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# Volumetric Analysis

misostudy



## 01. Introduction

A quantitative analysis is one in which the amount or concentration of a particular species in a sample is determined accurately and precisely.

Volumetric analysis is a quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution. The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as titration.

**Unknown solution :** The solution consisting the substance to be estimated is termed unknown solution. The substance is termed titrate.

### Standard solution :

The solution in which an accurately known amount of the reagent (titrant) has been dissolved in a known volume of the solution is termed standard solution. There are two types or reagents (titrants) :

- Primary standards :** These can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), silver nitrate ( $\text{AgNO}_3$ ), copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), ferrous ammonium sulphate [ $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ], sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), etc. are the examples of primary standards.
- Secondary standards :** The solutions of these reagents are to be standardised before use as these cannot be weighed accurately. The examples are sodium hydroxide ( $\text{NaOH}$ ), potassium hydroxide ( $\text{KOH}$ ), hydrochloric acid ( $\text{HCl}$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), iodine, etc.

### Law of equivalence :

It is applied in all volumetric estimations. According to it, the chemical substances react in the ration of their chemical equivalent masses.

$$\frac{\text{Mass of substance A}}{\text{Mass of substance B}} = \frac{\text{Chemical equivalent mass of substance A}}{\text{Chemical equivalent mass of substance B}}$$

$$\text{or } \frac{\text{Mass of substance A}}{\text{Chemical equivalent mass of substance A}} = \frac{\text{Mass of substance B}}{\text{Chemical equivalent mass of substance B}}$$

$$\text{or } \text{gram equivalent of A} = \text{gram equivalent of B}$$

$$\text{or } \text{milli-gram equivalent of A} = \text{milli-gram equivalent of B}$$

The point at which the amounts of the two reactants are just equivalent is known as equivalence point or end point. An auxiliary substance which helps in the usual detection of the completion of the titration or equivalence point or end point is termed as indicator, *i.e.* substances which undergo some easily detectable changes at the equivalence point are used as indicators.

## 02. Methods of Expressing Concentrations of Solutions

(i) **Per cent by mass :**

$$\% \text{ Solute} = \frac{\text{Mass of solute in grams}}{\text{Mass of solution in grams}} \times 100$$

(ii) **Molarity (Molar concentration) :**

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$$

$$\text{Molarity} = \frac{\text{Number of milli-moles of the solute}}{\text{Number of milli-litres of the solution}}$$

(iii) **Molarity :**

$$\text{Molarity} = \frac{\text{Number of gram moles of the solute}}{\text{Number of kilograms of the solvent}}$$

(iv) **Mole fraction :**

$$\text{Mole fraction of A, } (f_1) = \frac{\frac{w_1}{m_1}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}}$$

$$\text{Mole fraction of B, } (f_2) = \frac{\frac{w_2}{m_2}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}}$$

$$\text{Mole fraction of C, } (f_3) = \frac{\frac{w_3}{m_3}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}}$$

The sum of mole fraction of a solution is equal to 1, i.e.,  $f_1 + f_2 + f_3 = 1$

(v) **Normality :**

$$\text{Normality} = \frac{\text{Number of gram equivalent of the solution}}{\text{Number of litres of the solution}}$$

**Normality equation :**

So,  $N_1V_1 = N_2V_2$  (Normality equation)

**Relationship between normality and molarity :** We know that,  
Strength of the solution (g/L) = Normality  $\times$  Equivalent mass  
Similarly,

Strength of the solution (g/L) = Molarity  $\times$  Molecular mass

So,

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass of the substance}}{\text{Equivalent mass of the substance}} = n$$

or Normality =  $n \times$  Molarity

In the case of acids, 'n' is basicity of acids while in the case of bases, 'n' is acidity of bases.