



# STOICHIOMETRY-II

THEORY AND EXERCISE BOOKLET

# CONTENTS

S.NO.	TOPIC	PAGE NO.
1.	THEORY WITH SOLVED EXAMPLES	
2.	CLASS ROOM PROBLEMS	16 - 21
3.	EXERCISE - I	22 – 27
4.	EXERCISE - II	28 – 29
5.	EXERCISE - III	30 – 34
6.	EXERCISE - IV	35
7.	EXERCISE - V	36 – 38
8.	ANSWER-KEY	39 – 40

394 - Rajeev Gandhi Nagar Kota, Ph. No. 0744-2209671, 93141-87482, 93527-21564 www. motioniitjee.com , email-hr.motioniitjee@gmail.com

Page # 2 STOICHIOMETRY - II

# **JEE SYLLABUS:**

# STOICHIOMETRY - II

Oxidation number, Calculation for oxidation number, normality, law of equivalence, redox-reactions, titration,



# **OXIDATION & REDUCTION**

#### **Oxidation Number:**

It is the charge (real or imaginary) which an atom appears to have when it is in combination. It may be a whole no. or fractional. An element may have different values of oxidation number depending. It depends on nature of compound in which it is present. There are some operational rules to determine oxidation number.

## **Oxidation:**

Addition of oxygen, removal of hydrogen, addition of electro-negative element, removal of electropositive element, loss of electrons, increase in oxidation number (de – electronation).

#### Reduction:

Removal of oxygen, addition of hydrogen, removal of electronegative element, addition of electro +ve element, gain of electrons, decrease in oxid. no. (electronation).

#### **Redox Reactions:**

A reaction in which oxidation & reduction occur simultaneously.

#### **Oxidising Agents:**

(oxidants, oxidisors). They oxidise others, themselves are reduced & gain electrons. eg.  $O_2$ ,  $O_3$ ,  $HNO_3$ ,  $MnO_2$ ,  $H_2O_2$ , halogens,  $KMnO_4$ ,  $K_2Cr_2O_7$ ,  $KIO_3$ ,  $Cl(SO_4)_3$ ,  $FeCl_3$ , NaOCl, hydrogen ions.

[Atoms present in their higher oxidation state.]

#### **Reducing Agents:**

 $H_2$ , molecular form is weak reducing agent but Nascent hydrogen is powerful. C, CO,  $H_2S$ ,  $SO_2$ ,  $SnCl_2$ , sodium thio Sulphate, Al, Na,  $CaH_2$ ,  $NaBH_4$ ,  $LiAlH_4$ . They reduce others, themselves get oxidised & lose electrons. Also called reductants or reducers.

[Atoms present in their lower oxidation state.]

## **Both oxidising & Reducing Agents:**

SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>, etc.

#### **Balancing of Equations:**

- (i) <u>Ion electron method</u>
- (ii) Oxidation number method

[Concept involved that in any chemical reaction e<sup>-</sup> cannot be produced so no. of e<sup>-</sup> s in O.H. & R.H. should be same]

Note: To predict the product of reaction remember:

- (a) Free halogen on reduction gives halide ion  $(F_2 \rightarrow F^-)$
- (b) Alkali metals on oxidation give metallic ion with +1 oxidation state.
- (c) In alkaline medium it is reduced to K<sub>2</sub>MnO<sub>4</sub> but in strong alkaline or neutral medium it reduces of Mn<sup>+4</sup>
- (d) In acid solution KMnO₄ is reduced to Mn²+
- (e)  $H_2O_2$  on reduction gives water and on oxidation gives oxygen.
- (f) Dichromate ion in acid solution is reduced to Cr<sup>3+</sup>.



Page # 4 STOICHIOMETRY - II

## **Nature of Oxides Based on Oxidation Number:**

Lowest oxidation state  $\rightarrow$  Basic (MnO)

Intermediate oxidation state  $\rightarrow$  Amphoteric  $(Mn_3O_4, MnO_2)$ 

Highest oxidation state  $\rightarrow$  Acidic  $(Mn_2O_7)$ 

### **Rules For Assigning Oxidation Number:**

(i) Oxidation number of free elements or atoms is zero.

- (ii) Oxidation number of allotropes is zero.
- (iii) Oxidation number of atoms in homo-nuclear molecules is zero.
- (iv) Oxidation number of mono-atomic ions is equal to the algebric charge on them.
- (v) Oxidation number of F in compounds is -1
- (vi) Oxidation number of H in its compounds is +1, except in metalhydrides where it is -1
- (vii) Oxidation number of O is -2 in its compounds, but in  $F_2$  O it is +2 and in peroxides it is -1 and -0.5 in  $KO_2$
- (viii) Oxidation number of alkali metals in their compounds +1.
- (ix) Oxidation number of alkaline earth metals in their compounds is +2.
- (x) The sum of oxidation number of all the atoms in a molecule should be zero and in an ion equal to its charge.

# Average Oxidation Number: Find Oxidation Number of Fe in Fe<sub>3</sub>O<sub>4</sub>.

Fe<sub>3</sub>O<sub>4</sub> is FeO. Fe<sub>2</sub>O<sub>3</sub>

O.N. of Fe in FeO is +2; O.N. of Fe in Fe<sub>2</sub>O<sub>3</sub> is +3.

Therefore average O.N. of three Fe atoms =  $\frac{+2+2x(+3)}{3}$  =  $+\frac{8}{3}$ 

# **EQUIVALENT CONCEPT**

## (A) Volumetric analysis:

This mainly involve titrations based chemistry. If can be divided into two major category.

(I) Non-redox system (II) Redox system

#### (I) Non-redox system

This involve following kind of titrations:

- 1. Acid-Base titrations
  - 2. Back titration
- 3. Precipitation titration
- 4. Double indicator acid base titration

#### **Titrimetric Method of Analysis:**

A titrimetric method of analysis is based on chemical reaction such as.

$$aA + tT \rightarrow Product.$$

Where 'a' molecules of "analysis", A reacts with t molecules of reagent T.

T is called Titrant normally taken in buret in form of solution of known concentration. The solution of titrant is called "standard solution".

The addition of titrant is added till the amount of T, chemically equivalent to that of 'A' has been added. It is said equivalent point of titration has been reached. In order to know when to stop addition of titrant, a chemical substance is used called indicator, which respond to appearance of excess of



titrant by changing colour precisely at the equivalence point. The point in the titration where the indicator changes colour is termed the 'end point'. It is possible that end point be as close as possible to the equivalence point. The term titration refer's to process of measuring the volume of titrant required to reach the end point.

#### Law of Chemical equivalence:

It states that in any chemical reaction the equivalents of all the reactants and products must be same.

$$2A + 3B \rightarrow 4C$$

Eg. of A = Equivalents of 'B' = Equivalents of 'C'

Equivalents of 'A' = 
$$\frac{\text{Weight of 'A'}}{\text{Equivalent weight of 'A'}}$$

or Equivalents of 'A' = no. of moles of 'A'  $\times$  n-factor

$$A + B + C \rightarrow product$$

If A & B do not react with each other but C react with both A & B then

meq. of A + meq. of B = meq. of C

#### n - factor calculation

n factor here we mean a conversion factor by which we divide molar mass of substance to get equivalent mass and it depends on nature of substance which vary from one condition to another condition. We can divide n-factor calculations in two category.

- (1) In case of non-redox reaction.
  - (a) n factor of acid = basicity of the acid

**Basicity**: Number of replacible H<sup>+</sup> ion.

- **Ex.1** n factor of HCl = 1
  - n factor of CH<sub>3</sub>COOH = 1
  - n factor of  $H_2SO_4 = 2$
  - (b) n factor of base = acidity of the base

Acidity: Number of replaceble OH- ion.

- **Ex.2** n factor of NaOH = 1
  - n factor of  $Ca(OH)_{2} = 2$
  - n factor of AI(OH)<sub>3</sub> = 3 inturing potential through education
  - n factor of  $B(OH)_3 = 1$  (because it is a mono basic acid)
  - (c) n factor Salt: Total number of positive or negative charge.
- **Ex.3** n factor of NaCl = 1
  - n factor of  $Na_3SO_4 = 2$
  - n factor of  $K_2SO_4.AI_2(SO_4)_3.24H_2O = 8$
- **Ex.4** Find the n factor of H<sub>3</sub>PO<sub>4</sub> in the following reaction.

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 + 2H_2O$$

- **Sol.** Basicity of H<sub>3</sub>PO<sub>4</sub> in the above reaction is 2
  - ∴ the n factor of H<sub>3</sub>PO<sub>4</sub> is 2



# (2) In case of redox reaction.

# (a) From oxidation number

n factor of oxidising or redusing agent = change in oxidation number per molecule.

 $\Rightarrow$  consider a salt  $A_x B_y$  in which the O.S. of A is +c. It changes to a compound  $A_d E$  in which the O.S. of A is +f. Here we are assuming that B does not undergo any change in O.S.

 $A_x^{+c} B_y \to A_d^{+f} E$  (obviously  $A_x B_y$  must have reacted with some other substance to produce the product  $A_d E$ . That means other substance has the atom E in it.)

The 'n' factor is = |xc - xf|.

- **Ex.5** Find the n factor of KMnO<sub>4</sub> in different medium.
- **Sol.** (i) In acidic mediam

 $KMnO_4 \rightarrow Mn^{+2}$ 

Change in oxidation number of Mn = +7 - 2 = 5

- $\therefore$  the n factor of KMnO<sub>4</sub> = 5 **Ans.**
- (ii) basic medium

 $KMnO_4 \rightarrow K_2MnO_4$ 

n factor of  $KMnO_4 = +7 - 6 = 1$  **Ans.** 

(iii) neutral medium

 $KMnO_4 \rightarrow MnO_2$ 

n factor of  $KMnO_4 = +7 - 4 = 3$  **Ans.** 

- **Ex.6** Find the n factor of  $Na_2S_2O_3$  in the following reactions.
  - (a)  $Na_2S_2O_3 + I_2 \rightarrow NaI + Na_2S_4O_6$

sodium thio sodium tetra

sulphate thionate

- (b)  $Na_2S_2O_3 + I_2 \rightarrow NaI + Na_2SO_4$
- **Sol.** (a) Change in oxidation number of sulphur = |+2 2.5| = 0.5

Change in oxidation number per molecule =  $0.5 \times 2$ 

- $\therefore$  n factor of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 1
- (b) Change in oxidation number of sulphur = |2 6| = 4

Change in oxidation number per molecule =  $4 \times 2$ 

- $\therefore$  n factor of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 8
- $\Rightarrow$  Consider the salt  $A_x B_y$  to undergo a reaction so that the element A undergoes a change in O.S. but is present in more than one product with the same O.S. i.e.  $A_x^{+c}By \to A_a^{+f}B_y + A_g^{+f}H$  (the superscripts denote the oxidation state of the respective elements).

$$\therefore$$
 n =  $|xc - xf|$ 

 $\Rightarrow$  Salts that react in such a way that more than one type of atom in the salt undergoes O.S. change.

$$A_x^{+c}By \rightarrow A_a^{+f}E + J_xB^{-1}$$

In this case both A and B are changing their O.S.'s and both of them are either getting oxidised or reduced. In such a case n factor of the compound is the sum of the individual n factors of A and B. i.e. |xc - xf| + |-xC - (-yi)|. Then n factor of A can be undersood which is |xc - xf|. The n factor of B is |-xc - (-yi)|



# **Disproportionation Reactions:**

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disporportionation reactions.

n factor = 
$$2 = n_2$$

$$Cl_2(g) + 2OH^-(aq) \rightarrow C^{+1}O^-(aq) + Cl^-(aq) + H_2O(\ell)$$

$$n factor = 2 = n_1$$

n factor of overall reaction =  $n_1 \times n_2 / n_1 + n_2$ 

#### (b) From ion electron method:

n factor = total number of electrons transfered per mole of the reactant

**Ex.8** 
$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4 H_2O$$
  
n factor of KMnO<sub>4</sub> = 5

#### **Acid-Base titration.**

To find out strength or concentration of unknown acid or base it is titrated against base or acid of known strength. At the equivalence point we can know amount of acid or base used and then with the help of law of equivalents we can find strength of unknown.

Meq of acid at equivalence point = Meq of base at equivalence point

**Ex.9** One litre solution of alkali (NaOH) is prepared by dissolving impure solid of alkali which contain 5% Na<sub>2</sub>CO<sub>3</sub> and 8% CaCO<sub>3</sub> and 10% NaCl. A 10 ml portion of this solution required 9.8 mL of a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for neutralization. Calculate weight of alkali dissolved initially.

gm eq. of  $Na_2CO_3$  + gm eq. of  $CaCO_3$  + gm eq. of NaOH = gm eq. of  $H_2SO_4$ 

**Sol.** 
$$\frac{5x}{100} \times \frac{1}{53} + \frac{8x}{100} \times \frac{1}{50} + \frac{77x}{100} \times \frac{1}{40} = 0.98$$
  $x = 45 \text{ g Ans.}$ 

#### **Back titration**

Back titration is used in volumetric analysis to find out excess of reagent added by titrating it with suitable reagent. it is also used to find out percentage purity of sample. For example in acid-base titration suppose we have added excess base in acid mixture. To find excess base we can titrate the solution with another acid of known strength.

- **Ex.10** 20 g. of a sample of Ba(OH)<sub>2</sub> is dissolved in 50 ml. Of 0.1 N HCl solution. The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of Ba(OH)<sub>2</sub> in the sample.
- **Sol.** Milli eq. of HCl initially =  $50 \times 0.1 = 5$

Milli eq. of NaOH consumed = Milli eq. of HCl in excess =  $20 \times 0.1 = 2$ 

 $\therefore$  Milli eq. of HCl consumed = Milli eq. of Ba(OH)<sub>2</sub> = 5 - 2 = 3

 $\therefore$  eq. of Ba(OH)<sub>2</sub> = 3/1000 = 3 × 10<sup>-3</sup>

Mass of Ba(OH)<sub>2</sub> =  $3 \times 10^{-3} \times (171/2) = 0.2565$  g.

% Ba(OH)<sub>2</sub> =  $(0.2565/20) \times 100 = 1.28$  % **Ans.** 



**Ex.11** 4.0 g of monobasic, saturated carboxylic acid is dissolved in 100 mL water and its 10 mL portion required 8.0 mL 0.27 M NaOH to reach the equivalence point. In an another experiment, 5.0 g of the same acid is burnt completely and  $CO_2$  produced is absorbed completely in 500 mL of a 2.0 N NaOH solution. A 10 mL portion of the resulting solution is treated with excess of  $BaCl_2$  to precipitate all carbonate and finally titrated with 0.5 N  $H_2SO_4$  solution. Determine the volume of the acid solution that would be required to make this solution neutral.

**Sol.** meg. of NaOH = 
$$8 \times 0.27$$
 = meg. of acid for 10 ml of acid solution

meq. of acid for 100 ml of solution = 
$$\frac{8 \times 0.27 \times 100}{10} = \frac{4}{M} \times 10^3$$

M (acid) = 
$$\frac{4}{8 \times 0.27 \times 10} \times 1000 = 185.2$$

Formula of acid. =  $C_n H_{2n} O_2$ 

$$\Rightarrow$$
 M = 14n + 32 = 185.2

$$\Rightarrow$$
 n = 11

Now 5g acid will produce  $\frac{5}{185.2} \times 11 = \frac{55}{185.2}$  mol CO<sub>2</sub> after complete combustion.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Total mass of NaOH available =  $500 \times 2 \times 10^{-3} = 1.0$  mole

Moles of NaOH left unreacted = 
$$1 - \frac{2 \times 55}{185.2} = \frac{76}{185.2}$$
 in 500 mL

 $\Rightarrow$  Molarity of NaOH after precipitation of Na<sub>2</sub>CO<sub>3</sub> = 0.812

Therefore, 
$$0.812 \times 10 = 0.5 \times V$$

$$\Rightarrow$$
 V = 16.24 ml **Ans.**

## **Precipitation titration:**

In ionic reaction we can know strength of unknown solution of salt by titrating it against a reagent with which it can form precipitate. For example NaCl strength can be known by titrating it against  $AgNO_3$  solution with which it form white ppt. of AgCl.

So meq. of NaCl at equivalence point = meq. of AgNO<sub>3</sub> used = meq. of AgCl formed

**Ex.12** A complex of cobalt with ammonia is analyzed for determining its formula, by titrating it against a standardized acid as follows:

$$Co(NH_3)_x Cl_3(aq) + HCl \rightarrow NH_4^+(aq) + Co^{3+}(aq) + Cl^-(aq)$$

A 1.58 g complex required 23.63 mL 1.5 M HCl to reach the equivalence point. Determine formula. If the reaction mixture at equivalence point is trated with excess of  $AgNO_3$  solution, what mass of AgCl will precipitate out?

**Sol.** The balanced chemical reaction is:

$$Co(NH_3)_xCl_3 + xHCl \rightarrow xNH_4^+ + Co^{3+} + (x + 3) Cl^-$$

$$\frac{1.58}{165.5 + 17x} \frac{1.58x}{165.5 + 17x} \frac{1.58(x + 3)}{165.5 + 17x}$$

$$\Rightarrow \frac{1.58x}{165.5 + 17x} = \frac{23.63 \times 1.5}{1000} = moles of HCl$$

$$\Rightarrow x = 6$$

moles of CI = moles of AgCI = 
$$\frac{(x+3)\times1.58}{165.5+17x}$$
  
wt. of AgCI =  $\frac{(x+3)\times1.58}{165.5+17x}\times143.5=7.62$   
m(AgCI) =  $0.053\times143.5=7.62$  q **Ans.**

#### CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER

The weight % of available  $Cl_2$  from the given sample of balaching powder on reaction with dil acids or  $CO_2$  is called available chlorine.

$$\begin{aligned} &\mathsf{CaOCl}_2 + \mathsf{H}_2\mathsf{SO}_4 \to \mathsf{CaSO}_4 + \mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2 \\ &\mathsf{CaOCl}_2 + \mathsf{2HCl} \to \mathsf{CaCl}_2 + \mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2 \\ &\mathsf{CaOCl}_2 + \mathsf{2CH}_3\mathsf{COOH} \to \mathsf{Ca(CH}_3\mathsf{COO)}_2 + \mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2 \\ &\mathsf{CaOCl}_2 + \mathsf{CO}_2 \to \mathsf{CaCO}_3 + \mathsf{Cl}_2 \end{aligned}$$

#### Method of determination:

Bleaching powder + 
$$CH_3COOH + KI \frac{starch}{Hypo}$$
 end point meq. of  $I_2$  = meq. of  $CI_2$  = meq. of Hypo solution

% of  $CI_2 = \frac{3.55 \times x \times V(mL)}{W(q)}$ 

where x = molarity of hypo solution v = mL. of hypo solution used in titration.

**Ex.13** 10 gm sample of bleaching powder was dissolved into water to make the solution on litre. To this solution 35 mL of 1.0 M Mohr salt solution was added containing enough  $H_2SO_4$ . After the reaction was complete, the excess Mohr salt required 30 mL of 0.1 M KMnO<sub>4</sub> for oxidation. The % of available  $Cl_2$  approximately is (mol wt = 71)

**Sol.14** meg. of Mohr's salt = 
$$35 \times 1 \times 1 = 35$$

meq. of KMnO<sub>4</sub> = meq. of excess mohr salt =  $30 \times 0.1 \times 5 = 15$  The parameter meq. of Mohr salt reacted with bleaching powder = 35 - 15 = 20 Meq. of Cl<sub>2</sub> = 20

wt. of 
$$Cl_2 = 20 \times 10^{-3} \times \frac{71}{2} = 0.71 \text{ gm}$$

% of 
$$Cl_2 = \frac{0.71}{2} \times 100 = 7.1$$
 % **Ans.**

#### Double indicator acid-base titration:

In the acid-base titration the equivalence point is known with the help of indicator which changes its colour at the end point. In the titration of polyacidic base or polybasic acid there are more than one end point. One indicator is not able to give colour change at every end point. So to find out each end point we have to use more than one indicator. For example in the titration of  $Na_2CO_3$  against HCl there are two end points.



$$Na_2CO_3 + HCI \rightarrow NaHCO_3 + NaCI$$
  
 $NaHCO_3 + HCI \rightarrow H_2CO_3 + NaCI$ 

When we use phenolphthalein in the above titration it changes its colour at first end point when  $NaHCO_3$  is formed and with it we can not know second end point. Similarly with methyl orange it changes its colour at second end point only and we can not know first end point. it is because all indicator changes colour on the basis of pH of medium. So in titration of  $NaHCO_3$ ,  $KHCO_3$  against acid phenolphthalein can not be used.

Titration		Indicator	pH Range	n factor
Na <sub>2</sub> CO <sub>3</sub>	against acid	Phenolphthalein	8.3 – 10	1
Na <sub>2</sub> CO <sub>3</sub>	"	Methyl orange	3.1 – 4.4	2

A sample contains NaOH, Na<sub>2</sub>CO<sub>3</sub> & NaHCO<sub>3</sub>. This solution is titrated with HCl or H<sub>2</sub>SO<sub>4</sub>

(i) When Phenolphthalein (HPh) is used as indicator the reaction are given below.

This is the Half neutralisation of Na<sub>2</sub>CO<sub>3</sub>

$$NaHCO_3 + HCI \rightarrow X$$

Hence

Meq. of HCl = meq of NaOH + 
$$\frac{1}{2}$$
 meq. of Na<sub>2</sub>CO<sub>3</sub>

(ii) when methyl orange (MeOH) is used as indicator

$$Na_2CO_3 + 2HCI \rightarrow 2 NaCI + H_2O + CO_2$$

This is the complete neutralisation

$$NaHCO_3 + HCI \rightarrow NaCI + H_2O + CO_3$$

in this case

meq. of HCl = meq of NaOH + meq. of Na
$$_2$$
CO $_3$  + meq. of NaHCO $_3$ -JEE|ALEEE

(iii) If MeOH is added after the first end point obtained from HPh

$$NaHCO_3 + NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

Produced original

meq. of HCl = meq. of NaHCO<sub>3</sub> (produced) + meq. of NaHCO<sub>3</sub> (original)

#### Note:

When we carry out dilution of solution, meq eq. milli mole or mole of substance does not change because they represent amount of substance, however molar concentration may change.

**Ex.15** A solution contains a mixture of  $Na_2CO_3$  and NaOH. Using phenolphthalein as indicator 25 ml. of mixture required 19.5 ml of 0.995 N HCl for the end point. With methyl orange. 25 ml of solution required 25 ml. of the same. HCl for the end point. Calculate grams per litre of each substance in the mixture.



**Sol.** Let a & b are the meq. of Na<sub>2</sub>CO<sub>3</sub> and NaOH respectively when phenolphthale in is used as indicator

$$\frac{1}{2} \text{ meq. of Na}_2\text{CO}_3 + \text{meq. of NaOH} = \text{meq of HCI}$$

$$\frac{a}{2} + b = 19.5 \times 0.995$$

$$\frac{a}{2} + b = 19.4$$
 ...(1)

when MeOH is used as indicator

meq. of  $Na_2CO_3$  + Meq. of NaOH = meq. of HCl

$$a + b = 25 \times 0.995$$
  
 $a + b = 24.875$ 

from (1) & (2)

$$\frac{a}{2} = 5.475 \implies a = 10.95$$

$$b = 24.875 - 10.95 = 13.925$$

wt of Na<sub>2</sub>CO<sub>3</sub> /lit = 
$$\frac{10.95}{25} \times 10^{-3} \times \frac{106}{2} \times 1000 = 23.2 \text{ gm/lit}$$

wt of NaOH/lit =  $b \times 10^{-3} \times 84/25 \times 1000 = 22.28$  gm/lit **Ans.** 

- **Ex.16** 2.5 g of a mixture containing  $CaCO_3$ ,  $Ca(HCO_3)_2$  and NaCl was dissolved in 100 mL water and its 10 mL portion required 10 mL 0.05 M  $H_2SO_4$  solution to reach the phenolphthalein end point. An another 10 mL portion of the same stock solution required 32.35 mL of the same acid solution to reach the methyl orange end point. Determine mass percentage of  $CaCO_3$  and  $Ca(HCO_3)_2$  in the original mixture.
- **Sol.** Let a and b are the meq. of CaCO<sub>3</sub> and Ca(HCO<sub>3</sub>)<sub>2</sub> respectively.

When HPh is used is indicater then only CaCO<sub>3</sub> will react with H<sub>2</sub>SO<sub>4</sub>

meq. of  $H_2SO_4 = 1/2$  meq. of  $CaCO_3$ 

meq. of 
$$H_2SO_4 = \frac{10 \times 0.05 \times 100 \times 2}{10} = 10$$

meq. of 
$$CaCO_3 = 20$$

When MeOH is used as indicator

then meq. of  $CaCO_3$  + meq. of  $Ca(HCO_3)_2$  = meq. of  $H_2SO_4$ 

$$a + b = \frac{32.35 \times 0.05 \times 2}{10} \times 100$$
 potential through education

$$a + b = 32.35$$

$$b = 12.5$$

wt. of 
$$CaCO_3 = a \times 10^{-3} \times 100/2$$

wt. of 
$$Ca(HCO_3)_2 = b \times 10^{-3} \times 162/2 = 1 \text{ gm}$$

% of CaCO<sub>3</sub> = 
$$\frac{1}{2.5} \times 100 = 40\%$$

% of Ca(HCO<sub>3</sub>)<sub>2</sub> = 
$$\frac{1}{25} \times 100 = 40\%$$



**Ex.17** 6.4 g of a pure monobasic organic acid is burnt completely in excess of oxygen and  ${\rm CO_2}$  evolved is absorbed completely in one litre of an aqueous solution of NaOH. A 10 mL portion of this solution required 14.5 mL of a normal HCl solution to reach the phenolphthalein end point. An another 10 mL portion of the same solution required 18 mL of the same HCl solution to reach the methyl organe end point. If the organic acid contains 25% oxygen by weight, deduce the empirical formula of this acid and strength of original NaOH solution.

**Sol.** 
$$C_xH_yO_2 + O_2 \rightarrow xCO_2 \xrightarrow{2NaOH} xNa_2CO_3$$

$$\frac{6.4}{M} \xrightarrow{6.4x} \frac{6.4x}{M}$$

Let 100 ml of solution contains a meq. of NaOH & b meq. of  $\mathrm{Na_2CO_3}$ 

when HPh is used as indicator then

meq. of NaOH + 1/2 meq. of Na<sub>2</sub>CO<sub>3</sub> = Meq. of HCl

$$= \frac{14.5 \times 1}{10} \times 1000 = 40\%$$

$$a + b/2 = 14.5 \times 100$$

$$a + b/2 = 14.5 \times 100 = 1450 \dots (1)$$

when MeOH is used as indicator

meq. of NaOH + meq. of  $Na_2CO_3 = Meq.$  of HCl

$$a + b = 18 \times 1 \times \frac{1}{10} \times 100 = 1800$$
 ...(2)

$$b = 700$$

$$a = 100$$

moles of Na<sub>2</sub>CO<sub>3</sub> = 
$$\frac{b \times 10^{-3}}{2}$$
 =  $\frac{6.4}{M} \times x$ 

$$\Rightarrow \frac{700 \times 10^{-3}}{2} = 6.4 \frac{x}{M} \dots (1)$$

wt % of = 25

$$M \times \frac{25}{100} = 32 \implies M = 128$$

from (1) 
$$\frac{700 \times 10^{-3}}{2} = 6.4 \times \frac{x}{128}$$

$$\frac{700 \times 10^{-3}}{2} \times \frac{128}{6.4} = x = 7$$

formula C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>

Molarity of NaOH = 
$$\frac{1800}{1000}$$
 = 1.8 M **Ans.**

**Ex.18** A solution contains  $Na_2CO_3$  and  $NaHCO_3$ . 10 mL of the solution requires 2.5 mL of 0.1 M  $H_2SO_4$  for neutralisation using phenolphthalein as an indicator. Methyl organge is added when a further 2.5 mL of 0.2 M  $H_2SO_4$  was required. Calculate the amount of  $Na_2CO_3$  and  $NaHCO_3$  in one litre of the solution.

when HPh is used as indicator

then 
$$\frac{1}{2}$$
 meq. of Na<sub>2</sub>Cl<sub>3</sub> = meq. of H<sub>2</sub>SO<sub>4</sub>

$$\frac{a}{2} = 2.5 \times 0.1 \times 2 \implies \qquad a = 1$$

MeOH is added after the forst eard point the solution

Contains NaHCO<sub>3</sub> original & NaHCO<sub>3</sub> produced.

meq. of H<sub>2</sub>SO<sub>4</sub> = meq. of NaHCO<sub>3</sub> original + meq. of NaHCO<sub>3</sub> produced

$$2.5 \times 0.2 \times 2 = b + 1/2 \text{ meq. of Na}_2\text{CO}_3$$
  
=  $b + a/2$ 

$$b + a/2 = 1$$

$$b = 1 - 0.5 = 0.5$$

wt of 
$$Na_2CO_3/lit = a \times 10^{-3} \times \frac{106}{2} \times \frac{1}{10} \times 1000$$

$$= 1 \times \frac{53}{10} = 5.3 \text{ gm}$$

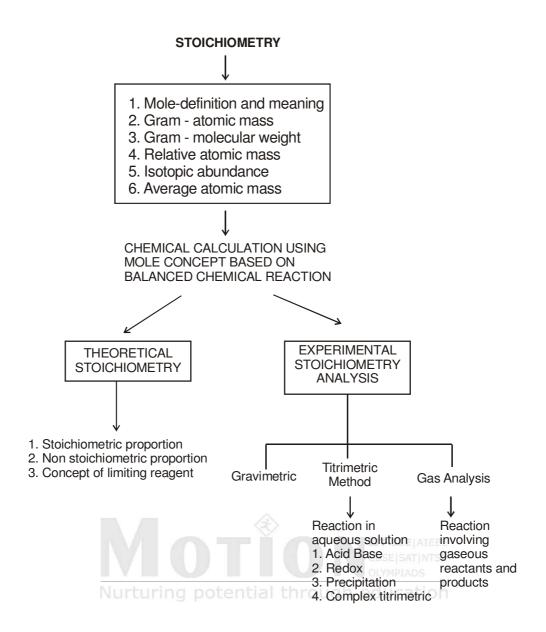
wt of NaHCO<sub>3</sub>/lit = b × 
$$10^{-3}$$
 × 84 ×  $\frac{1}{10}$  × 1000 = 4.2 gm **Ans.**





Page # 14 STOICHIOMETRY - II

## **THE ATLAS**



#### **GLOSSARY**

**Aliquot**. A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called as aliquot.

**Analytical concentration,** The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

**Equivalent.** The amount of a substance which furnishes or reacts with 1 mole of H<sup>+</sup> (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

**Equivalent weight.** The weight in grams of one equivalent of a substance.

**Equivalence point.** The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

**End point.** The point in a titration where an indicator changes color.

**Formula weight.** The number of formula weights of all the atoms in the chemical formula of a substance.

**Formality.** The number formula weights of solute per litre of solution; synonymous with analytical concentration.

**Indicator.** A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

**Normality.** The number of equivalents of solute per litre of solution.

**Primary standard.** A substance available in a pure form or state of known purity which is used in standardizing a solution.

**Standardization.** The process by which the concentration of a solution is accurately ascertained.

**Standard solution.** A solution whose concentration has been accurately determined.

**Titrant.** The reagent (a standard solution) which is added from a buret to react with the analyte.

