medium (i.e. neutral, acid or alkaline) in which reaction occurs.

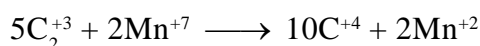
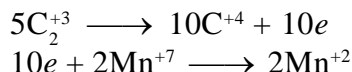
#### (a) Neutral medium :

e.g.,  $\text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 \longrightarrow \text{CO}_2 + \text{K}_2\text{O} + \text{MnO}_4 + \text{H}_2\text{O}$

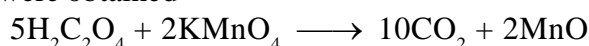
**Step 1.** Select the oxidatn, reductant atoms and write their half reactions, one representing oxidation and other reduction.



**Step 2.** Balance the no. of electrons and add the two equations.

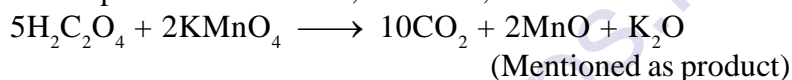


**Step 3.** Write complete molecule of the reductant and oxidant from which respective redox atoms were obtained



**Step 4.** Balance other atoms if any (except H and O)

In above example K is unbalanced, therefore,



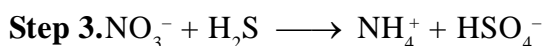
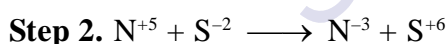
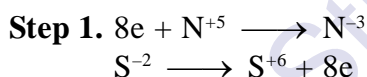
**Step 5.** Balance O atom using  $\text{H}_2\text{O}$  on desired side.



#### (b) Acidic medium :



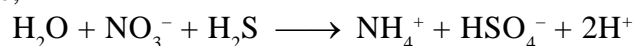
Produced like neutral medium for step 1 to 4.



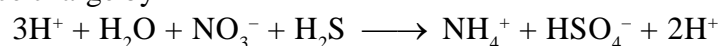
**Step 4.** No other atom (except H and O) is unbalanced and thus, no need for this step.

**Step 5. Balance O atom :** Balancing of O atom is made by using  $\text{H}_2\text{O}$  and  $\text{H}^+$  ions.

Add desired molecules of  $\text{H}_2\text{O}$  on the side deficient with O atom and double  $\text{H}^+$  on opposite side. Therefore,



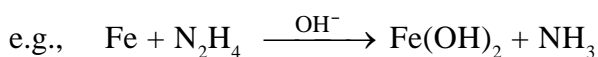
**Step 6.** Balance charge by  $\text{H}^+$



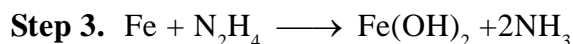
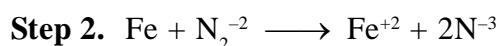
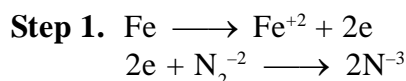
∴ Finally balanced equation is,



#### (c) Alkaline medium :



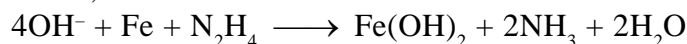
Proceed like neutral medium for step 1 to 4



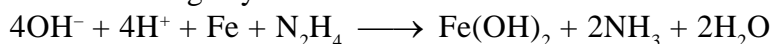
**Step 4.** No other atom (except H and O) is unbalanced and thus, no need for this step.

**Step 5.** Balance O atom: Balancing of O atom is made by using  $\text{H}_2\text{O}$  and  $\text{OH}^-$  ions.

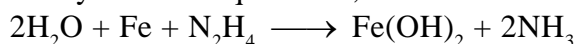
Add desired molecules of  $\text{H}_2\text{O}$  on the side rich with O atoms and double  $\text{OH}^-$  on opposite side. Therefore,



**Step 6.** Balance charge by  $\text{H}^+$ :



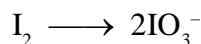
$\therefore$  finally balanced equation is,



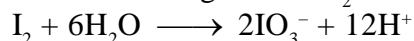
### Balancing of Half reactions



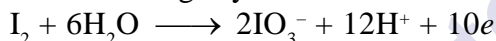
**Step 1.** Balance atoms other than O and H if needed i.e.,



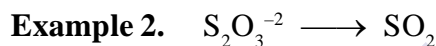
**Step 2.** Balance O atoms using  $\text{H}^+$  and  $\text{H}_2\text{O}$  as reported earlier.



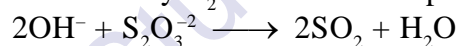
**Step 3.** Balance charge by electrons.



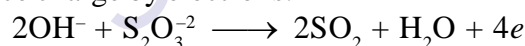
This is balanced half reaction.



**Step 2.** Balance O atom by  $\text{H}_2\text{O}$  and  $\text{OH}^-$  as reported earlier.



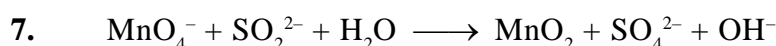
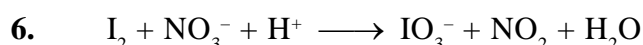
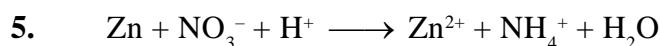
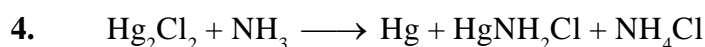
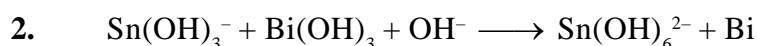
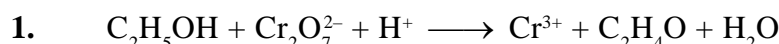
**Step 3.** Balance charge by electrons.



This is balanced half reaction

## 3. Daily Practice Problem Sheet

1. Balance the following equation using desired medium –





8.  $\text{H}_2\text{O}_2 + \text{ClO}_2 + \text{OH}^- \longrightarrow \text{ClO}_2^- + \text{O}_2 + \text{H}_2\text{O}$
9.  $\text{ClO}^- + \text{CrO}_2^- + \text{OH}^- \longrightarrow \text{Cl}^- + \text{CrO}_4^{2-} + \text{H}_2\text{O}$
10.  $\text{Cl}_2 + \text{KOH} \longrightarrow \text{KClO}_3 + \text{KCl} + \text{H}_2\text{O}$
11.  $\text{H}_2\text{O}_2 + \text{KMnO}_4 \longrightarrow \text{MnO}_2 + \text{KOH} + \text{O}_2 + \text{H}_2\text{O}$
12.  $\text{HNO}_2 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{HNO}_3 + \text{KMnO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
13.  $\text{N}_2\text{H}_4 + \text{AgNO}_3 + \text{KOH} \longrightarrow \text{N}_2 + \text{Ag} + \text{KNO}_3 + \text{H}_2\text{O}$
14.  $\text{P} + \text{HNO}_3 \longrightarrow \text{HPO}_3 + \text{NO} + \text{H}_2\text{O}$
15.  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} \longrightarrow \text{KCl} + \text{CrCl}_3 + \text{H}_2\text{O} + \text{Cl}_2$
16.  $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{CO}_2 + \text{Mn}^{2+} + \text{H}_2\text{O}$
17.  $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{Cr}^{3+} + \text{CO}_2 + \text{H}_2\text{O}$
18.  $\text{KMnO}_4 + \text{H}_2\text{S} + \text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{MnSO}_4 + \text{S} + \text{H}_2\text{O}$
19.  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 + \text{KCN} + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{Cu}(\text{CN})_3 + \text{NH}_3 + \text{KCNO} + \text{NH}_4\text{Cl} + \text{KCl}$
20.  $\text{Ag} + \text{KCN} + \text{H}_2\text{O} + \text{O}_2 \longrightarrow \text{KAg}(\text{CN})_2 + \text{KOH}$
21.  $\text{Fe}_3\text{O}_4 + \text{MnO}_4^- + \text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + \text{MnO}_2 + \text{OH}^-$
22.  $\text{C}_2\text{H}_5\text{OH} + \text{MnO}_4^- + \text{OH}^- \longrightarrow \text{C}_2\text{H}_3\text{O}^- + \text{MnO}_2 + \text{H}_2\text{O}$
23.  $\text{Cr}_2\text{O}_7^{2-} + \text{SO}_3^{2-} + \text{H}^+ \longrightarrow \text{Cr}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$
24.  $\text{ClO}_3^- + \text{SO}_2 + \text{H}^+ \longrightarrow \text{ClO}_2 + \text{HSO}_4^-$
25.  $\text{Mn}^{2+} + \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \longrightarrow \text{MnO}_4^- + \text{HSO}_4^- + \text{H}^+$

## 6. Methods of expressing the concentration of a solution

The concentration of a solution can be expressed in a number of ways. The important methods are:

### (i) Strength of solution :

Amount of solute present in one litre solution

$$S = \frac{\text{weight of solute}}{\text{volume of solution in litre}} = \frac{w}{V \text{ in } (l)}$$

$$= \text{Normality} \times \text{Equivalent weight}$$

$$= \text{Molarity} \times \text{Molecular weight}$$

### (ii) Mass percentage or per cent by mass :

$$\%(\text{w/w}) \text{ Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$= \frac{\text{Mass of solute} \times 100}{\text{Mass of solute} + \text{Mass of solvent}} = \frac{\text{Mass of solute} \times 100}{\text{Volume of solution} \times \text{Density of solution}}$$

### (iii) Percent mass by volume :

$$\%(\text{w/v}) = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(iv) **Parts per million (ppm) :**

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

(v) **Mole fraction :**

Let  $n$  moles of solute (A) and  $N$  moles of solvent (B) be present in a solution.

$$\text{Mole fraction of solute} = \frac{n}{N+n} = X_A, \text{ Mole fraction of solvent} = \frac{N}{N+n} = X_B$$

$$\text{In binary solution, } X_A + X_B = 1$$

Mole fraction is independent of temperature of the solution.

(vi) **Molality**

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{weight (in kg) of solvent}}$$

Let  $w_A$  grams of the solute of molecular mass  $m_A$  be present in  $w_B$  grams of the solvent, then

$$\text{Molality (m)} = \frac{w_A}{m_A \times w_B} \times 1000$$

**Relation between mole fraction and Molality :**

$$\frac{X_A \times 1000}{X_B \times m_B} = m = \frac{w_A \times 1000}{w_B \times m_B}$$

**Note :** Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

(vii) **Molarity (Molar concentration)**

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume (in litre) of solution}}$$

$$\text{Molarity of the solution} = \frac{w_A}{m_A \times V} \times 1000$$

**Relation between molarity and % solute by mass :**

Let  $d$  = density of solution in g/mL and let it contains  $x\%$  (w/w) solute by mass.

Number of moles of solute in 1 litre

$$= \frac{\text{mass of solute in gram}}{\text{grams molecular mass of solute}} = \frac{x \times d \times 10}{M_{\text{solute}}}$$

$$M = \frac{x \times d \times 10}{m_A}$$

**Molarity of dilution :**

$$\begin{array}{ccc} \text{Before dilution} & & \text{After dilution} \\ M_1 V_1 & = & M_2 V_2 \end{array}$$

**Molarity of mixing :**

$$M_1 V_1 + M_2 V_2 + M_3 V_3 = M_R (V_1 + V_2 + V_3) \quad M_R = \text{resultant molarity}$$

**Relationship between molality and molarity :**

$$\text{Molality (m)} = \frac{\text{molarity}}{d - \text{molarity} \times m_{\text{solute}}} = \frac{1000 \times M}{1000 \times d - M \times M_{\text{solute}}}$$

**(viii) Normality :**

It is define as no. of equivalent of a solute present in one litre of solution.

$$N = \frac{\text{Equivalent of solute}}{\text{Volume of solution in litre}} = \frac{\text{Weight of solute}}{\text{Equivalent weight of solute} \times V \text{ in litre}}$$

$$N = \frac{w}{E \times V \text{ in (l)}} = \frac{w \times 1000}{E \times V \text{ in mL}}$$

Also **Equivalent** =  $N \times V \text{ in l} = \frac{\text{Wt. of solute}}{\text{Eq. wt. of solute}}$

and **Milli equivalent** =  $N \times V \text{ in ml} = \frac{\text{Wt. of solute}}{\text{Eq. wt. of solute}} \times 1000$

**Note :** A striking fact regarding equivalent and milli equivalent is **equivalent and milli equivalent of reactants reacts in equal number to give same number of equivalent or milli equivalent of products separately.**

**(ix) Formality :**

Since molecular weight of ionic solids is not determined accurately experimentally due to their dissociation nature and therefore molecular weight of ionic solid is often referred as formula weight and molarity as formality.

$$\text{Formality} = \frac{\text{wt. of solute}}{\text{Formula wt.} \times V(\text{in l})} \text{ i.e., molarity}$$

**(x) Specific gravity of solution**

$$= \frac{\text{weight of solution}}{\text{volume of solution}} \text{ i.e., weight of 1 mL solution.}$$

**Note :**

- (1) Molality, % by weight, mole fractions are independent of temperature since these involve weights.
- (2) Rest all, i.e, Normality, molarity, % by vol., % by strength and strength are temperature dependent, normally decrease with increase in temperature since volume of solution increases with T.
- (3) Sometimes term formality is used in place of molarity.
- (4) Normal, molar solution means for solutions having normality 1 N and molarity 1 M respectively..
- (5) Standard solution is one whose N or M are known
- (6) On diluting a solution, eq, meq, mole or m mole of solute do not change however N an M change.

**Illustration 4.**

*The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity of the solution.*

**Solution :**

In solving such numericals, the following formula can be applied:

$$\text{Molarity} = \frac{\% \text{ strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$$

$$M = \frac{13 \times 1.09 \times 10}{98} = 1.445 \text{ M}$$

**Illustration 5.**

*The density of a 3 M sodium thiosulphate solution ( $\text{Na}_2\text{S}_2\text{O}_3$ ) is 1.25 g/mL. Calculate*

- (i) *the percentage by mass of sodium thiosulphate*
- (ii) *the mole fraction of sodium thiosulphate and*
- (iii) *molalities of  $\text{Na}^+$  and  $\text{S}_2\text{O}_3^{2-}$  ions.*

**Solution :**

$$(i) \quad M = \frac{x \times d \times 10}{m_A} \quad \Rightarrow \quad 3 = \frac{x \times 1.25 \times 10}{158}$$

$$\therefore x = 37.92$$

$$(ii) \quad \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{158} = 3$$

$$\text{Mass of water} = (1250 - 474) = 776 \text{ g}, \quad \text{No. of moles of water} = \frac{776}{18} = 43.1$$

$$\text{Mole fraction of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{3}{43.1 + 3} = \frac{3}{46.1} = 0.065$$

$$(iii) \quad \text{No. of moles of } \text{Na}^+ \text{ ions} = 2 \times \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3 = 2 \times 3 = 6$$

$$\text{Molality of } \text{Na}^+ \text{ ion} = \frac{\text{No. of moles of } \text{Na}^+ \text{ ions}}{\text{Mass of water in kg}} = \frac{6}{776} \times 1000 = 7.73 \text{ m}$$

$$\text{No. of moles of } \text{S}_2\text{O}_3^{2-} \text{ ions} = \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3$$

$$\text{Molality of } \text{S}_2\text{O}_3^{2-} \text{ ions} = \frac{3}{776} \times 1000 = 3.86 \text{ m}$$

**Illustration 6.**

*One litre of sea water weighs 1030 g and contains about  $6 \times 10^{-3}$  g of dissolved  $\text{O}_2$ . Calculate the concentration of dissolved oxygen in ppm.*

**Solution :**

$$\text{Mass of } \text{O}_2 \text{ in mg} = 6 \times 10^{-3} \text{ g} \times 10^3 \text{ mg/g} = 6 \text{ mg}$$

$$\text{ppm of } \text{O}_2 \text{ in 1030 g sea water} = \frac{\text{Mass of } \text{O}_2 \text{ in mg}}{\text{Mass of sea water in kg}} = \frac{6}{(1030/1000) \text{ kg}}$$

$$= \frac{6 \times 1000}{1030} = 5.8 \text{ ppm}$$

**Illustration 7.**

*A 100 mL solution of KOH contains 10 milliequivalents of KOH. Calculate its strength in normality and grams/liter.*

**Solution :**

$$\text{Normality} = \frac{\text{no. of m.e.}}{\text{volume in mL}} = \frac{10}{100} = 0.1$$

∴ Strength of the solution = N/10. Again,

$$\text{Strength in grams/ litre} = \text{normality} \times \text{eq. wt.} = \frac{1}{10} \times 56 = 5.6 \text{ grams/litre.}$$

$$\left( \text{eq. wt. of KOH} = \frac{\text{molecular wt}}{\text{acidity}} = \frac{56}{1} = 56 \right)$$

## 4. Daily Practice Problem Sheet

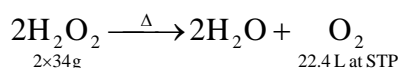
- 214.2 g of sugar syrup contains 34.2 g of sugar. Calculate :  
(a) molality of the solution and  
(b) mole fraction of sugar in the syrup.
- How many g of a 5.0 % by weight NaCl solution are necessary to yield 3.2 g NaCl ?
- Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 95 ml prepared by adding 50 ml of ethyl alcohol (density = 0.789 g ml<sup>-1</sup>) to 50ml water (density = 1.00 g ml<sup>-1</sup>).
- What volume of 96 % H<sub>2</sub>SO<sub>4</sub> solution (density 1.83 g/ml) is required to prepare 4 litre of 3.0 M H<sub>2</sub>SO<sub>4</sub> solution ?
- A litre of milk weighs 1.032 kg. The butterfat it contains to the extent of 4.0% by volume has a density of 865 kg/m<sup>3</sup>. What is the density of the fat-free “skimmed” milk ?
- Mole fraction of glucose in a solution (solvent is a liquid having molecular mass 25) is 0.2. If density of solution is 1.4 gm/ml, then calculate molarity of the solution.
- 10 ml of ethanol having density 0.7893 gm/ml is mixed with 20 ml of water having density 0.9971 g/ml. The resulting solution formed has density 0.9571 g/ml. Calculate  
(i) % change in volume on mixing      (ii) molarity of the solution  
(iii) molality of the solution
- A procedure calls for 100 cm<sup>3</sup> of 20.0 % H<sub>2</sub>SO<sub>4</sub>, density 1.14 g/cm<sup>3</sup>. How much concentrated acid, of density 1.84 g/cm<sup>3</sup> and containing 98.0 % H<sub>2</sub>SO<sub>4</sub> by weight, must be diluted with water to prepare 100 cm<sup>3</sup> acid of the required strength ?
- 100 g of 1 molal ethylene glycol solution is prepared in the laboratory. Determine % by mass of each component.
- What volume of dilute nitric acid, of density 1.11 g/mL and 19 % HNO<sub>3</sub> by weight, contains 10 g HNO<sub>3</sub>?
- What volume of 95.0 % alcohol by weight (density 0.809 g/cm<sup>3</sup>) must be used to prepare 150 cm<sup>3</sup> of 30.0% alcohol by weight (density 0.957 g/cm<sup>3</sup>) ?

12. Calculate the resulting molarity of the solution that is obtained by adding 5 g of NaOH to 200 mL of M/4 NaOH solution (density = 1.05 g cm<sup>-3</sup>). The density of resulting solution is 1.08 g cm<sup>-3</sup>.
13. A sample of drinking water was found to be severely contaminated with chloroform which is supposed to be carcinogen. The level of contamination was 15 ppm (by mass). Express this in percent by mass. Also find the molality of chloroform in water sample.
14. Calculate the volume of 80 % H<sub>2</sub>SO<sub>4</sub> by mass (density = 1.80 g cm<sup>-3</sup>) that is required to obtain one litre of 20 % H<sub>2</sub>SO<sub>4</sub> by mass (density = 1.25 g cm<sup>-3</sup>)
15. (a) The given sample of sulphuric acid was found to have mole fraction of H<sub>2</sub>SO<sub>4</sub> as 0.15. Calculate the molality of the solution.  
(b) In a solution of benzene and toluene, the mole fraction of toluene is 0.5. Calculate the mass % of the solution with respect to benzene ?

## 7. Volume Strength of H<sub>2</sub>O<sub>2</sub> Solution

The concentration of H<sub>2</sub>O<sub>2</sub> is usually represented in terms of volume. If a sample of H<sub>2</sub>O<sub>2</sub> is labeled as 'x volume', it means that 1 volume of H<sub>2</sub>O<sub>2</sub> solution gives 'x volumes' of O<sub>2</sub> gas at STP on complete decomposition.

Consider the decomposition of H<sub>2</sub>O<sub>2</sub> as



∴ 22400 ml of O<sub>2</sub> gas is liberated by 68g of H<sub>2</sub>O<sub>2</sub> solution

$$\therefore x \text{ ml of O}_2 \text{ gas will be liberated by } = \frac{68x}{22400} = \frac{17x}{5600} \text{ g of H}_2\text{O}_2$$

It means that  $\frac{17x}{5600}$  g of H<sub>2</sub>O<sub>2</sub> will be present in 1 ml of solution.

$$\therefore 1000 \text{ ml of solution contains H}_2\text{O}_2 = \frac{17x}{5600} \times 1000 = \frac{17x}{5.6}$$

Strength (g L<sup>-1</sup>) = Normality × Equivalent weight

$$\frac{17x}{5.6} = N \times \frac{34}{2} \quad (\ominus \text{ n-factor of H}_2\text{O}_2 = 2)$$

$$x = 5.6 \times N$$

i.e., Volume strength of H<sub>2</sub>O<sub>2</sub> = 5.6 × Normality

### Illustration 8:

A sample of H<sub>2</sub>O<sub>2</sub> is x% by mass. x ml of KMnO<sub>4</sub> are required to oxidize one gram of this H<sub>2</sub>O<sub>2</sub> sample. Calculate the normality of KMnO<sub>4</sub> solution.

### Solution :

Suppose, Mass of H<sub>2</sub>O<sub>2</sub> solution = 100g

Mass of H<sub>2</sub>O<sub>2</sub> present = x gram

Mass of H<sub>2</sub>O<sub>2</sub> solution taken = 1 gram

Mass of H<sub>2</sub>O<sub>2</sub> present in 1 gram solution =  $\frac{x}{100}$

Equivalents of H<sub>2</sub>O<sub>2</sub> =  $\frac{W}{E}$

$$= \frac{x}{100 \times 17} \quad \dots(1)$$

$$(E \text{ for H}_2\text{O}_2) = 17$$

Equivalents of  $\text{KMnO}_4 = N \times V \text{ (litre)} = N \times x \times 10^{-3}$

Putting equivalents of  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$  equal,

$$\frac{x}{100 \times 17} = N \times x \times 10^{-3}$$

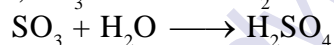
$$N = 0.59 \text{ (Normality of } \text{H}_2\text{SO}_4\text{)}$$

## 5. Daily Practice Problem Sheet

- Calculate the strength of "30 V"  $\text{H}_2\text{O}_2$  in the terms of :  
(a) % strength (w/v)      (b) normality      (c) molarity      (d) strength (g/L)
- Calculate the volume strength of 3.58 N  $\text{H}_2\text{O}_2$  solution.
- Calculate the strength of "56 V"  $\text{H}_2\text{O}_2$  in the terms of :  
(a) % strength (w/v)      (b) normality      (c) molarity      (d) strength (g/L)
- What is the mass of hydrogen peroxide present in 1 litre of 2M solution ? Calculate the volume of oxygen (at NTP) liberated upon the complete decomposition of 100 ml of the above solution.
- Calculate the strength in  $\text{gm/22.4 l}$  of '100 V' of  $\text{H}_2\text{O}_2$ .

## 8. Percentage Labeling of Oleum

Oleum or fuming sulphuric acid contains  $\text{SO}_3$  gas dissolved in sulphuric acid. When water is added to oleum,  $\text{SO}_3$  reacts with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$ , thus mass of the solution increases.



The total mass of  $\text{H}_2\text{SO}_4$  obtained by diluting 100g of sample of oleum with desired amount of water, is equal to the percentage labeling of oleum.

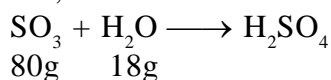
$$\begin{aligned} \therefore \% \text{ labeling of oleum} &= \text{Total mass of } \text{H}_2\text{SO}_4 \text{ present in oleum after dilution.} \\ &= \text{mass of } \text{H}_2\text{SO}_4 \text{ initially present} \\ &\quad + \text{mass of } \text{H}_2\text{SO}_4 \text{ produced on dilution.} \end{aligned}$$

### Illustration 9:

*Calculate the composition of 109% oleum.*

### Solution :

Let the mass of  $\text{SO}_3$  in the sample be 'w' g, then the mass of  $\text{H}_2\text{SO}_4$  would be  $(100 - w)$ g. On dilution,



$$\text{Moles of } \text{SO}_3 \text{ in oleum} = \frac{w}{80} = \text{Moles of } \text{H}_2\text{SO}_4 \text{ formed after dilution.}$$

$$\therefore \text{Mass of } \text{H}_2\text{SO}_4 \text{ formed on dilution} = \frac{98w}{80}$$

$$\text{Total mass of } \text{H}_2\text{SO}_4 \text{ present in oleum after dilution} = \frac{98w}{80} + (100 - w) = 109$$

$$\therefore w = 40$$

Thus oleum sample contains 40%  $\text{SO}_3$  and 60%  $\text{H}_2\text{SO}_4$ .

## 6. Daily Practice Problem Sheet

- Calculate % of free  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in 104.5 % oleum sample.
- Calculate % of free  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in 102.25% oleum sample.
- Calculate % of free  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in 118% oleum sample.
- Calculate the weight of  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$  in 200 g of oleum sample labelled as 109%.
- Calculate the composition of the final solution if 100g of oleum labelled as 118% is added with  
(a) 9 gm water                      (b) 18 g water                      (c) 1.20 g water

## 9. Hardness of Water

Hardness of water is due to the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in it. Hardness of water is of two types :

- Temporary Hardness :** It is due to the presence of dissolved  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  in water. To determine the temporary hardness a given volume of hard water is titrated with a strong acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ) using methyl orange indicator.
- Permanent Hardness :** It is due to the presence of dissolved  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgCl}_2$  and  $\text{MgSO}_4$  in water. A known volume of hard water is taken and an excess of known equivalents of  $\text{Na}_2\text{CO}_3$  are added in it.  $\text{Na}_2\text{CO}_3$  reacts with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  forming precipitates of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . These precipitates are filtered off. The filtrate is titrated with a strong acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ). Knowing the equivalents of  $\text{Na}_2\text{CO}_3$  added and left unreacted, the equivalents of  $\text{Na}_2\text{CO}_3$  consumed by hard water is known. The equivalents of  $\text{Na}_2\text{CO}_3$  consumed is equal to the total equivalents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water.

Hardness of water is represented in ppm (mg/litre) of  $\text{CaCO}_3$  i.e. milli grams of  $\text{CaCO}_3$  present per litre of hard water. But hard water does not contain  $\text{CaCO}_3$ . Hard water contains  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{Ca}(\text{HCO}_3)_2$  etc.

One mole  $\text{CaCl}_2 \equiv$  one mole  $\text{CaCO}_3$   
or                      111 g  $\text{CaCl}_2 \equiv$  100g  $\text{CaCO}_3$   
Similarly,        120g  $\text{MgSO}_4 \equiv$  100g  $\text{CaCO}_3$

Thus mass of  $\text{CaCO}_3$  corresponding to the mass of  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  etc., present in hard water is calculated. Milligrams of  $\text{CaCO}_3$  per litre of hard water is called hardness of water in ppm.

### Illustration 9:

*One liter of sample of hard water contains 1mg of  $\text{CaCl}_2$  and 1 mg of  $\text{MgCl}_2$ . Find the total hardness of water in terms of  $\text{CaCO}_3$  per  $10^6$  parts of water by weight*

**Solution:**

$$\text{m M of } \text{MgCl}_2 = \frac{1 \times 10^{-3} \times 10^3}{95} = \frac{1}{95} \quad \left( \text{milli mole} \frac{\text{wt.}}{\text{M.wt}} \times 1000 \right)$$

$$\text{m M of } \text{CaCl}_2 = \frac{1 \times 10^{-3} \times 10^3}{111} = \frac{1}{111}$$

$\therefore$  m M of  $\text{CaCO}_3$  if  $\text{MgCl}_2$  and  $\text{CaCl}_2$  are taken form of  $\text{CaCO}_3$   
( $\square$  Ca, Mg are both bivalent  $\therefore$  mole ratio is 1 : 1)

$$= \frac{1}{95} + \frac{1}{111} = \frac{206}{111 \times 95}$$

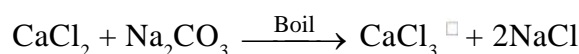


$$\begin{aligned}
 \therefore \text{Weight of CaCO}_3 \text{ in 1000 mL} &= \frac{206}{111 \times 95} \times \frac{100}{1000} \\
 \therefore \text{Hardness in ppm (part per million)} \\
 &= \frac{\text{g of CaCO}_3}{10^6 \text{ g of H}_2\text{O}} = \frac{206 \times 100 \times 10^6}{111 \times 95 \times 1000 \times 1000} = 1.953 \\
 \therefore \text{Hardness} &= \mathbf{1.953 \text{ ppm}}
 \end{aligned}$$

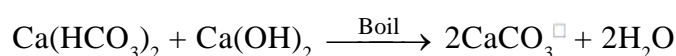
### Water Softeners :

The hardness may be removed by either of the reactants on treating with water.

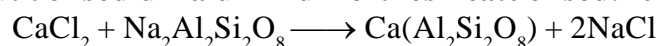
(a) **Washing soda :**



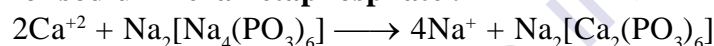
(b) **Slaked lime :**



(c) **Permutit or sodium aluminium orthosilicate or sod. zeolite :**



(d) **Calgon or sodium hexametaphosphate :**



## 7. Daily Practice Problem Sheet

- (a) Calculate the degree of hardness of water containing :

(i) 0.02 gm of  $\text{MgSO}_4$  per litre.      (ii) 0.005 moles of  $\text{MgSO}_4$  per litre

(b) 50 litre of water containing  $\text{Ca(HCO}_3)_2$  when converted into soft water required 22.2 g  $\text{Ca(OH)}_2$ .  
Calculate the amount of  $\text{Ca(HCO}_3)_2$  per litre of hard water.
- Calculate the degree of hardness of water containing :

(a) 0.04 g of  $\text{CaSO}_4$  per litre      (b) 0.001 moles of  $\text{CaCO}_3$  per litre  
 (c) 0.01 g of  $\text{CaCl}_2$  per litre      (d) 0.12 g of  $\text{MgCl}_2$  per litre
- A water sample obtained from a tube well contains 88.2 ppm of  $\text{SO}_4^{2-}$  and 149 ppm of  $\text{HCO}_3^-$  with  $\text{Ca}^{2+}$  ions as the only cation in  $10^6$  g. Calculate :

(a) the concentration of  $\text{Ca}^{2+}$  expressed in ppm.  
 (b) the No. of moles of  $\text{CaO}$  consumed in removing  $\text{HCO}_3^-$  from  $1.0 \times 10^6$  g of given water sample.  
 (c) the concentration (in ppm) of residual  $\text{Ca}^{2+}$  ions left after the treatment with  $\text{CaO}$ .
- What mass of  $\text{CaO}$  will be required to soften 1000 litre of a hard water sample containing 122.0 ppm of  $\text{HCO}_3^-$ . If all the cations associated with  $\text{HCO}_3^-$  ions are  $\text{Ca}^{2+}$ , what will the total mass of  $\text{CaCO}_3$  obtained as white precipitate.
- A sample of hard water has its hardness due to  $\text{CaSO}_4$  only. When this water is passed through an anion exchange resin,  $\text{SO}_4^{2-}$  ions are replaced by  $\text{OH}^-$ . 25.0 ml of hard water sample so treated requires 21.58 ml of  $10^{-3}$  M  $\text{H}_2\text{SO}_4$  for its titration. What is the hardness of water expressed in terms of ppm of  $\text{CaSO}_4$ ? Assume density of hard water = 1 g/ml.

## 10. Significance of Chemical Equations

Let us consider a balanced chemical equations

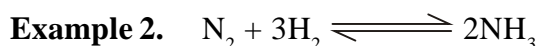


This equation will provide us various quantitative informations:

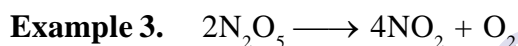
1. The molar ratio of reactants, i.e., PbS and  $\text{H}_2\text{O}_2$  in which they react together is 1:4.
2. The molar ratio of the two products i.e.,  $\text{PbSO}_4$  and  $\text{H}_2\text{O}$  being formed in the reaction is also 1:4.
3. The initial moles of PbS and  $\text{H}_2\text{O}_2$  for the reaction to take place not necessarily be 1 and 4 respectively or also should not be in the molar ratio of 1:4.
4. One can start the reaction with PbS and  $\text{H}_2\text{O}_2$  in any molar ratio, but the ratio of PbS and  $\text{H}_2\text{O}_2$  which are reacting will always be in the ratio of 1:4.
5. One mole of  $\text{PbSO}_4$  and 4 moles of  $\text{H}_2\text{O}$  will be formed for each mole of PbS being consumed.

**The stoichiometric coefficients of a balanced chemical equation is the molar ratio and not the weight ratio.**

One can use the balanced chemical equation for quantitative (gravimetrically or volumetrically) estimation of reactants and products. But if one does not have the balanced equation, it is very difficult to calculate the amounts of reactants consumed or products being formed.



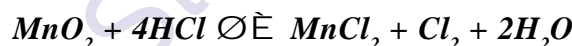
Above balanced chemical equation gives idea that 1 mole of  $\text{N}_2$  (28 g) reacts with 3 mole of  $\text{H}_2$  (6 g) to give 2 mole of  $\text{NH}_3$



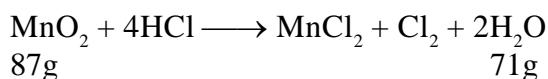
Above balanced equation indicates that 2 mole of  $\text{N}_2\text{O}_5$  ( $2 \times 108$  g) will decompose to give 4 mole of  $\text{NO}_2$  ( $4 \times 46$  g) and 1 mole of  $\text{O}_2$  (32 g).

### Illustration 10:

*Calculate the mass of 90% pure  $\text{MnO}_2$  to produce 35.5g of  $\text{Cl}_2$  according to the following reaction.*



**Solution:**



Q 71g  $\text{Cl}_2$  is produced by 87g of  $\text{MnO}_2$

$$\therefore 35.5\text{g } \text{Cl}_2 \text{ is produced} = \frac{87 \times 35.5}{712} = 43.5\text{g}$$

Q 90g pure  $\text{MnO}_2$  is present in 100g sample

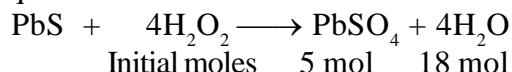
$$\therefore 43.5\text{g pure } \text{MnO}_2 = \frac{100 \times 43.5}{90} = 48.3\text{g}$$

## 11. The Limiting Reagent

The reactions in which more than one reactants are reacting and if they are not present in the same molar ratio as the balanced equation requires, then one has to find out the limiting reagent i.e., the reagent which is completely consumed in the reaction. All quantitative calculations are carried out with the help of limiting reagent only. Now, how to decide the limiting reagent of a reaction? Consider the following example.

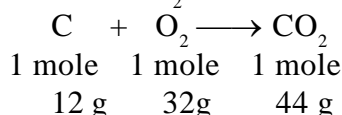
**Example 1.** Suppose you are given 5 moles of PbS and 18 moles of  $\text{H}_2\text{O}_2$  and you have to calculate the maximum amount of  $\text{PbSO}_4$  being produced.

The balanced equation is :



Now since 1 mol of PbS reacts completely with 4 moles of  $\text{H}_2\text{O}_2$  to produce 1 mol of  $\text{PbSO}_4$ . Therefore, 5 moles of PbS will react with 20 moles of  $\text{H}_2\text{O}_2$ . But since moles of  $\text{H}_2\text{O}_2$  is only 18. So,  $\text{H}_2\text{O}_2$  will be the reagent which will be consumed first, and hence  $\text{H}_2\text{O}_2$  is the limiting reagent. If PbS have been the limiting reagent 5 mole of it would have given 5 moles of  $\text{PbSO}_4$  but it is not so. As one can see from the balanced chemical equation that 1 mol of  $\text{PbSO}_4$  is produced from 4 moles of  $\text{H}_2\text{O}_2$ . So 18 moles of  $\text{H}_2\text{O}_2$  will produce 4.5 moles of  $\text{PbSO}_4$ .

**Example 2.** Suppose you are given 12 g of C and 40 gm of  $\text{O}_2$  and you have to calculate maximum amount of  $\text{CO}_2$  formed. The balance chemical equation is :



For complete reaction of 40 g of  $\text{O}_2$  (1.25 mole) 15 g of C (1.25 mole) is required but only 12 g of C is present therefore C is limiting reagent and 12 g of C will give 44 g of  $\text{CO}_2$  and the  $\text{O}_2$  is excess reagent.

So, one can define limiting reagent in another way,

**“The reagent producing the least number of moles of products is the limiting reagent”.**

### Calculation of limiting reagent :

- By calculating the required amount by the equation and comparing it with given amount.  
[Useful when only two reactant are there]
- By Calculating amount of any one product obtained taking each reactant one by one irrespective of other reactants. The one giving least product is *limiting reagent*.
- Divide given moles of each reactant by their stoichiometric coefficient, the one with least ratio is *limiting reagent*. [Useful when number of reactants are more than two]

### Percentage yield :

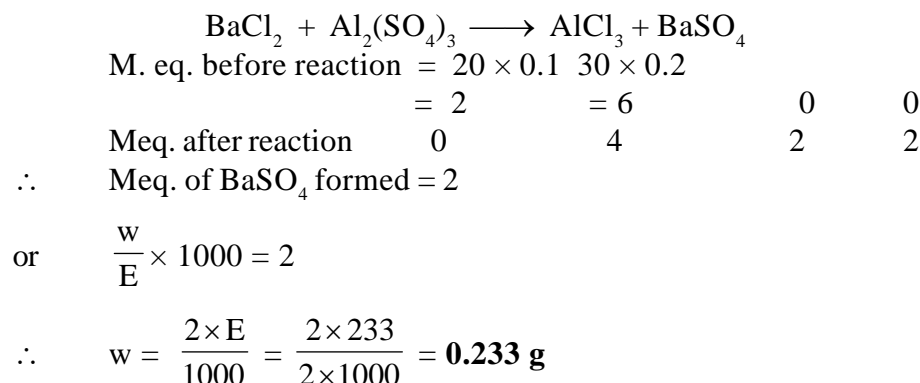
$$\text{The percentage yield of product} = \frac{\text{actual yield}}{\text{the theoretical maximum yield}} \times 100$$

- The actual amount of any limiting reagent consumed in such incomplete reactions is given by : [ % yield  $\times$  given moles of limiting reagent ] [ for reversible reactions ]
- For irreversible reaction with % yield less than 100, the reactant is converted to product [desired and waste]

**Illustration 11.**

20 mL of 0.1 N  $\text{BaCl}_2$  is mixed with 30 mL of 0.2 N  $\text{Al}_2(\text{SO}_4)_3$ . How many g of  $\text{BaSO}_4$  are formed?

**Solution :**

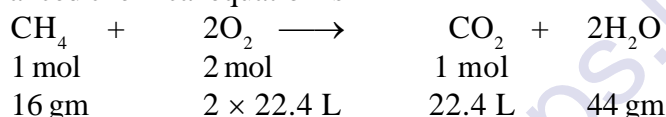


**Illustration 12.**

8 gm of methane is burnt with 4.48L of  $\text{O}_2$  at STP. Find out the volume of  $\text{CO}_2$  gas produced at STP and also the weight of  $\text{CO}_2$  gas.

**Solution :**

The balanced chemical equation is



$$\text{No. of moles of } \text{CH}_4 = \frac{8}{16} = 0.5 \text{ mol}$$

$$\text{No. of moles of } \text{O}_2 = \frac{4.48\text{L}}{22.4\text{L}} = 0.2 \text{ mol}$$

Now since 1 mole of  $\text{CH}_4$  requires 2 mol (i.e. 44.8 L) of  $\text{O}_2$  for complete combustion. But the given moles of  $\text{O}_2$  is only 0.2 mol. So,  $\text{O}_2$  is the limiting reagent.

Again, since 2 moles of  $\text{O}_2$  reacts with 1 mol of  $\text{CH}_4$  to give 22.4 L of  $\text{CO}_2$  at STP.

So 0.2 mole of  $\text{O}_2$  will react with 0.1 mol of  $\text{CH}_4$  to give 2.24 L of  $\text{CO}_2$ .

$$\begin{aligned}
 \text{Wt. of } \text{CO}_2 \text{ produced} &= 0.1 \text{ mol} \times 44 \\
 &= 4.4 \text{ gms of } \text{CO}_2
 \end{aligned}$$

## 8. Daily Practice Problem Sheet

- According to the reaction,  $\text{SO}_2 + \text{H}_2\text{S} \longrightarrow \text{S} + \text{H}_2\text{O}$ , when 6.4 g of  $\text{SO}_2$  is reacted with 4 g  $\text{H}_2\text{S}$ . Calculate :
  - The limiting reagent
  - Maximum amount of sulphure which can be produced
  - The amount of excess reagent remaining after the reaction is complete ?
- According to the reaction  $\text{K}_2\text{Cr}_2\text{O}_7 + 14 \text{HCl} \longrightarrow 2\text{CrCl}_3 + 2\text{KCl} + 3\text{Cl}_2 + 7\text{H}_2\text{O}$  when 2.98g of  $\text{K}_2\text{Cr}_2\text{O}_7$  and 5.84 g of  $\text{HCl}$  were reacted. Then calculate :
  - The limiting reagent
  - Maximum amount of  $\text{CrCl}_3$  which can be produced
  - The amount of excess reagent remaining after the reaction is complete ?
  - How much ml of  $\text{Cl}_2$  will be evolved at STP after the reaction is complete ?

3. A sample of  $\text{KClO}_3$  on decomposition yielded 448 mL of oxygen gas at NTP. Calculate :  
 (a) weight of oxygen produced.                      (b) weight of  $\text{KClO}_3$  originally taken, and  
 (c) weight of  $\text{KCl}$  produced.
  
4. In a process for producing acetic acid, oxygen gas is bubbled into acetaldehyde containing manganese (II) acetate (catalyst) under pressure at  $60^\circ\text{C}$ .  

$$2\text{CH}_3\text{CHO} + \text{O}_2 \longrightarrow 2\text{CH}_3\text{COOH}$$
 In a laboratory test of this reaction, 20g of  $\text{CH}_3\text{CHO}$  and 10g of  $\text{O}_2$  were put into a reaction vessel  
 (a) How many gram of  $\text{CH}_3\text{COOH}$  can be produced?  
 (b) How many grams of the excess reactant remain after the reaction is complete?
  
5. What weight of  $\text{CO}$  is required to form  $\text{Re}_2(\text{CO})_{10}$  from 2.50 g of  $\text{Re}_2\text{O}_7$  according to the unbalanced reaction:  $\text{Re}_2\text{O}_7 + \text{CO} \rightarrow \text{Re}_2(\text{CO})_{10} + \text{CO}_2$
  
6. 1 g of dry green algae absorbs  $4.7 \times 10^{-3}$  mole of  $\text{CO}_2$  per hour by photosynthesis. If the fixed carbon atoms were all stored after photosynthesis as starch,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , how long would it take for the algae to double their own weight, assuming photosynthesis takes place at a constant rate ?
  
7. When a mixture of  $\text{NaBr}$  and  $\text{NaCl}$  is repeatedly digested with sulphuric acid, all the halogens are expelled and  $\text{Na}_2\text{SO}_4$  is formed quantitatively. With a particular mixture, it was found that the weight of  $\text{Na}_2\text{SO}_4$  obtained was precisely the same as the weight of  $\text{NaBr}$ - $\text{NaCl}$  mixture taken. Calculate the ratio of the weights of  $\text{NaCl}$  and  $\text{NaBr}$  in the mixture.
  
8. Equal weights of phosphorus and oxygen are heated in a closed vessel producing  $\text{P}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  in 1 : 1 mole ratio. If the limiting component is exhausted, find what fraction of which component is left over.
  
9. 0.75 mole of solid ' $\text{A}_4$ ' and 2 mole of gaseous  $\text{O}_2$  are heated in a sealed vessel, completely using up the reactants and producing only one compound. It is found that when the temperature is reduced to the initial temperature, the contents of the vessel exhibit a pressure equal to half the original pressure. What conclusions can be drawn from these data about the product of the reaction.
  
10. Equal weights of  $\text{Zn}$  metal and iodine are mixed together and the iodine is completely converted to  $\text{ZnI}_2$ . What fraction by weight of the original zinc remains unreacted ?
  
11. From the following reaction sequence,  

$$\text{CaC}_2 + \text{H}_2\text{O} \longrightarrow \text{CaO} + \text{C}_2\text{H}_2$$

$$\text{C}_2\text{H}_2 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_4$$

$$n\text{C}_2\text{H}_4 \longrightarrow (\text{C}_2\text{H}_4)_n$$
 Calculate the mass of polyethylene which can be produced from 10 kg of  $\text{CaC}_2$ .
  
12. From the following reactions,  

$$2\text{CoF}_2 + \text{F}_2 \longrightarrow 2\text{CoF}_3$$

$$(\text{CH}_2)_n + 4n \text{CoF}_3 \longrightarrow (\text{CF}_2)_n + 2n \text{HF} + 4n \text{CoF}_2$$
 Calculate how much  $\text{F}_2$  will be consumed to produce 1 kg of  $(\text{CF}_2)_n$ .

## 12. Stoichiometry

### (A) Gravimetric Analysis :

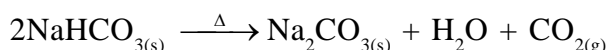
Gravimetric analysis is an analytical technique based on the measurements of mass of solid substances and/or volume of gaseous species. Gravimetric analysis is divided into three parts.

- (a) Mass-Mass relationship                      (b) Mass-volume relationship  
(c) Volume-volume relationship

#### (a) Mass-Mass Relationship :

It relates the mass of a species (reactant or product) with the mass of another species (reactants or product)

Let us consider a chemical reaction,



Suppose the mass of  $\text{NaHCO}_3$  being heated is 'a' g and we want to calculate the weight of  $\text{Na}_2\text{CO}_3$  being produced by heating of 'a' g of  $\text{NaHCO}_3$ .

The moles of  $\text{NaHCO}_3 = \frac{a}{84}$

According to the above balanced equation 2 moles of  $\text{NaHCO}_3$  upon heating gives 1 mole of  $\text{Na}_2\text{CO}_3$ . So,

The no. of moles of  $\text{Na}_2\text{CO}_3$  produced =  $\frac{1}{2} \times \frac{a}{84}$

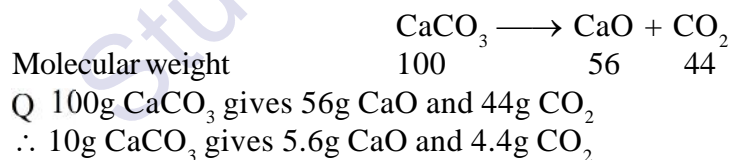
Thus, wt. of  $\text{Na}_2\text{CO}_3$  produced = moles of  $\text{Na}_2\text{CO}_3 \times \text{Molecular weight of } \text{Na}_2\text{CO}_3$

$$= \frac{1}{2} \times \frac{a}{84} \times 106 = \frac{53a}{84} \text{ gms}$$

#### Illustration 13 :

*By heating 10g of  $\text{CaCO}_3$ , 5.6g  $\text{CaO}$  is formed. What is the weight of  $\text{CO}_2$  obtained in this reaction?*

**Solution :**



#### (b) Mass-Volume Relationship :

It relates the mass of a species (reactant or product) and the volume of a gaseous species (reactant or product) involved in a chemical reaction. Suppose we are provided with 'a' gms of  $\text{NaHCO}_3$  in a vessel of capacity V L and the vessel is heated, so that  $\text{NaHCO}_3$

decomposes as  $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$

Now, we want to calculate the volume of  $\text{CO}_2$  gas being produced.

Moles of  $\text{NaHCO}_3$  taken =  $\frac{a}{84}$

Now, since 2 moles of  $\text{NaHCO}_3$  gives 1 mole of  $\text{CO}_2$  at STP. Thus

Moles of  $\text{CO}_2$  produced =  $\frac{1}{2} \times \frac{a}{84}$

As we know that 1 mole of any gas at STP occupies a volume of 22.4 L.

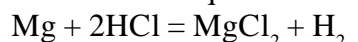
So, volume of  $\text{CO}_2$  produced =  $\left( \frac{1}{2} \times \frac{a}{84} \times 22.4 \right) \text{L}$

**Illustration 14 :**

*Calculate the volume of hydrogen liberated at 27°C and 760 mm pressure by treating 1.2g of magnesium with excess of hydrochloric acid.*

**Solution :**

The balanced equation is



1 mole                      1 mole

24g                          22.4 litre at NTP

24g of Mg liberate hydrogen = 22.4 litre

$$1.2\text{g of Mg will liberate hydrogen} = \frac{22.4}{24} \times 1.2 = 1.12 \text{ litre}$$

Volume of hydrogen under given condition can be calculated by applying

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 760 \text{ mm}$$

$$P_2 = 760 \text{ mm}$$

$$T_1 = 273 \text{ K}$$

$$T_2 = (27 + 273) = 300\text{K}$$

$$V_1 = 1.12 \text{ litres}$$

$$V_2 = ?$$

$$V_2 = \frac{760 \times 1.12}{273} \times \frac{300}{760} = 1.2308 \text{ litres}$$

**(c) Volume-Volume Relationship :**

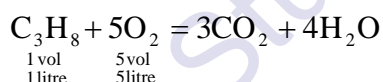
It relates the volume of gaseous species (reactants or products) with the volume of another gaseous species (reactant or product) involved in a chemical reaction.

**Illustration 15 :**

*What volume of oxygen gas at NTP is necessary for complete combustion of 20 litre of propane measured at 0°C and 760 mm. pressure.*

**Solution :**

The balanced equation is



1 vol  
1 litre      5 vol  
5 litre

1 litre of propane requires = 5 litre of oxygen

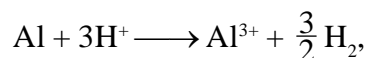
20 litre of propane will require = 5 × 20 = 100 litre of oxygen at 760 mm pressure and 0°C.

## 9. Daily Practice Problem Sheet

1. Calculate the volume of  $\text{CO}_2$  formed at STP by heating 4.2 g of  $\text{NaHCO}_3$ .
2. Calculate the amount of  $\text{CaCO}_3$  required to be heated in order to collect 1.12 litre of  $\text{CO}_2$  at STP.
3. Anhydrous sodium sulphate can absorb water vapour and be converted to the decahydrate. By how many grams would the mass of a 1-g sample of the thoroughly dried  $\text{Na}_2\text{SO}_4$  increase if exposed to sufficient water vapour to be converted to the decahydrate ?
4. 100 ml mixture of  $\text{O}_2$  and  $\text{O}_3$  when passed through pyrogallol (absorbs only  $\text{O}_3$ ) volume reduced by 20ml. 100 ml of this mixture when heated calculate the increase in total volume.
5. Calculate the volume of  $\text{O}_2$  required for complete combustion of 1 litre  $\text{CH}_4$  gas at STP.



6. 5 g of  $\text{CaCO}_3$  when heated the  $\text{CO}_2$  liberated was found 1 litre at STP. Calculate the percentage purity of the  $\text{CaCO}_3$  sample.
7. When 5 g mixture of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  was heated, 560 ml of  $\text{CO}_2$  was collected at STP. Calculate percentage of composition of the mixture.
8. 1 g mixture of cuprous oxide and cupric oxide was quantitatively reduced to 0.839 g of metallic copper. What was the weight of cupric oxide in the original sample ?
9. A 1-g sample of  $\text{KClO}_3$  was heated under such conditions that a part of it decomposed according to the equation :
  - (a)  $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$   
and the remaining underwent change according to the equation
  - (b)  $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 If the amount of  $\text{O}_2$  evolved was 146.8 mL at NTP, calculate the percentage by weight of  $\text{KClO}_4$  in the residue.
10. A solid mixture (5 g) consisting of lead nitrate and sodium nitrate was heated below  $600^\circ\text{C}$  until the weight of the residue is constant. If the loss in weight is 28 %, find the amount of the lead nitrate and sodium nitrate in the mixture ?
11. A 2-g sample containing  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  loses 0.248 g when heated to  $300^\circ\text{C}$ , the temperature at which  $\text{NaHCO}_3$  decomposes to  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . What is the percentage of  $\text{Na}_2\text{CO}_3$  in the given mixture ?
12. An alloy of aluminium, and copper was treated with aqueous HCl. The aluminium dissolved according to the reaction :



but the copper remained as pure metal. A 0.350 g sample of the alloy gave 415 cc of  $\text{H}_2$  measured at 273 K and 1 atm pressure. What is the weight percentage of Al in the alloy ?

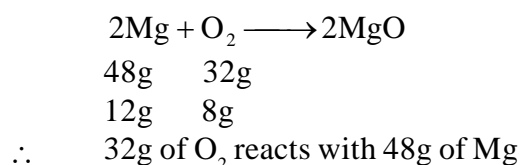
## (B) Volumetric Analysis

**Titration :** The process of determination of concentration of a solution of unknown concentration with the help of a solution of known concentration i.e., standard solution, is known as **TITRATION**.

Note : No. of equivalent of solute = Volume of solution (in litre)  $\times$  normality of solution

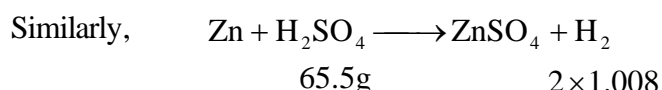
No. of milli equivalents of solute = Normality of solution  $\times$  Volume of solution in milliliters

**Equivalent Weight :** Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of that element e.g.



$$\therefore 8\text{g of O}_2 = \frac{48 \times 8}{32} = 12\text{g}$$

$$\therefore \text{Equivalent weight of Mg} = 12$$

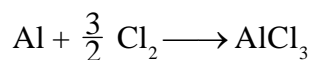


$$\ominus \quad 2 \times 1.008\text{g of hydrogen is displaced by } 65.5\text{g}$$



$$\therefore 1.008 \text{ g of H} = \frac{65.5}{2 \times 1.008} = 32.75 \text{ g}$$

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



32 g  $\frac{3}{2}$  × 71 g ⇌ 111.5 g chlorine reacts with 27 g of Al

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

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

As we can see from the above examples that equivalent weight is the ratio of atomic weight and a factor (say n-factor) which is in above three cases is their respective valencies. So,

$$\text{equivalent weight} = \frac{\text{atomic weight}}{\text{n - factor}}$$

In a similar way, the equivalent weight of acid/base is the ratio of molecular weight and the basicity/acidity and for oxidizing agents and reducing agent it is the ratio of molecular weight and the number of moles of electrons gained or lost. So in case of acid/base the n-factor is basicity/acidity (i.e. number of dissociable  $\text{H}^+$  ions/number of dissociable  $\text{OH}^-$  ion and in case of oxidizing agent/reducing agent, n-factor is number of moles of electrons gained/lost per mole of oxidizing agent/reducing agent. Therefore, in general, we can write.

$$\text{Equivalent weight (E)} = \frac{\text{Atomic or molecular weight}}{\text{n - factor}}$$

$$\text{No. of equivalents of solute} = \frac{\text{Wt}}{\text{Eq. wt.}} = \frac{\text{W}}{\text{E}} = \frac{\text{W}}{\text{M/n}}$$

$$\text{No. of equivalents of solute} = \text{No. of moles of solute} \times \text{n-factor}$$

$$\text{And also Normality} = \text{n-factor} \times \text{molarity of solution}$$

## 10. Daily Practice Problem Sheet

- \* Equivalent weight of any substance is the weight in gram which combines with 1 gram of hydrogen, 8 grams of oxygen, 35.5 grams of Cl and 108 grams of Ag.
- \* 
$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{'n' factor}}$$
- 1. The equivalent weight of a metal is 36. What weight of the metal would give 9.322 gm of its chloride ?
- 2. On heating  $5 \times 10^{-3}$  equivalent of  $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$ , 0.18 gm of water is obtained, what is the value of x ?
- 3. The equivalent weight of a metal is double that of oxygen. How many times is the weight of its oxide greater than the weight of the metal ?

4. 0.224 gm of a metal when dissolved in dilute acid liberates 285 cc of hydrogen, measured at 17°C and 78 cm of mercury pressure. Find the equivalent weight of the metal.
5. 1.82 g of a metal required 32.5 mL of N HCl to dissolve it. What is equivalent weight of metal ?
6. The equivalent weight of a metal is 30. What volume of chlorine would be liberated at 27°C and 750 mm pressure by 0.6 gm of the metal ? [ Aqueous tension at 27°C = 26.6 mm ]
7. The molecular formula of an oxide of an element X is  $X_m O_n$  what is the equivalent weight of the metal ? [ Given atomic weight of X = a ]
8. 12 g of an element combines with 32 g of oxygen. What is the equivalent weight of the element if the equivalent weight of oxygen is 8 ?
9. Equivalent weight of sulphur in  $SCl_2$  is 16, what is the equivalent weight of S in  $S_2Cl_2$  ? [ S = 32 , Cl = 35.5 ]
10. 1.60 gm of a metal were dissolved in  $HNO_3$  to prepare its nitrate. The nitrate was strongly heated to give 2 g oxide. Calculate equivalent weight of metal.
11. From 3.36 gm of Fe, 4.80 gm of iron oxide is obtained. What is the equivalent weight of Fe ?
12. 1.0 g of metal nitrate gave 0.86 g of metal sulphate. Calculate equivalent weight of metal.
13. An element forms two oxides, the weight ratio composition in them, A : O = x : y in the first oxide and y : x in the second oxide. If the equivalent weight of A in the first oxide is 10.33, Calculate the equivalent weight of A in the second oxide .

### Calculation of n-factor

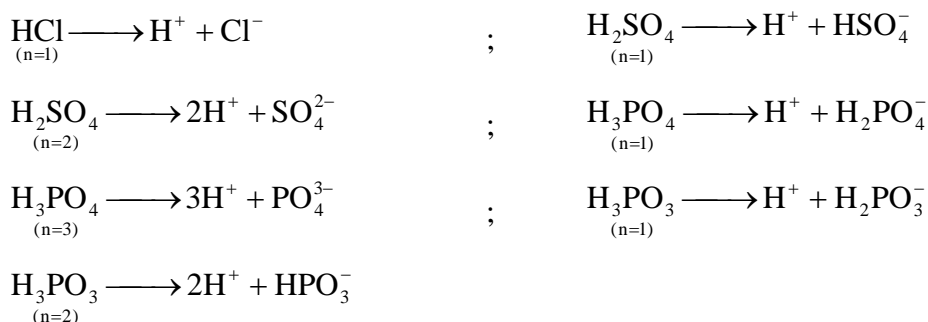
For calculating the n-factor of any reactant in any reaction. One must know the kind of reaction it is, the reactions may be classified into the following three types .

- (a) Acid-Base Reactions/Neutralization reactions
- (b) Redox Reactions
- (c) Precipitation Reactions/Double decomposition reactions

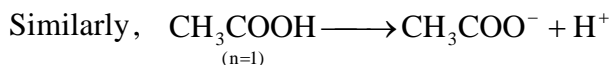
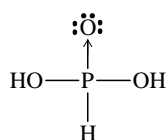
#### (a) Acid-Base Reaction :

According, to the Arrhenius, an acid is a substance that furnishes  $H^+$  ion(s) in solution, a base is a substance that furnishes  $OH^-$  ion(s) in solution and neutralization is a reaction in which  $H^+$  ion furnished by acid combines with  $OH^-$  ions furnished by base. The number of  $H^+$  ion(s) furnished per molecule of the acid is its n-factor also called basicity. Similarly the number of  $OH^-$  ion(s) furnished by the base per molecule is its n-factor, also called acidity.

#### Some Examples

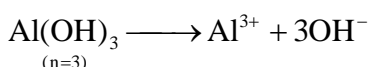
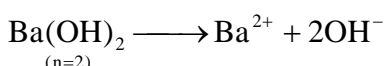
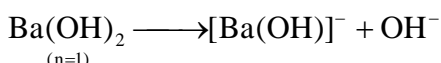
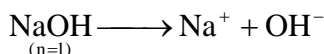


The n-factor of  $H_3PO_3$  cannot be 3 as it has only two dissociable  $H^+$  ions. So, its n-factor or dissociable protons is 1 or 2 as one of the H-atoms is linked with P atom directly.



n-factor of  $\text{CH}_3\text{COOH}$  is 1, because it contains only one dissociable  $\text{H}^+$  ion.

Now, we will consider the n-factor of some bases.



Similarly, n-factor of  $\text{Al(OH)}_3$  can also be 1 or 2 or 3, depending upon the number of  $\text{OH}^-$  released.

## 11. Daily Practice Problem Sheet

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{'n' factor}}$$

**Note :** Molecular weight is the mass of 1 mole of any substance hence 'n' factor is always calculated for 1 mole of substance.

Acids :

1. Calculate the 'n' factor of following acids :

- |   |                              |
|---|------------------------------|
| (a) $\text{H}_2\text{C}_2\text{O}_4$  | (b) $\text{H}_2\text{SO}_4$  |
| (c) $\text{H}_3\text{PO}_2$   | (d) $\text{KHC}_2\text{O}_4$ |
| (e) $\text{H}_3\text{BO}_3$   | (f) $\text{H}_3\text{PO}_4$  |
| (g) $\text{NaHC}_2\text{O}_4 \cdot \text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$                                 | (h) $\text{HNO}_2$           |
| (i) $\text{H}_2\text{S}$  | (j) $\text{CH}_3\text{COOH}$ |
| (k) $\text{Al}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{C}_2\text{O}_4$   | (l) $\text{H}_3\text{PO}_3$  |
| (m) $\text{H}_2\text{SO}_3$   | (n) $\text{HNO}_3$           |
| (o) $\text{SnC}_2\text{O}_4 \cdot 2\text{NaHC}_2\text{O}_4 \cdot 3\text{KHC}_2\text{O}_4 \cdot 4\text{H}_2\text{C}_2\text{O}_4$ |                              |

2. Find equivalent weight of  $\text{H}_2\text{SO}_4$  in the following cases :

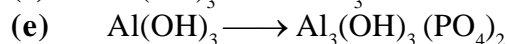
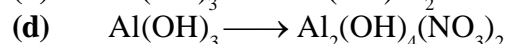
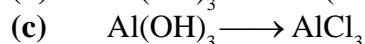
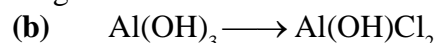
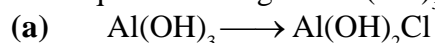
- |  |  |
|--|--|
| (a) $\text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4$                     | (b) $\text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4$     |
| (c) $\text{H}_2\text{SO}_4 \longrightarrow \text{Na}_3\text{H}(\text{SO}_4)_2$ | (d) $\text{H}_2\text{SO}_4 \longrightarrow \text{KH}_3(\text{SO}_4)_2$ |

Bases :

3. Calculate the 'n' factor and equivalent weight of following bases :

- |                                  |                            |  |
|----------------------------------|----------------------------|--|
| (a) $\text{NaOH}$                | (b) $\text{NH}_4\text{OH}$ | (c) $\text{Al(OH)}_3$                        |
| (d) $\text{Mg(OH)}_2$            | (e) $\text{MgAl(OH)}_5$    | (f) $\text{Fe(OH)}_3$                        |
| (g) $\text{Na}_3\text{Al(OH)}_6$ | (h) $\text{KOH}$           | (i) $\text{Ca}_2\text{Al}_3(\text{OH})_{13}$ |
| (j) $\text{Zn(OH)}_2$            |                            |  |

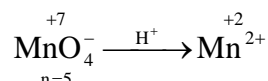
4. Find equivalent weight of  $\text{Al}(\text{OH})_3$  in the following reactions :



## (B) Redox Reactions

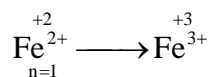
Those reactions which involve the exchange of electrons are called redox reactions. For the calculation of n-factor of oxidising agent or reducing agent, the method depends upon the change in oxidation state of the species considered. We will discuss them one by one.

(i) When only one atom undergoing either reduction or oxidation e.g.

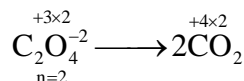


In such a case, we consider the change in oxidation state of atom undergoing oxidation or reduction change per molecule as the n-factor of the species.

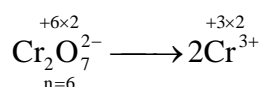
$$\text{n-factor} = |(+2) \times 1 - (+7) \times 1| = 5$$



$$\text{n-factor} = |(+3) \times 1 - (+2) \times 1| = 1$$



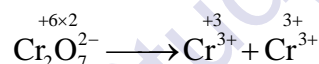
$$\text{n-factor} = |(+4) \times 2 - (+3) \times 2| = 2$$



$$\text{n-factor} = |(+3) \times 2 - (+6) \times 2| = 6$$

(ii) Salts which reacts in such a way that only one atom undergoes change in oxidation state but appears in two products with the same oxidation state :

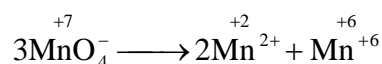
In such a case the method of calculation of n-factor remains the same i.e., we will calculate the change in oxidation state of the atom per mole of that substance (reactant).



In this example, oxidation state of Cr changes from +6 to +3 in both the products. So

$$\text{n-factor} = |(+6) \times 2 - (+3) \times 2| = 6$$

(iii) Salts which react in such a way that only one atom undergoes change in oxidation state but goes in two products with different oxidation state as a result of either only oxidation or only reduction.



In such a case, it is impossible to calculate the n-factor until and unless one knows that how much of  $\text{MnO}_4^-$  is changing to  $\text{Mn}^{2+}$  and how much to  $\text{Mn}^{6+}$  and if one knows the balanced equation then there is no need of calculation of n-factor. Nevertheless in such case the n-factor can be calculated by deducing the total change in oxidation state divided by total number of atom undergoing reduction/oxidation change. So, for the calculation of n-factor in the above example, out of three moles of  $\text{MnO}_4^-$ , two moles are being converted to  $\text{Mn}^{2+}$  and one mole changes to  $\text{Mn}^{6+}$ . So total decrease in oxidation state of Mn.

$$= |2 \times (+2) - 2 \times (+7)| + |1 \times (+6) - 1 \times (+7)|$$

$$= |4 - 14| + |6 - 7| = 11$$

$$\text{So, n-factor} = \frac{11}{3}$$

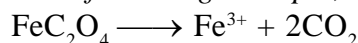
- (iv) *Salts which react in such a way that only one atom undergoes change in oxidation state in two product, in one product with changed oxidation state and in other product with same oxidation state as that of reactant.*

In such case also one cannot calculate the n-factor without knowing the balanced chemical equation because one must know how much of atom has changed its oxidation state. For example,



Let us calculate the n-factor of HCl. Out of 14 moles of  $\text{Cl}^-$  (in HCl) only 6 moles of  $\text{Cl}^-$  are changing its oxidation state from  $-1$  to  $0$  in the product  $\text{Cl}_2$  and the oxidation state of remaining 8  $\text{Cl}^-$  ions remains same in KCl and  $\text{CrCl}_3$ . So, total no. of moles of electrons lost by 14 moles of HCl is 6. So each mole of HCl takes up  $6/14$  i.e.,  $3/7$  moles of electrons and hence n-factor of HCl is  $3/7$ .

- (v) *Salts which react in such a way that two or more atoms in the salt undergoes change in oxidation states as a result of either oxidation or reduction. Let us consider the following example,*



In this case, the oxidation of both  $\text{Fe}^{2+}$  and  $\text{C}^{3+}$  are changing from  $+2$  and  $+3$  to  $+3$  and  $+4$  respectively. In such a case we will calculate the n-factor of the salt as the total increase or decrease in oxidation state per mole of the salt. As one can see that one mole of  $\text{FeC}_2\text{O}_4$  contains one mole of  $\text{Fe}^{2+}$  and one mole of  $\text{C}_2\text{O}_4^{2-}$  (i.e. 2 carbon atoms per mole of  $\text{C}_2\text{O}_4^{2-}$ ).

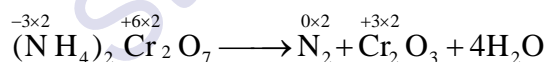
Total change in oxidation state

$$= |1 \times (+2) - 1 \times (+3)| + |2 \times (+3) - 2 \times (+4)|$$

$$= 1 + 2 = 3$$

So, n-factor of  $\text{FeC}_2\text{O}_4$  is 3

- (vi) *Salts which react in such a way that two atoms undergoing change in oxidation state but one undergoing oxidation and other reduction reaction. In such a case one has to calculate the change in oxidation state of either the atom being oxidized or the atom being reduced. For example,*



In this reaction, the oxidation state of N is increasing by 6 units and that of Cr is decreasing by 6 unit. So, we can consider either oxidation or reduction product for the calculation of n-factor and it will be the same.

n-factor of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  considering oxidation

$$= |(-3) \times 2 - (0) \times 2| = 6$$

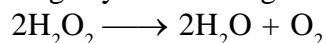
n-factor of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  considering reduction

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

- (vii) *Species which undergoes disproportionation reaction: Those reaction in which oxidant and reductant are the same species or the same element from the species is getting oxidized as well as reduced.*

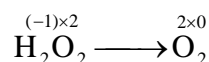
When the number of moles of atoms being oxidized is equal to the number of moles of atoms being reduced.

The n-factor can be calculated by knowing the balanced chemical equation and considering any of the change taking place. Say for example,



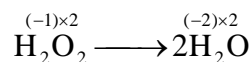
Out of 2 moles of  $\text{H}_2\text{O}_2$  consumed in the reaction, one mole of  $\text{H}_2\text{O}_2$  is being oxidized ( $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2$ ) and one mole of  $\text{H}_2\text{O}_2$  is being reduced ( $\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ ). First

consider the oxidation reaction



$$\text{n-factor} = |2 \times 0 - (-1) \times 2| = 2$$

Again, considering reduction reaction

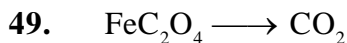
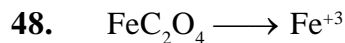
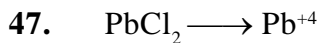
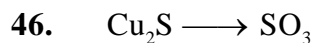
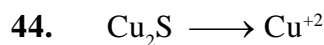
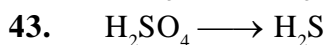
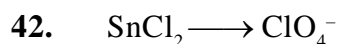
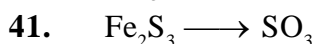
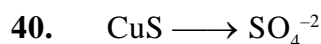
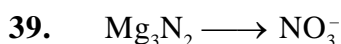
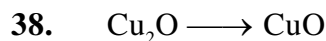
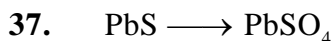
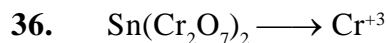
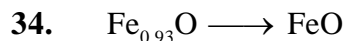
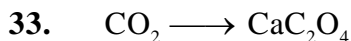
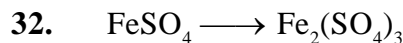
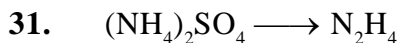
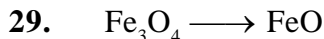
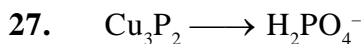
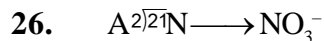
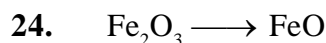
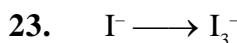
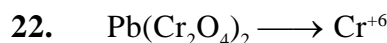
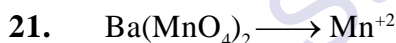
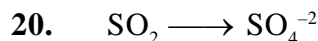
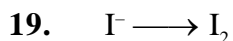
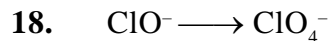
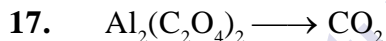
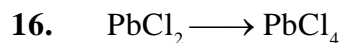
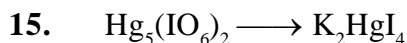
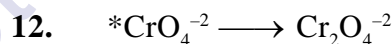
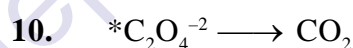
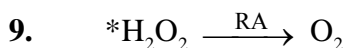
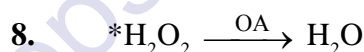
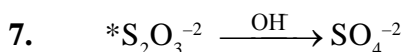
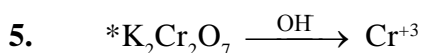
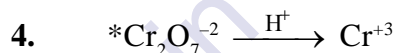
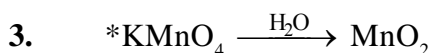
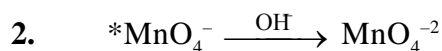
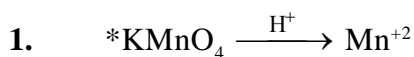


$$\text{n-factor} = |(-2) \times 2 - (-1) \times 2| = 2$$

So, n-factor of  $\text{H}_2\text{O}_2$  either considering oxidation or reduction reaction is same i.e. 2.

## 12. Daily Practice Problem Sheet

**I** Calculate n factor of the reactants in the following reaction in which only 1 atom undergo change in oxidation state



**II** Calculate 'n' factor of reactants in the following reactions in which more than 1 atoms undergo change in oxidation state :

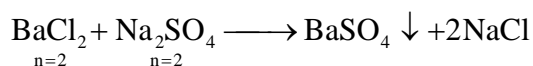
- $\text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{+3} + \text{CO}_2$
- $\text{Cu}_2\text{S} \longrightarrow \text{Cu}^{+2} + \text{SO}_4^{-2}$
- $\text{Pb}(\text{N}_3)_2 \longrightarrow \text{Pb}_3\text{O}_4 + \text{NO}$
- $\text{As}_2\text{S}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{SO}_3$
- $\text{Cu}_3\text{P} \longrightarrow \text{Cu}^{+2} + \text{H}_3\text{PO}_4$
- $\text{CrI}_3 \longrightarrow \text{CrO}_4^{-2} + \text{IO}_4^{-}$
- $\text{FeS}_2 \longrightarrow \text{Fe}^{+3} + \text{SO}_2$
- $\text{Co}(\text{MnO}_4)_3 \longrightarrow \text{CoO} + \text{MnO}_2$
- $\text{FeCr}_2\text{O}_4 \longrightarrow \text{Fe}_2\text{O}_3 + \text{K}_2\text{CrO}_4$
- $\text{SnC}_2\text{O}_4 \longrightarrow \text{Sn}^{+4} + \text{CO}_2$

**III** Calculate 'n' factor of reactants in the following disproportionation reactions

- $\text{Br}_2 \longrightarrow \text{Br}^- + \text{BrO}_3^-$
- $\text{ClO}_3^- \longrightarrow \text{ClO}_4^- + \text{Cl}^-$
- $\text{S} \longrightarrow \text{S}^{-2} + \text{S}_2\text{O}_3^{-2}$
- $2\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
- $2\text{Cu}^+ \longrightarrow \text{Cu}^{+2} + \text{Cu}$

### (c) Precipitation/Double Decomposition Reactions :

In such reaction, there is no change in oxidation state of any atom. The n-factor of the salt can be calculated by multiplying the oxidation state of the cation/anion by total no. of atoms per molecule of the salt. For example



for  $\text{BaCl}_2$

n-factor = Oxidation state of Ba atom in  $\text{BaCl}_2 \times$  number of Ba atoms in 1 molecule of  $\text{BaCl}_2$

$$= (+2) \times 1 = 2$$

for  $\text{Na}_2\text{SO}_4$

n-factor = Oxidation state of Na  $\times$  number of Na-atoms in 1 molecule of  $\text{Na}_2\text{SO}_4$   
 $= (+1) \times 2 = 2$

## 13. Titration

The process of determination of concentration of a solution with the help of a solution of known concentration (standard solution) is called titration.

Titration is divided into following three categories.

- Simple Titration
  - Acid base titration
  - Double Titration
  - Redox titration
- Back Titration
- Iodimetric and Iodometric Titration

### (a) Simple Titration :

A known volume of the solution of unknown concentration is taken in a flask and required reagents are added to it. The solution of known concentration is added from the burette in the solution of unknown concentration till the latter reacts completely. This process is called titration. At the end point (equivalence point) the equivalents or milliequivalents of the two reacting substances are equal.

$$\text{Volume of solution (A)} = V_A \text{ litres}$$

$$\text{Normality of solution (A)} = N_A$$

$$\text{Equivalents of substance (A)} = N_A V_A$$

$$\text{Similarly equivalents of substance (B)} = N_B V_B$$

At the equivalence point (end point) the equivalents (not the moles) of the two substance are equal.

$$N_A V_A \text{ (litre)} = N_B \times V_B \text{ (litre)}$$

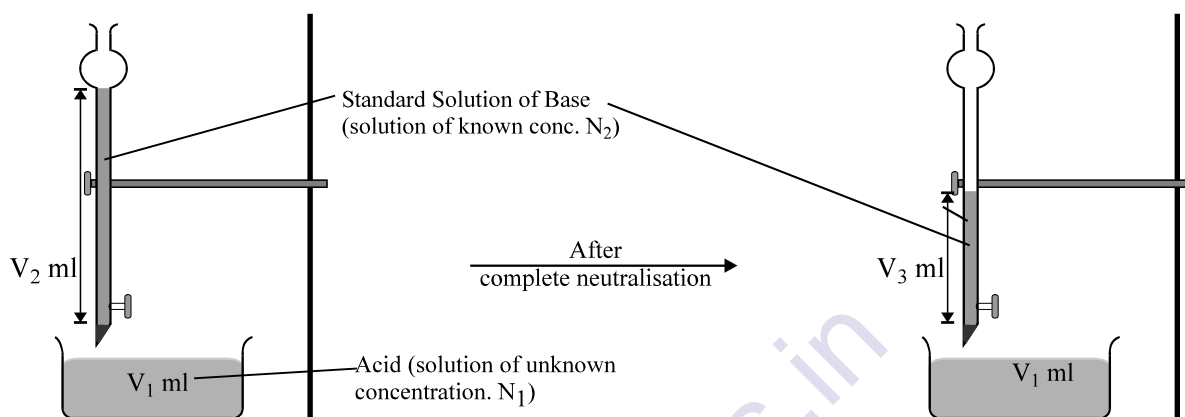
**Simple titrations can be studied under following three headings :**

(i) Acid base titration      (ii) Double Titration      (iii) Redox titration

**(i) ABT (Acid Base Titration) :**

In this type of titration an acid is reacted with base

For ABT,      **Meq. of acid = Meq. of base**



In the above figure

$$\begin{aligned} \text{Meq. of acid} &= N_1 V_1 \\ \text{Meq. of acid} &= N_2 (V_2 - V_3) \\ \therefore N_1 V_1 &= N_2 (V_2 - V_3) \end{aligned}$$

**Illustration 16 :**

**40 ml N/10 HCl and 60 ml N/20 KOH are mixed together. Calculate the normality of the acid or base left. What is the normality of the salt formed in the solution?**

**Solution :**

$$\text{Milli equivalents of HCl} = N \times V \text{ (ml)} = \frac{1 \times 40}{10} = 4$$

$$\text{Milli equivalents of KOH} = N \times V \text{ (ml)} = \frac{1 \times 60}{20} = 3$$

One milli equivalent of an acid neutralizes one milli equivalent of a base

$$\text{Milli equivalent of HCl left} = 4 - 3 = 1$$

$$\text{Total volume of the solution} = 40 + 60 = 100 \text{ ml}$$

$$\text{Milli equivalents of HCl} = N \times V \text{ (ml)}$$

$$1 = N \times 100$$

$$\text{Normality (N) of HCl left in solution} = 0.01$$

Salt formed = Milli equivalent of acid or base neutralized

$$\text{Milli equivalents of the salt formed} = N \times V \text{ (ml)}$$

$$3 = N \times 100$$

$$\text{Normality (N) of salt formed} = 0.03$$



## 13. Daily Practice Problem Sheet

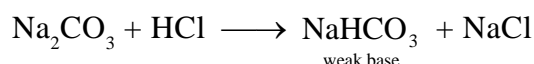
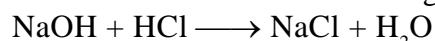
1. A solution containing 4.2 g of KOH and  $\text{Ca}(\text{OH})_2$  is neutralized by an acid. If it consumes 0.1 equivalent of acid, calculate composition of sample in solution.
  2. Gastric juice contains 3.0 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day, how many antacid tablets each containing 400 mg of  $\text{Al}(\text{OH})_3$  are needed to neutralize all the HCl produced in one day ?
  3. 2.5 g of a double sulphate of iron and ammonia on boiling with NaOH liberated  $\text{NH}_3$  gas which exactly neutralised 12.8 mL of normal  $\text{H}_2\text{SO}_4$ . Determine the percentage of  $\text{NH}_3$  in the double salt. [8.71 %]
  4. The formula weight of an acid is 82.0. 100  $\text{cm}^3$  of a solution of this acid containing 39.0 g of the acid per litre were completely neutralized by 95.0  $\text{cm}^3$  of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid ?
  5. What volume at NTP of ammonia gas will be required to be passed into 30 mL of  $\text{NH}_2\text{SO}_4$  solution to bring down the acid normality to 0.2 N ?
  7. What volume of a solution of hydrochloric acid containing 73 g of acid per litre would suffice for the exact neutralization of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water ?
  8. Calculate the volume of a dibasic acid of normality 0.1 N which is just sufficient to neutralize 1 g of base which furnishes 0.04 mole of  $\text{OH}^-$  in solution.
  9. Two acids  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  are neutralized separately by the same amount of an alkali when sulphate and dihydrogen phosphates are formed respectively. Find the ratio of the masses of  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ .
  10. 100 g of HCl solution of specific gravity 1.17 g/mL contains 33.4 g of HCl. What volume of this HCl solution will be required to exactly neutralize 5 litres of 0.1 N NaOH solution ?
  11. 2.505 g of hydrated dibasic acid requires 35 mL of 1 N NaOH solution for complete neutralization. When 1.01 g of the hydrated acid is heated to constant weight, 0.72 g of the anhydrous acid is obtained. Calculate degree of hydration of the acid.
  12. Oxalic acid,  $(\text{COOH})_2$ , reacts with NaOH according to  

$$(\text{COOH})_2 + 2\text{NaOH} \longrightarrow (\text{COONa})_2 + 2\text{H}_2\text{O}$$
 If 0.816 g of oxalic acid dihydrate,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , is dissolving in water and titrated with 0.120 M NaOH solution, what volume of NaOH will be needed ?
  13. A mixture of NaOH and  $\text{Mg}(\text{OH})_2$  weighs 2.325 g. It requires 3 g of  $\text{H}_2\text{SO}_4$  for its neutralization. What is % composition of mixture ?
  14. 0.9698 g of an acid are present in 300 mL of a solution. 10 mL of this solution requires exactly 20 mL of 0.05 N KOH solution. Calculate equivalent weight of acid. If molecular weight of acid is 98, calculate no. of neutralizable protons.
- (b) **Double Titration :**  
 If an aqueous solution contains a mixture of any two of the three NaOH,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  and it has to be titrated against an acid HCl or  $\text{H}_2\text{SO}_4$ , it will require two indicators to determine the strength of the bases present. The two indicators used are phenolphthalein and methyl orange.

**Method :** A given volume of the aqueous solution of the bases is taken and phenolphthalein indicator is added to it. This solution is titrated with an acid of known normality to the end point the volume of the acid used is noted. This end point is called first end point. Now in the same solution methyl orange is added and again titrated with an acid of known strength to the end point. It is called second end point. The volume of acid, used in the second end point is also noted. The normality of the bases present is then calculated.

**Principle :** In the presence of phenolphthalein indicator

- (i) NaOH is completely neutralized by the acid.
- (ii) Only half of the milliequivalents of  $\text{Na}_2\text{CO}_3$  present are titrated as the phenolphthalein will show the colour change when only  $\text{NaHCO}_3$  (weak base) and neutral species are left in the reaction mixture. The following reactions take place,



Since phenolphthalein is a weak organic acid, and it changes its colour in weakly basic medium ( $\text{NaHCO}_3$ ), so as soon as the  $\text{Na}_2\text{CO}_3$  is converted to  $\text{NaHCO}_3$  phenolphthalein shows the colour change indicating the completion of the reaction.

In the presence of methyl orange, all the basic substances left in the mixture will be neutralized by acid and methyl orange will show the colour change when the medium is weakly acidic ( $\text{H}_2\text{O} + \text{CO}_2$  i.e.  $\text{H}_2\text{CO}_3$ ).

### 1. **Titration of the solution containing both NaOH and $\text{Na}_2\text{CO}_3$ :**

A given volume of the aqueous solution is titrated with an acid of known normality using phenolphthalein indicator. Suppose 'a' milli equivalents of acid are used in the first end point then,

$$\text{milli equivalent of NaOH} + \frac{1}{2} \text{ milli equivalent of Na}_2\text{CO}_3 = \text{milli equivalent of acid} = a \quad \dots(1)$$

Now in the same already titrated solution methyl orange indicator is added and again titrated to the end point. Suppose 'b' milli equivalents of the acid are used at the second end point.

$$\frac{1}{2} \text{ milli equivalents of Na}_2\text{CO}_3 = \text{milli equivalents of acid} = b \quad \dots(2)$$

From equation (1) and (2)

$$\begin{aligned} \text{Milli equivalents of acid used by Na}_2\text{CO}_3 &= 2b \\ &\equiv \text{milli equivalents of Na}_2\text{CO}_3 \\ \text{Milli equivalents of acid used by NaOH} &= a - b \\ &= \text{milli equivalent of NaOH} \end{aligned}$$

Knowing the milli equivalents of  $\text{Na}_2\text{CO}_3$  or NaOH and the volume of the solution titrated, their normality can be calculated.

### Illustration 17 :

*NaOH and  $\text{Na}_2\text{CO}_3$  are dissolved in 200 ml aqueous solution. In the presence of phenolphthalein indicator. 17.5 ml of 0.1 N HCl are used to titrate this solution. Now methyl orange is added in the same solution titrated and it requires 2.5 ml of the same HCl. Calculate the normality of NaOH and  $\text{Na}_2\text{CO}_3$  and their mass present in the solution.*

### Solution :

Milli equivalents (a) of HCl used in the presence of phenolphthalein indicator.

$$\begin{aligned} &= N \times V \text{ (ml)} \\ &= 0.1 \times 17.5 = 1.75 \end{aligned}$$

$$1.75 \text{ (a)} = \text{milli. eq. of NaOH} + \frac{1}{2} \text{ milli eq. of Na}_2\text{CO}_3 \quad \dots(1)$$

Milli eq. (b) of HCl used in the presence of methyl orange indicator

$$= N \times V \text{ (ml)}$$

$$= 0.1 \times 2.5 = 0.25$$

$$0.25 \text{ (b)} = 1/2 \text{ milli equivalents of } \text{Na}_2\text{CO}_3 \quad \dots(2)$$

**For  $\text{Na}_2\text{CO}_3$  solution:** From equation(2)

$$\text{Milli eq. of acid used by } \text{Na}_2\text{CO}_3 = 2b$$

$$= 2 \times 0.25 = 0.5$$

$$\text{Volume of } \text{Na}_2\text{CO}_3 \text{ solution} = 200 \text{ ml}$$

$$\text{Suppose, Normality of } \text{Na}_2\text{CO}_3 = N$$

$$\text{Milli equivalents of } \text{Na}_2\text{CO}_3 = N \times V \text{ (ml)} = 200N$$

Putting equivalents of acid and  $\text{Na}_2\text{CO}_3$  equal.

$$200N = 0.5$$

$$\text{or (Normality of } \text{Na}_2\text{CO}_3 \text{ solution) } N = \frac{1}{400}$$

$$\text{Mass of } \text{Na}_2\text{CO}_3 = N \times E \times V \text{ (litre)}$$

$$(\text{E for } \text{Na}_2\text{CO}_3 = 53) = \frac{1}{400} \times 53 \times 0.2$$

$$= \mathbf{0.0265 \text{ gram}}$$

**For NaOH solution:** From equation (1) and (2)

$$\text{Milli eq. acid used by NaOH} = a - b = 1.75 - 0.25$$

$$= 1.50$$

$$\text{Volume of NaOH solution} = 200 \text{ ml}$$

$$\text{Suppose, Normality of NaOH solution} = N$$

$$\text{Mili eq. of NaOH} = N \times V \text{ (ml)} = 200 N$$

Putting the mili eq. of NaOH and acid used equal

$$200 N = 1.5$$

$$(\text{Normality of NaOH solution}) \quad N = \frac{1.5}{200}$$

$$\text{Mass of NaOH} = N \times E \times (V \text{ litres})$$

$$= \frac{1.5}{200} \times 40 \times 0.2$$

$$(\text{E for NaOH} = 40) = \mathbf{0.06g}$$

## 2. **Titration of the solution containing both $\text{Na}_2\text{CO}_3$ and $\text{NaHCO}_3$ :**

Given volume of the solution is titrated by an acid using phenolphthalein indicator. Suppose 'a' milli equivalents of acid are used in the first end point. Then

$$1/2 \text{ milli equivalent of } \text{Na}_2\text{CO}_3 = \text{milli equivalents of acid} = a \dots(1)$$

Now in the same already titrated solution methyl orange indicator is added and again titrated to the end point. Suppose 'b' milli equivalents of the acid are used at the second end point. Then

$$1/2 \text{ milli equivalents of } \text{Na}_2\text{CO}_3 + \text{milli equivalents of } \text{NaHCO}_3$$

$$= \text{milli equivalents of acid} = b \dots(2)$$

From equation (1) and (2)

$$\text{Milli equivalents of acid used by } \text{Na}_2\text{CO}_3 = 2a$$

$$\equiv \text{milli equivalents of } \text{Na}_2\text{CO}_3$$

$$\text{Milli equivalents of acid used by } \text{NaHCO}_3 = b - a$$

$$= \text{milli equivalent of } \text{NaHCO}_3$$

Knowing the milli equivalents of the base and volume of the solution titrated, the normality (strength) of the bases can be calculated.

**Illustration 18 :**

*Both  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  are present in an aqueous solution. In the presence of phenolphthalein indicator 10 ml of this solution requires 2.5 ml of 0.1M  $\text{H}_2\text{SO}_4$  for titration. After this methyl orange is added in the same solution and titration requires 5 ml M  $\text{H}_2\text{SO}_4$ . Calculate the concentration of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in g/litre.*

**Solution :**

Milli eq. (a) of  $\text{H}_2\text{SO}_4$  used in the presence of phenolphthalein indicator  
 $= N \times V \text{ (ml)} = 0.1 \times 2 \times 2.5 = 0.5$

$$a = 0.5 = \frac{1}{2} \text{ milli equivalents of } \text{Na}_2\text{CO}_3 \quad \dots(1)$$

Milli. eq. (b) of  $\text{NaHCO}_3 + \frac{1}{2}$  milli eq. of  $\text{Na}_2\text{CO}_3 \quad \dots(2)$

**For  $\text{Na}_2\text{CO}_3$  solution:** From equation (1)

Milli eq. of acid used by  $\text{Na}_2\text{CO}_3 \quad = 2 \times 0.5 = 1$

Suppose, Normality of  $\text{Na}_2\text{CO}_3$  solution = N

Volume of  $\text{Na}_2\text{CO}_3$  solution taken = 10 ml

Milli eq. of  $\text{Na}_2\text{CO}_3$  taken =  $N \times V \text{ (ml)} = 10 N$

Putting the milli eq. of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  equal,

$$1 = 10 N$$

or (Normality of  $\text{Na}_2\text{CO}_3$ )  $N = 0.1$

Strength (S) in g/litre =  $N \times E$

$$= 0.1 \times 53 \text{ (E for } \text{Na}_2\text{CO}_3 = 53)$$

$$= \mathbf{5.3 \text{ g/litre}}$$

**For  $\text{NaHCO}_3$  solution:** From equations (1) and (2) milli eq. of acid used by

$$\text{NaHCO}_3 = b - a = 1.0 - 0.5 = 0.5$$

Suppose, Normality of  $\text{NaHCO}_3$  solution = N

Volume of  $\text{NaHCO}_3$  solution taken = 10 ml

Milli equivalents of  $\text{NaHCO}_3$  taken = 10 N

Putting the milli eq. of  $\text{H}_2\text{SO}_4$  and  $\text{NaHCO}_3$  equal,

$$0.5 = 10 N$$

or (Normality of  $\text{NaHCO}_3$  solution)  $N = 0.05$

Strength (S) in g/litre =  $N \times E$

$$\text{(E for } \text{NaHCO}_3 = 84) \quad = 0.05 \times 84 = \mathbf{4.2 \text{ g/litre}}$$

## 14. Daily Practice Problem Sheet

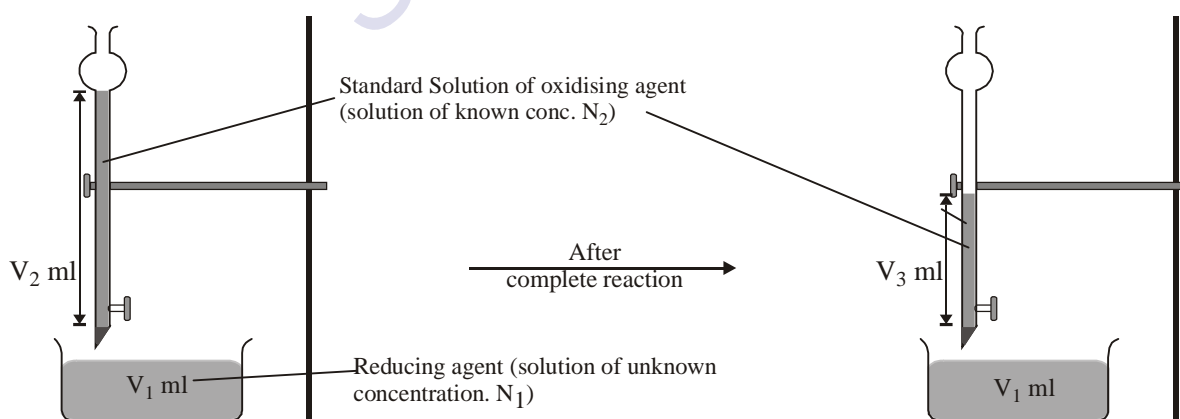
- A solution of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  is prepared 25 ml of this solution required for neutralization :
  - 25 ml of 0.08 N  $\text{HCl}$  when phenolphthalein is used as indicator
  - 35 ml of 0.08 N  $\text{HCl}$  when methyl orange is used as indicator. Find the strength of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .
- 8 gram of a mixture of anhydrous  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  was dissolved in water and made upto 1000 ml. 25 ml of this solution required for neutralization :
  - 32.51 ml of N/10  $\text{HCl}$  using methyl orange &
  - 11.80 ml of N/10  $\text{HCl}$  using phenolphthalein. Find the strength of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ .
- 25 ml of a mixture of  $\text{NaOH} + \text{Na}_2\text{CO}_3$ , when titrated with 0.1 N  $\text{HCl}$  using phenolphthalein indicator required 25 ml  $\text{HCl}$  to decolourise phenolphthalein. At this stage methyl orange was added and addition of acid was continued. The second end point was reached after further addition of 5 ml of the acid. Calculate the amount of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  per litre of the solution.

4. A solution contained  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . 25 ml of this solution required 5 ml of 0.1 N HCl for titration with phenolphthalein as indicator. The titration was repeated with the same volume of the solution but with methyl orange 12.5 ml of 0.1 N HCl was required this time. Calculate the amount of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in the solution.
5. A mixed solution of KOH and  $\text{Na}_2\text{CO}_3$  required 20 ml of N/20 HCl solution when titrated with phenolphthalein as indicator. But the same amount of solution when titrated with methyl orange as indicator required 30 ml of the same acid. Calculate the amount of KOH and  $\text{Na}_2\text{CO}_3$ .
6. 50 ml of a solution, containing 1 g each of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and NaOH, was titrated with N HCl. What will be the titre reading if :
  - (a) only phenolphthalein is used as indicator ?
  - (b) only methyl orange is used as indicator from the very beginning ?
  - (c) methyl orange is added after the first end point with phenolphthalein ?
7. 20 mL of a mixed solution of  $\text{Na}_2\text{CO}_3$  and NaOH required 17.5 mL of N/10 HCl when titrated within phenolphthalein as indicator. But when methyl orange added, a second end point was observed on the further addition of 2.4 mL of HCl. Calculate the amount of  $\text{Na}_2\text{CO}_3$  and NaOH in one lit. of the solution.
8. A solution contains  $\text{Na}_2\text{CO}_3$  and NaOH. Using phenolphthalein as indicator, 25 ml of a mixture requires 719.5 ml of 0.005 N HCl for the end point. If methyl orange is indicator, then 25 ml of solution requires 25.9 ml of the same HCl for end point. Calculate concentration of each substance in g per litre.
9. A certain solution consists of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , 30 ml of this solution required 12 ml of 0.1 N  $\text{H}_2\text{SO}_4$  using phenolphthalein as indicator. In presence of methyl orange, 30 ml of same solution required 40 ml of 0.1 N  $\text{H}_2\text{SO}_4$ . Calculate the amount of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  per litre in mixture.

**(c) Redox titration :**

It is a type of simple titration in which a solution of oxidising agent is reacted with a solution of reducing agent

For redox titration , **Meq. of reducing agent = Meq. of oxidising agent**



In the above figure

$$\begin{aligned}
 \text{Meq. of reducing agent} &= N_1 V_1 \\
 \text{Meq. of oxidising agent} &= N_2 (V_2 - V_3) \\
 \therefore N_1 V_1 &= N_2 (V_2 - V_3)
 \end{aligned}$$

## 15. Daily Practice Problem Sheet

- 20 mL of 0.2 M  $\text{MnSO}_4$  are completely oxidized by 16 mL of  $\text{KMnO}_4$  of unknown normality, each forming  $\text{Mn}^{+4}$  oxidation state. Find out the normality and molarity of  $\text{KMnO}_4$  solution.
- 1 g of  $\text{H}_2\text{O}_2$  solution containing X%  $\text{H}_2\text{O}_2$  by weight requires X mL of  $\text{KMnO}_4$  for complete oxidation in acid medium. Calculate normality of  $\text{KMnO}_4$  solution.
- Find out the % of oxalate ion in given sample of oxalate salt of which 0.3 g dissolved in 100 mL of water required 90 mL of N/20  $\text{KMnO}_4$  for complete oxidation.
- 25 g of a sample of  $\text{FeSO}_4$  was dissolved in water containing dil.  $\text{H}_2\text{SO}_4$  and the volume made upto 1 litre. 25 mL of this solution required 20 mL of N/10  $\text{KMnO}_4$  for complete oxidation. Calculate % of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in given sample.
- A solution of 0.1 M  $\text{KMnO}_4$  is used for the reaction :  

$$\text{S}_2\text{O}_3^{2-} + 2\text{MnO}_4^- + \text{H}_2\text{O} \longrightarrow \text{MnO}_2 + \text{SO}_4^{2-} + \text{OH}^-$$
 What volume of solution in mL will be required to react with 0.158 g of  $\text{Na}_2\text{S}_2\text{O}_3$  ?
- A solution contains mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$ . 25 mL of this solution requires 35.5 mL of N/10 NaOH for neutralization and 23.45 mL of N/10  $\text{KMnO}_4$  for oxidation. Calculate :  
 (a) Normality of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{SO}_4$   
 (b) Strength of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{SO}_4$   
 Assume molecular weight of  $\text{H}_2\text{C}_2\text{O}_4 = 126$
- 0.5 g sample of iron containing mineral mainly in the form of  $\text{CuFeS}_2$  was reduced suitably to convert all the ferric ions into ferrous ions ( $\text{Fe}^{+3} \longrightarrow \text{Fe}^{+2}$ ) and was obtained as solution. In the absence of any interfering radical, the solution required 42 mL of 0.01 M  $\text{K}_2\text{Cr}_2\text{O}_7$  for titration. Calculate % of  $\text{CuFeS}_2$  in sample.
- 0.2828 g of iron wire was dissolved in excess dilute  $\text{H}_2\text{SO}_4$  and the solution was made upto 100 mL. 20 mL of this solution required 30 mL of N/30  $\text{K}_2\text{Cr}_2\text{O}_7$  solution of exact oxidation. Calculate % purity of Fe in wire.
- Mg can reduce  $\text{NO}_3^-$  to  $\text{NH}_3$  in basic solution :  

$$\text{NO}_3^- + \text{Mg(s)} + \text{H}_2\text{O} \longrightarrow \text{Mg(OH)}_2\text{(s)} + \text{OH}^-\text{(aq)} + \text{NH}_3\text{(g)}$$
 A 25.0 mL sample of  $\text{NO}_3^-$  solution was treated with Mg. The  $\text{NH}_3\text{(g)}$  was passed into 50 mL of 0.15 N HCl. The excess HCl required 32.10 mL of 0.10 M NaOH for its neutralisation. What was the molarity of  $\text{NO}_3^-$  ions in the original sample ?
- A polyvalent metal weighing 0.1 g and having atomic weight 51.0 reacted with dil.  $\text{H}_2\text{SO}_4$  to give 43.9 mL of  $\text{H}_2$  at STP. The solution containing the metal in the lower oxidation state was found to required 58.8 mL of 0.1 N  $\text{KMnO}_4$  for complete oxidation. What are valencies of metal.
- A mixture of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  weighing 0.24 g on being treated with KI in acid solution liberates just sufficient  $\text{I}_2$  to react with 60 mL of 0.1 N hypo. Find out % of Cr and Mn in mixture.
- 1.5 g of brass containing Cu and Zn reacts with 3 M  $\text{HNO}_3$  solution, the following reaction take place  

$$\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}^{+2} + \text{NO}_2\text{(g)} + \text{H}_2\text{O}$$

$$\text{Zn} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{NH}_4^+ + \text{Zn}^{+2} + \text{H}_2\text{O}$$
 The liberated  $\text{NO}_2\text{(g)}$  was found to be 1.04 litre at  $25^\circ\text{C}$  and one atm.  
 (a) Calculate the percentage composition of brass.  
 (b) How many mL of 3M  $\text{HNO}_3$  will be required for completely reacting 1g of brass ?

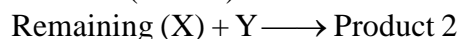
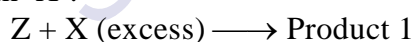


13. 10 mL of  $\text{H}_2\text{O}_2$  solution when reacted with KI solution produced 0.5 g of iodine. Calculate % purity of  $\text{H}_2\text{O}_2$  (by volume).
14. How many mL of 0.24 M solution of  $\text{Na}_2\text{SO}_3$  will be oxidized by 180 mL of 0.32 M  $\text{KMnO}_4$  in acid medium ?
15. What is the strength of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, whose 10 mL required 15 mL of N/10 hypo solution for neutralization?
16. A solution containing 1.984 g of crystalline  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  in water required 40 mL of N/5 iodine solution for complete reaction. Calculate the value of x.
17. 0.2274 g sample of copper ore containing CuS liberated iodine when treated with excess of KI in acid solution. The liberated iodine required 28.6 mL of 0.035 N  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution for complete reaction. Determine the percentage of CuS in ore.
18. 100 mL of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (10 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  per litre) and 75 mL of ferrous salt solution (80 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per litre) are mixed in presence of excess of  $\text{H}_2\text{SO}_4$  & the resulting solution titrated with 0.2121 N  $\text{KMnO}_4$  solution. What will be the volume of  $\text{KMnO}_4$  needed?
19. In analysis of 0.1 g iron oxide of unknown composition, is dissolved and all the iron is reduced to divalent state and then titrated with 0.0993 N solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , 13.05 mL of which is used for titration. What is the formula of iron oxide ?
20. 15 mL sample of a solution of 0.04 M  $\text{Sn}^{+2}$  and X.M  $\text{Fe}^{+2}$ . Both ions are easily oxidized by  $\text{Cr}_2\text{O}_7^{-2}$  in acidic solution and the redox products are  $\text{Sn}^{+4}$ ,  $\text{Fe}^{+3}$  and  $\text{Cr}^{+3}$ . If 18 mL of 0.1250 M  $\text{Cr}_2\text{O}_7^{-2}$  is required for oxidation what is X ?

### (B) Back Titration :

Let us consider that we have an impure solid substance 'Z' weighing 'w' g and we are required to calculate the percentage purity of 'Z' in the sample. We are also provided with two solutions 'X' and 'Y', where the concentration of 'Y' is known ( $N_1$ ) and that of 'X' is unknown. For the back titration to work, following conditions are to be satisfied

- (a) Compounds 'X', 'Y' and 'Z' should be such that 'X' and 'Y' reacts with each other.
- (b) 'X' and pure 'Z' also reacts with each other but the impurity present in 'Z' does not react with 'X'.



**Note : Product 1 should not react with Y**

$$\text{Milli equivalent of Y} = N_2 V_2$$

Where  $N_2$  and  $V_2$  (ml) is the normality and volume of Y

$$\text{Initial milli equivalent of X} = N_1 V_1$$

Where  $N_1$  and  $V_1$  (ml) is the normality and volume of X

$$\text{Remaining milli equivalents of X after reacting with Y} = N_1 V_1 - N_2 V_2$$

$$\text{Remaining milli equivalents of X} = \text{milli equivalents of Z}$$

$$N_1 V_1 - N_2 V_2 = \frac{a \times 1000}{\text{Equivalent weight}} \quad \text{where 'a' is the weight of pure Z which is reacted.}$$

$$a = \frac{\text{Molecular weight (} N_1 V_1 - N_2 V_2 \text{)}}{n - \text{factor}}$$

$$\therefore \text{Percentage purity of 'Z'} = \frac{(N_1 V_1 - N_2 V_2)}{n - \text{factor}} \times \frac{\text{Molar Mass of 'Z'}}{W} \times 100$$

### Illustration 19 :

20 g of a sample of  $\text{Ba}(\text{OH})_2$  is dissolved in 10 ml. of 0.5N HCl solution. The excess of HCl was titrated with 0.2N NaOH. The volume of NaOH used was 10 cc. Calculate the percentage of  $\text{Ba}(\text{OH})_2$  in the sample.

**Solution :**

Milli eq. of HCl initially	=	$10 \times 0.5 = 5$
Milli eq. of NaOH consumed	=	Milli eq. of HCl in excess
	=	$10 \times 0.2 = 2$
$\therefore$ Milli eq. of HCl consumed	=	Milli eq. of $\text{Ba}(\text{OH})_2$
	=	$5 - 2 = 3$
$\therefore$ eq. of $\text{Ba}(\text{OH})_2$	=	$3/1000 = 3 \times 10^{-3}$
Mass of $\text{Ba}(\text{OH})_2$	=	$3 \times 10^{-3} \times (171/2) = 0.2565 \text{ g.}$
% $\text{Ba}(\text{OH})_2$	=	$(0.2565/20) \times 100 = 1.28\%$

## 16. Daily Practice Problem Sheet

- 1 g sample of washing soda was dissolved in 50 mL of 1.0 M HCl. The excess acid required for neutralization 21.13 mL of 1.018 M  $\text{Ba}(\text{OH})_2$ . Compute the degree of hydration of washing soda.
- 1 mL solution containing  $(\text{NH}_4)_2\text{SO}_4$  was treated with excess of NaOH. The  $\text{NH}_3$  released was absorbed in 50 mL of 0.1 N HCl solution. The solution after passage of  $\text{NH}_3$  in it requires 20 mL of 0.1 N NaOH for complete neutralisation. Calculate the strength of  $(\text{NH}_4)_2\text{SO}_4$  solution.
- A mixture of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{Cl}$  in the ratio 43.7 % and 56.3 % respectively was dissolved in water to prepare 1 litre solution. 25 mL of this solution was boiled with 50 mL of N/10 NaOH until all the  $\text{NH}_3$  was evolved. The excess of NaOH was neutralized by 24.3 mL of N/10 HCl. Calculate the weight of each component in mixture.

### (C) Iodimetric and Iodometric Titrations

The redox-titration using iodine directly or indirectly as an oxidizing agent are called Iodine Titrations. These are of two types.

#### (a) Iodimetric Titrations :

Iodimetric titrations are defined as those iodine titrations in which a standard iodine solution is used as an oxidant and iodine is directly titrated against a reducing agent. Iodimetric procedures are used for the determination of strength of reducing agent like thiosulphates, sulphites, arsenites and stannous chloride etc., by titrating them against standard solution of iodine taken in a burette. Some cases of oxidation-reduction reactions are given as under :

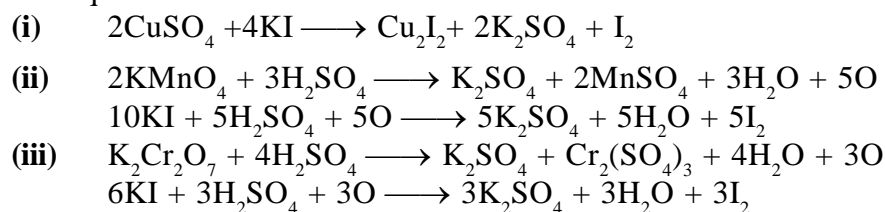
- $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
- $\text{Na}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HI}$
- $\text{Na}_3\text{AsO}_3 + \text{H}_2\text{O} \longrightarrow \text{Na}_3\text{AsO}_4 + 2\text{HI}$

#### (b) Iodometric Titrations :

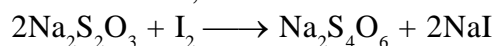
Iodometric titrations are defined as those iodine titrations in which some oxidizing agent liberates iodine from an iodine solution and then liberated iodine is titrated with a standard solution of a reducing agent added from a Burette. In such titrations, a neutral or an acidic solution of oxidizing agent is employed. The amount of iodine liberated from an iodide, (i.e. KI) is equivalent to the quantity of the oxidizing agent present. Iodometric titrations are used for the determination of  $\text{CuSO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ , ferric ions, antimonite ions,  $\text{H}_2\text{O}_2$ ,  $\text{MnO}_2$ , bromine and chlorine etc.



The equations for some of the reactions are as follows :



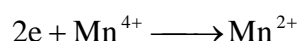
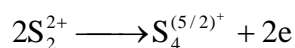
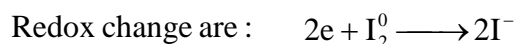
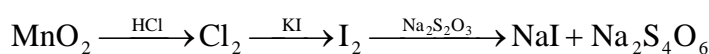
In the above reactions, the liberated iodine is titrated with a standard sodium thiosulphate.



### Illustration 20 :

0.5 g sample containing  $\text{MnO}_2$  is treated with  $\text{HCl}$ , liberating  $\text{Cl}_2$ . The  $\text{Cl}_2$  is passed into a solution of  $\text{KI}$  and  $30.0 \text{ cm}^3$  of  $0.1 \text{ M Na}_2\text{S}_2\text{O}_3$  are required to titrate the liberated iodine. Calculate the percentage of  $\text{MnO}_2$  in sample. (At. Wt. of  $\text{Mn} = 55$ ).

**Solution :**



The reactions suggest that,

$$\begin{aligned} \text{Meq. of MnO}_2 &= \text{Meq. of Cl}_2 \text{ formed} = \text{Meq. of I}_2 \text{ liberated} \\ &= \text{Meq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \end{aligned}$$

$$\therefore \frac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30$$

$$[\Theta \text{ N}_{\text{Na}_2\text{S}_2\text{O}_3} = M_{\text{Na}_2\text{S}_2\text{O}_3} \text{ since valency factor} = 1, \text{ see redox changes for Na}_2\text{S}_2\text{O}_3]$$

$$\text{or } w_{\text{MnO}_2} = \frac{0.1 \times 1 \times 30 \times M}{2000} = \frac{0.1 \times 1 \times 30 \times 87}{2000} \quad (\text{Q } M_{\text{MnO}_2} = 87)$$

$$w_{\text{MnO}_2} = 0.1305$$

$$\therefore \text{Purity of MnO}_2 = \frac{0.1305}{0.5} \times 100 = 26.1 \%$$

## 17. Daily Practice Problem Sheet

- 2.480 g of  $\text{KClO}_3$  are dissolved in conc.  $\text{HCl}$  and the solution was boiled. Chlorine gas evolved in the reaction was then passed through a solution of  $\text{KI}$  and liberated iodine was titrated with 100 mL of hypo. 12.3 mL of same hypo solution required 24.6 mL of 0.5 N iodine for complete neutralization. Calculate % purity of  $\text{KClO}_3$  sample.
- 0.32 g sample of impure  $\text{KI}$  was dissolved in 1.1 millimole of  $\text{K}_2\text{CrO}_4$  and 25 mL of 5 N  $\text{H}_2\text{SO}_4$ . Iodine formed was expelled off by boiling and the solution is now mixed with excess of pure  $\text{KI}$  and  $\text{I}_2$  liberated again, which on titration required 14 mL of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Calculate % purity of original  $\text{KI}$  sample.
- 0.3521 g of a mixture of  $\text{KMnO}_4$  and  $\text{K}_2\text{CrO}_4$  were treated with excess of  $\text{KI}$  in acid medium and liberated iodine required 25 mL of 0.32N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Determine % of  $\text{Mn}$  in mixture.

## SOLVED PROBLEMS

### SUBJECTIVE

#### Problem 1 :

*P and Q are two elements which forms  $P_2Q_3$  and  $PQ_2$ . If 0.15 mole of  $P_2Q_3$  weighs 15.9g and 0.15 mole of  $PQ_2$  weighs 9.3g, what are atomic weights of P and Q?*

#### Solution :

Let atomic weight of P and Q are a and b respectively

$$\therefore \text{Molecular weight of } P_2Q_3 = 2a + 3b$$

$$\text{and Molecular weight of } PQ_2 = a + 2b$$

Now given that 0.15 mole of  $P_2Q_3$  weigh 15.9g

$$(2a + 3b) = \frac{15.9}{0.15} \quad \left( \because \frac{\text{wt.}}{\text{mol. wt.}} = \text{mole} \right) \quad \text{Similarly, } (a + 2b) = \frac{9.3}{0.15}$$

Solving these two equations **b = 18, a = 26**

#### Problem 2 :

*Potassium selenate is isomorphous with potassium sulphate and contains 45.52% selenium by weight. Calculate the atomic weight of selenium. Also report the equivalent weight of potassium selenate.*

#### Solution :

Potassium selenate is isomorphous to  $K_2SO_4$  and thus its molecular formula is  $K_2SeO_4$ .

$$\text{Now molecular weight of } K_2SeO_4 = (39 \times 2 + a + 4 \times 16) \\ = (142 + a)$$

where a is atomic weight of Se

$$(142 + a)g K_2SeO_4 \text{ has Se} = a \text{ g}$$

$$\therefore 100g K_2SeO_4 \text{ has Se} = \frac{a \times 100}{142 + a}$$

$$\ominus \quad \% \text{ of Se} = 45.52 \quad \therefore \frac{a \times 100}{142 + a} = 45.52 \quad \therefore a = 118.2$$

$$\text{Also equivalent of } K_2SeO_4 = \frac{\text{Mol. wt.}}{2} = \frac{2 \times 39 + 118.2 + 64}{2} = 130.1$$

#### Problem 3 :

*A sample of  $H_2SO_4$  (density  $1.787g mL^{-1}$ ) is labeled as 86% by weight. What is molarity of acid? What volume of acid has to be used to make 1 litre of 0.2M  $H_2SO_4$ ?*

#### Solution :

$H_2SO_4$  is 86 % by weight

$$\therefore \text{Weight of } H_2SO_4 = 86g, \quad \text{Weight of solution} = 100g$$

$$\therefore \text{Volume of solution} = \frac{100}{1.787} \text{ mL} = \frac{100}{1.787 \times 1000} \text{ litre}$$

$$\therefore M_{\text{H}_2\text{SO}_4} = \frac{86}{98 \times \frac{100}{1.787 \times 1000}} = 15.68$$

Let V mL of this  $\text{H}_2\text{SO}_4$  are used to prepare 1 litre of 0.2 M  $\text{H}_2\text{SO}_4$

$\therefore$  mM of conc.  $\text{H}_2\text{SO}_4$  = mM of dilute  $\text{H}_2\text{SO}_4$

$$V \times 15.68 = 1000 \times 0.2 \quad \therefore V = \mathbf{12.75 \text{ mL}}$$

**Problem 4 :**

*The molecular mass of an organic acid was determined by the study of its barium salt. 4.290g of salt was quantitatively converted to free acid by the reaction with 21.64 ml of 0.477 M  $\text{H}_2\text{SO}_4$ . The barium salt was found to have two mole of water of hydration per  $\text{Ba}^{2+}$  ion and the acid is mono basic. What is molecular weight of anhydrous acid?*

**Solution :**

$$\text{Meq. of barium salt} = \text{Meq. of acid} ; \frac{4.290}{M/2} \times 1000 = 21.64 \times 0.4777 \times 2$$

$$\text{Molecular weight of salt} = 415.61$$

$$\text{Molecular weight of anion} = \frac{415.61 - 137 - 36}{2} = 121.31$$

$$\therefore \text{Molecular weight of acid} = 121.31 + 1 = \mathbf{122.31}$$

**Problem 5 :**

*25 mL of a solution of  $\text{Na}_2\text{CO}_3$  having a specific gravity of  $1.25 \text{ g mL}^{-1}$  required 32.9 mL of a solution of HCl containing 109.5gm of the acid per litre for complete neutralization. Calculate the volume of 0.84 N  $\text{H}_2\text{SO}_4$  that will be completely neutralized by 125g of  $\text{Na}_2\text{CO}_3$  solution.*

**Solution :**

$$N_{\text{HCl}} = \frac{109.5}{36.5 \times 1} = 3$$

Since  $\text{Na}_2\text{CO}_3$  is completely neutralized by HCl

$$\therefore \text{Meq. of } \text{Na}_2\text{CO}_3 = \text{Meq. of HCl} \Rightarrow N \times 25 = 32.9 \times 3 \quad \therefore N_{\text{Na}_2\text{CO}_3} = 3.948$$

Now  $\text{Na}_2\text{CO}_3$  fresh solution reacts with  $\text{H}_2\text{SO}_4$

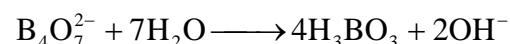
$$\therefore \text{Volume of } \text{Na}_2\text{CO}_3 \text{ solution} = \frac{125}{1.25} = 100 \text{ ml}$$

$$\therefore \text{Meq. of } \text{H}_2\text{SO}_4 = \text{Meq. of } \text{Na}_2\text{CO}_3 \Rightarrow 0.84 \times V = 100 \times 3.948$$

$$\therefore \text{Volume of } \text{H}_2\text{SO}_4 = \mathbf{470 \text{ mL}}$$

**Problem 6 :**

*Borax in water gives:*



*How many gram of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) are required to?*

(a) Prepare 50 mL of 0.2 M solution

(b) neutralize 25 mL of 0.1934 M of HCl and  $\text{H}_2\text{SO}_4$  separately

**Solution :**

$$\left( Q \text{ Molarity} = \frac{\text{Normality}}{\text{No. of replaceable OH}^-} \right) \quad \therefore \quad N = M \times 2$$

$$\text{Thus Meq. of borax in solution} = 50 \times 0.2 \times 2 = 20$$

$$\therefore \quad \frac{w}{M/2} \times 1000 = 20 \quad \therefore \quad \frac{w}{382/2} \times 1000 = 20 \quad \therefore \quad w = 3.82\text{g}$$

$$\text{For neutralization of HCl, Meq. of HCl} = \text{Meq. of borax} \Rightarrow 25 \times 0.1934 = \frac{w}{382/2} \times 1000$$

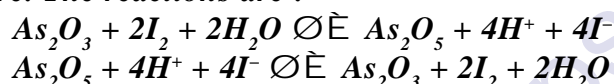
$$\therefore \quad \text{Weight of borax} = 0.09235\text{g}$$

$$\text{For neutralization of H}_2\text{SO}_4, \text{ Meq. of borax} = \text{Meq. of H}_2\text{SO}_4$$

$$\Rightarrow \quad \frac{w}{382/2} \times 1000 = 25 \times 0.1934 \times 2 \quad \therefore \quad \text{Weight of borax} = \mathbf{1.847\text{g}}$$

**Problem 7 :**

*A mixture containing  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$  required 20.10 mL of 0.05N iodine for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.113g hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) for complete reaction. Calculate mass mixture. The reactions are :*



**Solution :**

$$\text{Meq. of I}_2 \text{ used} = 20.10 \times 0.05 = 1.005$$

Let Meq. of  $\text{As}_2\text{O}_3$  and Meq. of  $\text{As}_2\text{O}_5$  in mixture be a and b respectively. On addition of  $\text{I}_2$  to mixture,

$\text{As}^{+3}$  is converted to  $\text{As}^{+5}$ .

$$\therefore \text{Meq. of } \text{As}_2\text{O}_3 = \text{Meq. of I}_2 \text{ to mixture used} = 1.005 = \text{Meq. of As}^{5+} \text{ formed.}$$

$$\text{or} \quad a = 1.005 \quad \dots(1)$$

After the reaction with  $\text{I}_2$ , mixture contains all the arsenic in +5 oxidation state which is then titrated using KI + hypo. Thus,

$$\text{Meq. of } \text{As}_2\text{O}_3 \text{ as As}^{+5} + \text{Meq. of } \text{As}_2\text{O}_5 \text{ as As}^{+5} = \text{Meq. of liberated I}_2 = \text{Meq. of hypo used}$$

$$\text{or} \quad a + b = \frac{1.113}{248} \times 1000 \Rightarrow a + b = 4.481$$

$$\text{By equations (1) and (2), } b = 4.481 - 1.005 = 3.476$$

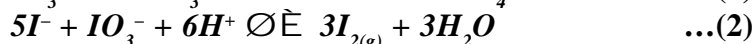
$$\therefore \text{Wt. of } \text{As}_2\text{O}_3 = \frac{\text{Meq.} \times \text{Eq. Wt}}{1000} = \frac{1.005 \times 198}{4 \times 100} = 0.0497\text{g}$$

$$\text{and} \quad \text{Wt. of } \text{As}_2\text{O}_5 = \frac{3.476 \times 230}{4 \times 1000} = 0.1999\text{g}$$

$$\therefore \text{Wt. of mixture} = 0.0497 + 0.1999 = \mathbf{0.2496\text{g}}$$

**Problem 8 :**

Chile salt peter, a source of  $\text{NaNO}_3$  also contains  $\text{NaIO}_3$ . The  $\text{NaIO}_3$  can be used as source of iodine, produced in the following reactions.



One litre of chile salt peter solution containing 5.80g  $\text{NaIO}_3$  is treated with stoichiometric quantity of  $\text{NaHSO}_3$ . Now an additional amount of same solution is added to reaction mixture to bring about the second reaction. How many grams of  $\text{NaHSO}_3$  are required in step I and what additional volume of chile salt peter must be added in step II to bring in complete conversion of  $\text{I}^-$  to  $\text{I}_2$ ?

**Solution :**

$$\therefore \text{Meq. of NaHSO}_3 = \text{Meq. of NaIO}_3 = N \times V = \frac{5.8}{198/6} \times 1000$$

$$[\text{Et. wt. of NaI} = M/6 \text{ because } \text{I}^{5+} + 6e \rightarrow \text{I}^-]$$

$$\text{Meq. of NaHSO}_3 = 175.76$$

$$\therefore W_{\text{NaHSO}_3} = \frac{175.76 \times 104}{2000} = 9.14\text{g}$$

Also Meq. of  $\text{I}^-$  formed in I step using valence factor 6 = 175.76

In II step valence factor of  $\text{I}^-$  is 1 and valence factor of  $\text{IO}_3^-$  is 5

$$\text{Thus, Meq. of I}^- \text{ formed using valence factor 1} = \frac{175.76}{6}$$

$$\text{Also Meq. of NaIO}_3 \text{ used in step II} = \frac{175.76}{6}$$

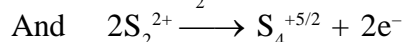
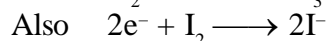
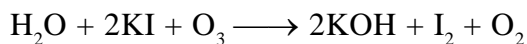
$$\therefore N \times V = \frac{175.76}{6} \Rightarrow \frac{5.8}{198/5} \times V = \frac{175.76}{6} \therefore V_{\text{NaIO}_3} = 200 \text{ mL}$$

**Problem 9 :**

For estimating ozone in the air, a certain volume of air is passed through an acidified or neutral  $\text{KI}$  solution when oxygen is evolved and iodide is oxidized to give iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution. In an experiment, 10 litre of air at 1 atm and  $27^\circ\text{C}$  were passed through an alkaline  $\text{KI}$  solution, at the end, the iodine entrapped in a solution on titration as above required 1.5 mL of 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Calculate volume % of  $\text{O}_3$  in sample.

**Solution :**

The reactions are :



$$\therefore \text{Meq. of I}_2 = \text{Meq. of Na}_2\text{S}_2\text{O}_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$$

$$\text{or mM of I}_2 = \frac{1.5 \times 10^{-2}}{2} = 7.5 \times 10^{-3}$$

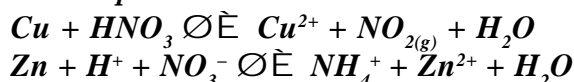
$$\therefore \text{mM of O}_3 = \text{mM of I}_2 = 7.5 \times 10^{-3} \quad (\ominus \text{ Mole ratio of O}_3 : \text{I}_2 :: 1 : 1)$$

$$\therefore P_{\text{O}_3} = \frac{7.5 \times 10^{-6} \times 0.0821 \times 300}{10} = 184.725 \times 10^{-7} \text{ atm}$$

$$\therefore \text{Volume \% of O}_3 = 184.725 \times 10^{-7} \times 100 = 1.847 \hat{=} 10^{-3} \%$$

**Problem 10 :**

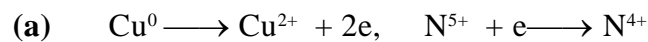
1.5g of brass containing Cu and Zn reacts with 3M HNO<sub>3</sub> solution, the following reactions take place.



The liberated NO<sub>2(g)</sub> was found to be 1.04 litre at 25°C and one atm.

- (a) Calculate the percentage composition of brass.  
 (b) How many mL of 3M HNO<sub>3</sub> will be required for completely reacting 1g of brass?

**Solution :**



$\therefore \text{Eq. of Cu} = \text{Eq. of NO}_2$

$$\frac{w}{63.6/2} = \frac{1 \times 1.04}{0.0821 \times 298} \left( Q \text{ mole of NO}_2 = \text{Eq. of NO}_2 = \frac{PV}{RT} \right)$$

$\therefore w_{\text{Cu}} = 1.35\text{g}, \quad \therefore w_{\text{Zn}} = 1.50 - 1.35 = 0.15\text{g}$

$\therefore \% \text{ of Cu} = \frac{1.35}{1.5} \times 100 = 90\% \quad \text{and} \quad \% \text{ of Zn} = \frac{0.15}{1.5} \times 100 = 10\%$

- (b) Thus, 1 g brass contains 0.9g Cu and 0.1g Zn

$\therefore \text{Meq. of HNO}_3 = \text{Meq. of Zn} \Rightarrow 3 \times 8 \times V_1 = \frac{0.1}{65/2} \times 1000$

$\therefore V_1 = 0.128\text{mL}$

$(Q \text{ N}^{+5} + 8e^- \longrightarrow \text{N}^{-3}) \quad \text{and} \quad \text{Meq. of HNO}_3 = \text{Meq. of Cu}$

or  $3 \times V_2 = \frac{0.9}{63.6/2} \times 1000 \quad \therefore V_2 = 9.43 \text{ mL}$

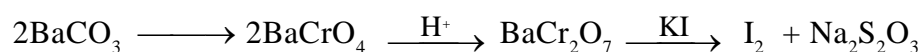
$\therefore \text{Total volume of HNO}_3 \text{ used} = 0.128 + 9.43 = 9.558 \text{ mL}$

**Problem 11 :**

1.249 g of a sample of pure BaCO<sub>3</sub> and impure CaCO<sub>3</sub> containing some CaO was treated with dil.HCl and it evolved 168 ml of CO<sub>2</sub> at NTP. From this solution, BaCrO<sub>4</sub> was precipitated, filtered and washed. The precipitate was dissolved in dilute sulphuric acid and diluted to 100 ml. 10 ml of this solution, when treated with KI solution, liberated iodine which required exactly 20 ml of 0.05N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Calculate the percentage of CaO in the sample.

**Solution :**

$$n_{\text{CaCO}_3} + n_{\text{BaCO}_3} = n_{\text{CO}_2} = \frac{168}{22400} = 7.5 \times 10^{-3} \quad \text{--- (1)}$$



$$\begin{aligned} \text{eq. of Na}_2\text{S}_2\text{O}_3 &= \text{eq. of I}_2 = \text{eq of BaCr}_2\text{O}_7 = \frac{20 \times 10^{-3} \times 0.05 \times 100}{10} \\ &= 1 \times 10^{-2} \end{aligned}$$

Moles of BaCr<sub>2</sub>O<sub>7</sub> =  $\frac{1}{6} \times 10^{-2}$ , Moles of BaCrO<sub>4</sub> =  $\frac{2}{6}$  ( $1 \times 10^{-2}$ )

Moles of BaCO<sub>3</sub> =  $\frac{1}{3} \times 10^{-2} = 3.33 \times 10^{-3}$  --- (2)

Weight of BaCO<sub>3</sub> = 0.650 gm

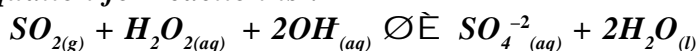
From equation (1) and (2) we get  $\Rightarrow n_{\text{CaCO}_3} = 4.17 \times 10^{-3}$

weight of  $\text{CaCO}_3 = 100 \times 4.17 \times 10^{-3} = 0.417 \text{ g}$

weight of  $\text{CaO} = 1.249 - 0.656 - 0.417 = 0.176$  % of  $\text{CaO} = \frac{0.176}{1.249} \times 100 = 14.09 \%$

### Problem 12 :

*In a quality control analysis for sulphur impurity 5.6g steel sample was burnt in a stream of oxygen and sulphur was converted into  $\text{SO}_2$  gas. The  $\text{SO}_2$  was then oxidized to sulphate by using  $\text{H}_2\text{O}_2$  solution to which had been added 30 mL of 0.04M NaOH. The equation for reaction is :*



*22.48 mL of 0.024M HCl was required to neutralize the base remaining after oxidation reaction. Calculate % of sulphur in given sample.*

**Solution :** Meq. of alkali added =  $30 \times 0.04 = 1.2$

Meq. of alkali left =  $22.48 \times 0.024 = 0.54$

$\therefore$  Meq. of alkali for  $\text{SO}_2$  and  $\text{H}_2\text{O}_2 = 1.2 - 0.54 = 0.66$

$\therefore$  Weight of alkali used =  $\frac{0.66 \times 40}{1000} = 0.0264$

Q 80g NaOH reacts with 64g  $\text{SO}_2$

$\therefore$  0.0264g NaOH reacts =  $\frac{64 \times 0.0264}{80} = 0.021 \text{ g SO}_2$

Now Q 64g  $\text{SO}_2$  required = 32g S

$\therefore$  0.021g  $\text{SO}_2$  required =  $\frac{32 \times 0.021}{64} = 0.0105 \text{ g}$

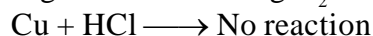
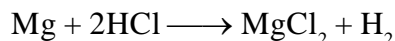
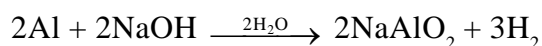
$\therefore$  % of S =  $\frac{0.0105}{5.6} \times 100 = 0.1875\%$

### Problem 13 :

*A granulated sample of aircraft alloy (Al, Mg, Cu) weighing 8.72g was first treated with alkali and then with very dilute HCl, leaving a residue. The residue after alkali boiling weighed 2.10g and the acid insoluble residue weighed 0.69g. What is the composition of the alloy?*

### Solution :

Let Al, Mg and Cu be a, b and c g respectively.



i.e., only Al reacts with NaOH and then only Mg reacts with HCl

$\therefore a + b + c = 8.72$

$b + c = 2.10$  (Residue left after alkali treatment)

$c = 0.69$  (Residue left after acid treatment)

$\therefore b = 6.62 \text{ g}$

$\therefore$  % of Al =  $\frac{6.62}{8.72} \times 100 = 75.9$  % of Mg =  $\frac{1.41}{8.72} \times 100 = 16.2$

% of Cu =  $\frac{0.69}{8.72} \times 100 = 7.9$

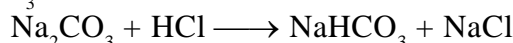


**Problem 14 :**

25 ml from a stock solution containing  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  was diluted to 250 ml with  $\text{CO}_2$  free distilled water. 25 ml of the diluted solution when titrated with 0.12 M HCl required 8 ml when phenolphthalein was used as an indicator. When 20 ml of diluted solution was titrated with same acid required 18 ml when methyl orange was used as an indicator. Calculate concentration of  $\text{NaHCO}_3$  in the stock solution in gm/litre and in mole/litre. To 100 ml of the stock solution how much NaOH should be added so that all bicarbonate will be converted into carbonate?

**Solution :**

When phenolphthalein used,  $\text{NaHCO}_3$  remains unaffected and  $\text{Na}_2\text{CO}_3$  will be converted into  $\text{NaHCO}_3$



$$\frac{1}{2} \text{ eq of } \text{Na}_2\text{CO}_3 = \text{eq. of HCl} \Rightarrow \frac{1}{2} \frac{w}{53} = 0.12 \times 8 \times 10^{-3} \times 10$$

$$w = 1.017 \text{ gm in 25 ml} = 40.7 \text{ gm / litre} = 0.38 \text{ mole / litre}$$

When methyl orange is used  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  both will be converted into  $\text{CO}_2$

$$\text{Eq. } (\text{Na}_2\text{CO}_3) + \text{eq}(\text{NaHCO}_3) = \text{eq (HCl)}$$

$$\left( 1.92 \times 10^{-3} + \frac{W}{84} \right) = 18 \times 0.12 \times 10^{-3} \times \frac{250}{20}$$

$$1.92 \times 10^{-2} + \frac{W}{84} = 2.7 \times 10^{-2}$$

$$\text{For } \text{NaHCO}_3 \text{ } W = 0.6552 \text{ gm in 250 ml} = 26.2 \text{ gm / litre} = 0.312 \text{ M}$$

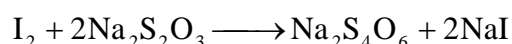
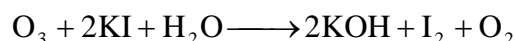
$$\text{eq. of bicarbonate} = \text{eq of NaOH}$$

$$0.78 \times 10^{-2} \times \frac{100}{25} = \frac{W}{40} \Rightarrow W = 1.248 \text{ gm}$$

**Problem 15 :**

One litre of a mixture of  $\text{O}_2$  and  $\text{O}_3$  at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the weight per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

**Solution :**



$$\therefore \text{ Milli mole of } \text{O}_3 = \text{milli mole of } \text{I}_2 = \frac{1}{2} \times \text{mM of } \text{Na}_2\text{S}_2\text{O}_3 (\text{mM} = \text{M} \times V_{\text{in ml}})$$

$$= \frac{1}{2} \times 40 \times \frac{1}{10} = 2\text{mM} = 0.002\text{mole}$$

Total milli mole of  $\text{O}_2$  and  $\text{O}_3$  in mixture are calculated from  $\text{PV} = n\text{RT}$

$$1 \times 1 = n \times 0.0821 \times 273 \quad \therefore n = 0.044 \text{ mole}$$

$$\therefore \text{ Mole of } \text{O}_2 = 0.044 - 0.002 = 0.042$$

Now weight of  $O_2 = 0.042 \times 32g = 1.344g$ ,      Weight of  $O_3 = 0.002 \times 48g = 0.096g$

$$\therefore \% \text{ of } O_3 = \frac{0.096}{1.344} \times 100 = 6.7 \%$$

$$\text{No. of photon or molecules of ozone} = \frac{0.096 \times 6.023 \times 10^{23}}{48} = 1.2 \times 10^{21}$$

## OBJECTIVE

### Problem 1 :

*It takes  $2.56 \times 10^{-3}$  equivalent of KOH to neutralize 0.1254g  $H_2XO_4$ . The number of neutrons in is*

- (a) 16                      (b) 8                      (c) 7                      (d) 32

**Solution :** (a)

$$\text{Mole of } H_2XO_4 = \frac{0.1254}{M_x + 66} [M_x = \text{Atomic mass of } x]$$

'n' factor of  $H_2XO_4 = 2 \Rightarrow [Q H_2XO_4 \text{ is dibasic acid}]$

$$\therefore 2.56 \times 10^{-3} = \frac{0.1254}{M_x + 66} \times 2 \Rightarrow M_x = 31.96 \text{ g/mol} = 32 \text{ g/mol}$$

Then X is sulphur which has 16 neutrons

### Problem 2 :

*How many grams of sodium bicarbonate are required to neutralize 10.0 ml of 0.902 M vinegar?*

- (a) 8.4g                      (b) 1.5g                      (c) 0.75g                      (d) 1.07g

**Solution :** (c)



$$\text{Equivalent of acid} = \frac{10 \times 0.902}{1000} ; \quad \text{Equivalent of } NaHCO_3 = 9.02 \times 10^{-5}$$

$$\text{Amount of } NaHCO_3 = 9.02 \times 10^{-5} \times \frac{1000}{10} \times 84 = 0.758$$

### Problem 3 :

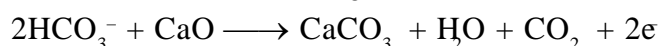
*A sample of hard water contains 244 ppm of  $HCO_3^-$  ions. What is the minimum mass of CaO required to remove  $HCO_3^-$  ions completely from 1 kg of such water sample*

- (a) 56 mg                      (b) 112 mg                      (c) 168 mg                      (d) 244 mg

**Solution :** (b)

Mass of  $HCO_3^-$  in 1 kg or  $10^6$  mg water = 244 mg

$$\text{Millimoles of } HCO_3^- = \frac{244}{61} = 4$$



millimoles of CaO = 2, mass of CaO =  $56 \times 2 = 112$  mg

**Problem 4 :**

100 ml of each of 0.5 N NaOH, N/5 HCl and N/10 H<sub>2</sub>SO<sub>4</sub> are mixed together. The resulting solution will be

- (a) Acidic (b) Neutral (c) Alkaline (d) None

**Solution:** (c)

$$\text{Meq. of NaOH} = 100 \times 0.5 = 50$$

$$\text{Meq. of HCl} = \frac{1}{5} \times 100 = 20;$$

$$\text{Meq. of H}_2\text{SO}_4 = \frac{1}{10} \times 100 = 10$$

$$\text{Total meq. of acid} = 20 + 10 = 30$$

$$\text{Total meq. of NaOH} = 50$$

$$\therefore \text{meq. of NaOH left} = 50 - 30 = 20$$

[Hence solution is alkaline]

**Problem 5 :**

The chloride of a metal (M) contains 65.5% of chlorine. 100 ml of the vapour of the chloride of the metal at STP weight 0.72g. the molecular formula of the metal chloride is :

- (a) MCl<sub>3</sub> (b) MCl (c) MCl<sub>2</sub> (d) MCl<sub>4</sub>

**Solution :** (a)

Molecular mass of chloride of metal = weight of 22,400 ml vapour of metal at STP

$$= \frac{0.72 \times 22,400}{100} = 161.28\text{g}$$

100g of metal chloride contains = 65.5 g chloride

$$\therefore 161.28\text{g metal chloride contains} = \frac{65.5 \times 161.28}{100} = 105.6\text{g}$$

Therefore, the number of mole of chlorine atoms per mole of metal chloride

$$= 105.6/35.5 = 3$$

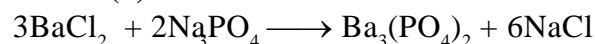
Hence the molecular formula of metal chloride is MCl<sub>3</sub>

**Problem 6 :**

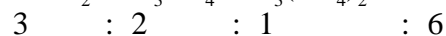
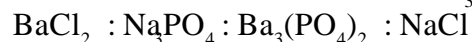
If 0.5 mole of BaCl<sub>2</sub> is mixed with 0.2 mole of Na<sub>3</sub>PO<sub>4</sub> the maximum number of moles of Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> that can be formed is

- (a) 0.7 (b) 0.5 (c) 0.3 (d) 0.1

**Solution :** (d)



From the molar ratio we see that Na<sub>3</sub>PO<sub>4</sub> is limiting reagent



□ 2 mole of Na<sub>3</sub>PO<sub>4</sub> gives = 1 mole of Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

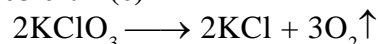
∴ 0.2 mole of Na<sub>3</sub>PO<sub>4</sub> gives = 0.1 mole of Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

**Problem 7 :**

The percent loss in weight after heating a pure sample of potassium chlorate (Molecular weight = 122.5) will be

- (a) 12.25 (b) 24.50 (c) 39.18 (d) 49

**Solution :** (c)

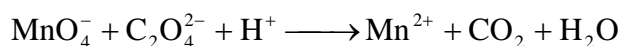


245 g KClO<sub>3</sub> on heating shows a weight loss of 96 gm

$$\therefore 100\text{g KClO}_3 \text{ on heating shows a weight loss of} = \frac{96 \times 100}{245} = 39.18\%$$

**Problem 8 :**

*For the reaction*



*the correct coefficients of the reactants for the balanced reaction are*

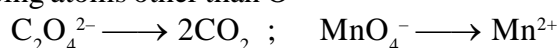
	$\text{MnO}_4^-$	$\text{C}_2\text{O}_4^{2-}$	$\text{H}^+$
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

**Solution : (a)**

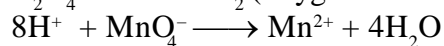
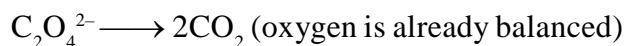
The above reaction can be balanced by using the ion electron method as under:



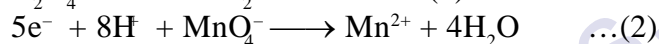
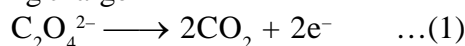
Balancing atoms other than O



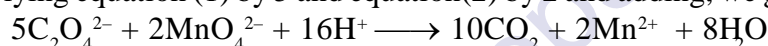
Since medium is acidic



Balancing charge



Multiplying equation (1) by 5 and equation(2) by 2 and adding, we get



**Alternatively**

'n' factor of  $\text{C}_2\text{O}_4^{2-}$  is 2 and that of  $\text{MnO}_4^-$  is 5

$\therefore$  they would react in the molar ratio of 5:2

**Problem 9 :**

*In an experiment, 50 ml of 0.1 M solution of a salt reacted with 25 ml of 0.1 M solution of sodium sulphite. The half equation for the oxidation of sulphite ion :*



*If the oxidation number of the metal in the salt was 3, what would be the new oxidation number of the metal?*

- (a) 0                      (b) 1                      (c) 2                      (d) 4

**Solution : (c)**

$\text{SO}_3^{2-}$  get oxidised and its 'n' factor is 2

The metal must have been reduced

Applying the law of equivalence

$$50 \times 0.1 \times (3 - n) = 25 \times 0.1 \times 2 \Rightarrow n = 2$$

**Problem 10 :**

*A mixture of magnesium chloride and magnesium sulphate is known to contain 0.6 moles of chloride ions and 0.2 moles of sulphate ions. The number of moles of magnesium ions present is*

- (a) 0.4                      (b) 0.5                      (c) 0.8                      (d) 1.0

**Solution : (b)**

In  $\text{MgCl}_2$ , the ratio of moles of  $\text{Mg}^{+2}$  to  $\text{Cl}^-$  is 1:2. Therefore, 0.6 moles of chloride combine with 0.3 moles of magnesium. In  $\text{MgSO}_4$ , 0.2 moles of sulphate combine with 0.2 moles of magnesium. Therefore, the number of moles of magnesium ion present is  $0.3 + 0.2 = 0.5$ .

**Problem 11 :**

3.0 molal NaOH solution has a density of 1.110 g/ml. The molarity of the solution is

- (a) 2.97                      (b) 3.05                      (c) 3.64                      (d) 3.050

**Solution :** (a)

Mole = 3, weight of solvent = 1000g

∴ wt. of solution = 100 + 3 × 40 = 1120g

$$\therefore \text{volume of solution} = \frac{1120}{1.110} \text{ ml} \quad \therefore M = \frac{3}{\frac{1120}{1.110 \times 1000}} = 2.97$$

**Problem 12 :**

The chloride of a metal contains 71% chlorine by weight and the vapour density of it is 50. The atomic weight of the metal will be

- (a) 29                      (b) 58                      (c) 35.5                      (d) 71

**Solution :** (a)

Molecular weight of metal chloride = 50 × 2 = 100

Let metal chloride be  $\text{MCl}_n$  then, Eq. of metal = eq. of chloride, or  $\frac{29}{E} = \frac{71}{35.5}$

$$\therefore E = \frac{29}{2}$$

Now  $a + 35.5n = 100$  or  $n.E + 35.5n = 100 \Rightarrow n = 2$

Therefore  $a = 2 \times E = 2 \times 29/2 = 29$

**Problem 13 :**

Element X reacts with oxygen to produce a pure sample of  $\text{X}_2\text{O}_3$ . In an experiment it is found that 1.00g of X produces 1.16g of  $\text{X}_2\text{O}_3$ . Calculate the atomic weight of X.

Given: atomic weight of oxygen, 16.0 g mol<sup>-1</sup>.

- (a) 67                      (b) 100.2                      (c) 125                      (d) 150

**Solution:** (d)

The mass of O atoms = 1.16 – 1.00 = 0.160g

$$\text{Number of moles of O atom} = \frac{0.160}{16} = 0.01$$

$$\text{In } \text{X}_2\text{O}_3, \quad \frac{\text{No. of moles of X}}{\text{No. of moles of O}} = \frac{2}{3}$$

$$\text{No. of moles of X} = \frac{2}{3} \times 0.01 = \frac{0.02}{3} = 0.00666$$

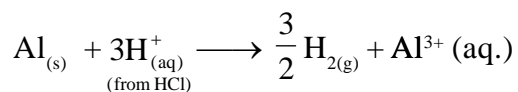
$$\text{Atomic weight of X} = \frac{\text{mass in g}}{\text{no. of moles}} = \frac{1.0}{0.00666} = 150$$

**Problem 14 :**

*The reaction between aluminium metal and dilute hydrochloric acid produces  $H_{2(g)}$  and  $Al^{3+}$  ions. The molar ratio of aluminium used to hydrogen produced is*

- (a) 1:2                      (b) 2:1                      (c) 2:3                      (d) 3:2

**Solution:** (c)



The molar ratio of  $Al_s$  used to  $H_2$  produced is  $1: \frac{3}{2}$  or 2:3.

**Problem 15 :**

*In an aqueous solution of barium nitrate, the  $[NO_3^-]$  is 0.80M. This solution is labelled as*

- (a) 0.080 N  $Ba(NO_3)_2$                       (b) 0.160 M  $Ba(NO_3)_2$   
 (c) 0.040 M  $Ba(NO_3)_2$                       (d) 0.080 M  $NO_3^-$

**Solution:** (c)

In  $Ba(NO_3)_2$ , the molar ratio of  $Ba(NO_3)_2$  to  $NO_3^-$  is 1:2. Therefore, the molarity of the  $Ba(NO_3)_2$

solution is  $\frac{1}{2} \times 0.080 = 0.040M$ .