

Volumetric Analysis : Definition and Principle

In practical chemistry, based on chemical analysis the nature and amount of a substance ion can be determined. This chemical analysis is of two types' quantitative analysis and qualitative analysis. Quantitative analysis deals with the volumetric and massive analysis of elements of a substance. Quantitative analysis is of two types.

1. Quantitative Analysis-

In the quantitative analysis the substance or radicals, which has to be determined, is converted into the temporary compound. This temporary compound is either measure into its original form or it is burn to convert into the other compound, which is appropriate for measurement . Now the weight of the substance or radicals is determined by the physical method. The ppt. method is the most useful method for the quantitative analysis.

Note-Quantitative analysis is not included into the syllabus of Higher Secondary.

2. Volumetric Analysis-

It is a sub-branch of quantitative analysis. It is a simple and accurate method of analysis. This method can determine amount of substance in terms of volume accurately the, hence the name volumetric analysis. In this type of analysis ,a solution of a substance whose concentration is to be calculated is taken and a known volume of another substance whose concentration is known. The volume of the solution is measured when the chemical reaction is completed. The end point of such reaction is indicated by change in colour or precipitation etc. Thus in this ,method of calculation, known volume of two substances are taken and the concentration of one of them is known then the concentration of the other is easily calculated. This method is called Titration.

Solution:-The homogenous mixture of any substance is given into the water or any liquid in solution.

Concentration or Strength-Amount of a substance in grams dissolved in a one-litre solution is called concentration or strength. Example-If the 2 grams of caustic soda is dissolved in 1 litre then the concentration Example-If the 2 grams of caustic soda is dissolved in 1 litre then the concentration of the solution will be 2gm/litre.

Normality-Amount of a substance in grams equal to its 1 gm equivalent weight in 1 litre solution is called Normality of that solution.

Or

Normality can be express by the following formula, which is a ratio between concentration of that solution and gram equivalent weight of that substance. It is denoted by N. It is a number. It does not have any limit.

Normality = Concentration / Equivalent weight

Example-(1) Concentration of Caustic Soda solution is 4 gm/litre and equivalent weight of Caustic Soda is 40 .Normality of this solution will be.
 $= \frac{4}{40} = \frac{1}{10} = \frac{N}{10} = 0.1N$

Example-(2) 2N Caustic Soda solution will have 80 gm of it dissolved in 1 litre because:

$2xN=2x40$ i.e. 80 gm/litre.

Molarity or Gram Molecular Weight : The amount of substance equal to its gram molecular weight dissolved in one litre solution, is called as Molar Solution. For example, 20 gm of caustic soda dissolved in one litre solution will form 0.5 M solution of Caustic Soda.

Percentage : Amount of solute dissolved in 100 parts of the solution is called percentage of that Solution.

Example : 10 percent solution of NaOH means 10 gram of NaOH dissolved in 100 gram of NaOH.

Gram Molecular Weight : Amount of a substance in grams equal to molecular weight of that substance is called 1 gram molecular weight of that substance.

Example : Molecular weight of Sodium Carbonate is 106 then its 1 gram molecular weight is 106 gram and the molecular weight of 2 gram is 212 gram.

Standard solution : Solution of known concentration (the solution in which the quantity of solvent is known in its known volume) is called a standard solution. Concentration of standard solution is expressed in terms of gram per litre or normality.

Normal Solution : A solution containing 1 gram equivalent of a solute dissolved in 1 litre of solution is called a Normal Solution.

Example : In the normal solution of Na_2CO_3 , 53 gram solvent substance is dissolved into the 1 litre (equivalent weight of Na_2CO_3 is 53).

Acid : Those substance which, when dissolved in water give Hydrogen ion (H^+) as the only positive ion are acids.

Example : $\text{HCl} = \text{H}^+ + \text{Cl}^-$

$\text{H}_2\text{SO}_4 = 2\text{H}^+ + \text{SO}_4^{2-}$

Strength of Acid : The acid, which gives more H^+ ions its strength, will be more. Two acids having same normality may have different degree of ionization and therefore the strengths will also differ.

Example : N/10 HCl is 92% ionized where as for acetic acid it is 1.3%. Therefore hydrochloric acid is a strong acid where as acetic acid is a weak acid.

Relative strength of weak acids :

$\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{CH}_3\text{COOH}$

Basisity of acids : Basisity of acids means can be express its strength to react with bases. Amount of Hydrogen ions given by one molecule of an acid is its basisity. It depends on the number of atoms of the H in acid. Therefore, number of atom of replaceable

hydrogen of any molecule of acid is basicity of acid.

HCl, HNO₃, CH₃COOH are monobasic acids, H₂SO₄ is a dibasic acid and H₃PO₄ is a Tri-basic acid.

Base : Those substances which when dissolve in water give Hydroxide ion (OH⁻) as the only negative ion are called bases.

Example : NaOH=Na⁺ + OH⁻ NH₄OH=NH₄⁺ + OH⁻

Strengths of Bases : The base those which give more OH⁻ ions will have more strength. Two bases having same Normality may have different degree of ionization. Therefore, they have different strength.

For example for same normality of N/10 NaOH is 84% ionized where as N/10 NH₄OH is only 1.3% ionized.

Relative strength of few bases -

KOH > NaOH > NH₄OH > Ba(OH)₂.

Acidity of Bases : Amount of Hydroxide ions (OH⁻) present in one molecule of base, is called the acidity.

Example : NH₄OH, NaOH are mono acidic bases. Ba(OH)₂ is a di-acidic base.

Equivalent Weight : Amount of substances which combines with or displaces 1.008 part of hydrogen or 8 part of oxygen or 35.5 part of chlorine is called equivalent weight of that substances.

Gram Equivalent Weight : Equivalent weight of a substance expressed in gram is called 1 gm equivalent weight of the substance.

Example : Equivalent of H₂SO₄ is 49. So 1 gram equivalent of H₂SO₄ will weigh 49 gram and 0.1 gm equivalent of H₂SO₄ acid will weigh 4.9 gram.

1. Equivalent weight of acid : The equivalent weight of acid is that which has one position for replaceable hydrogen atom is equivalent weight of acid. For example, one molecule of HCl has (gram molecular weight) one replaceable hydrogen atom. Therefore the equivalent weight of HCl is 36.5. Similarly one molecule of H₂SO₄ has 2 replaceable hydrogen atoms (molecular weight 98). Therefore the equivalent weight of H₂SO₄ is 49 (98/2). Equivalent weight of acid = Molecular weight of acid / Basicity of acid

2. Equivalent weight of base : The part of the base which has one portion for replaceable OH radicals or the number of weights which completely neutralize the one equivalent weight of any acid. For example in the following reaction 36.5 gram, HCl (1 gm equivalent weight) completely neutralized 40 gm NaOH. Therefore the equivalent weight of NaOH is 40.
NaOH + HCl = NaCl + H₂O

40gm 36.5gm Equivalent weight of base=Molecular weight of base/Acidity of base

3. Equivalent weight of salt : The equivalent weight of salt is the sum of the equivalent weight of the radicals. Generally the equivalent weight of acid, base or salt can be determined by the ratio of its molecular weight to the total positive valency.

The equivalent weight of Na_2CO_3 is $23+60/2=53$ or $106/2=53$

Similarly the equivalent weight of $\text{HCl}=36.5/1=36.5$

4. The equivalent weight of oxidation and reduction agents : The equivalent weight of any oxidising agent is that weight which makes available the 8 weight oxygen for reaction with 1 weight of hydrogen. Similarly the equivalent weight of the reduction agents is that weight which makes available one part of hydrogen or reacts with 8 part of oxygen.

1. KMnO_4 (Potassium Permanganate)-

This reacts in acidic medium in following ways-



Therefore, the 2 molecule of the KMnO_4 produces 5 atoms of oxygen in acidic medium

i.e.

$$2[39+55=16 \times 4] = 5 \times 16 = 10 \times 1$$

$$\text{Or } 2[158] = 10 \times 8 = 10 \times 1$$

$$\text{Or } 316/10 = 8 = 1 \quad \text{Or } 31.6 = 8 = 1$$

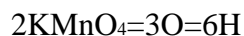
Therefore, the equivalent weight of KMnO_4 is 31.6 in the acidic medium. In the similar way.

The equivalent weight of oxidation agent = Molecular weight of substance $\times 2x$

Number of atom of the obtain oxidation agent.

(Note- Hence 2 is multiplied in formula because the atomic weight of oxygen is 16 is eight times more than the equivalent weight of oxygen).

Equivalent weight of KMnO_4 in the neutral medium-

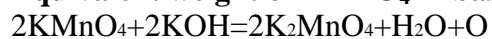


$$2 \times 158 = 3 \times 16 = 6\text{H}$$

$$316 = 6 \times 8 = 6\text{H} \quad \text{Or } 316/6 = 52.66 = 8 = 1$$

Therefore the equivalent weight of KMnO_4 in the neutral medium is 52.66.

Equivalent weight of KMnO_4 in basic medium-



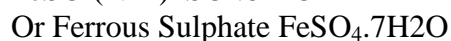
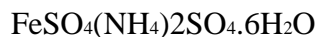
$$2 \times 158 = 16 = 2 \times 8$$

$$\text{Equivalent weight} = 2 \times 158 / 2 = 158.$$

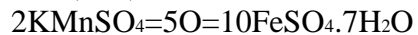
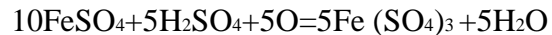
In this way, the equivalent weight of KMnO_4 in the basic medium is 158.

The example shows that the equivalent weight of any substance does not remain constant. It depends upon the reaction and the nature of the medium.

Ferrous ammonium sulphate :



(i) Equivalent weight of iron :



Therefore the equivalent weight of

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is 278.

Generally Ferrous sulphate is used in place of Ferrous ammonium sulphate $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in titration because the ferrous sulphate oxidized into the ferric sulphate in the air. Therefore the equivalent weight of ferrous ammonium sulphate is 399 (the molecular weight of the ferrous ammonium sulphate).