B.Sc. II Year (Inorganic Practical)

What is Titration?

Titration is a quantitative chemical analysis. It is used to determine an unknown concentration of a known substance in a sample.

The basic principle of the titration is the following:

A solution - a so called titrant or standard solution - is added to sample to be analyzed. The titrant contains a known concentration of a chemical which reacts with the substance to be determined. The titrant is added by means of a burette. A burette is a device which allows to exactly measure the quantity (volume) of the titrant added. Due to the chemical reaction taking place in the sample to be analysed, the characteristics of the sample changes. Hence it is volumetric analysis.

Burette

This change of the characteristics can be detected either by a so called color indicator or a sensor:

- A color indicator changes its color as soon as all the substance contained in the sample has reacted with the titrant added.

The concentration of the substance contained in the sample can then be calculated based on the volume of the titrant which was required to add until all the substance had reacted.

Terms for varieties of titration can reflect the nature of the reaction between A and B. Thus, there are acid-base, complexometric and oxidation-reduction titrations.

Conical flask

Standard solutions are prepared using standard substances in one of several ways. A primary standard is a substance of known high purity which may be dissolved in a known volume of solvent to give a primary standard solution. If stoichiometry is used to establish the strength of a titrant, it is called a secondary standard solution. The term secondary standard can also be applied to a substance whose active agent contents have been found by comparison against a primary standard.

End point and Equivalent point:

The main difference between **equivalence** and **endpoint** is that the **equivalence point** is a **point** where the chemical reaction comes to an **end** while the **endpoint** is the **point** where the colour change occurs in a system.

For a reaction, a stage which shows the completion of a particular reaction is known as end point. Equivalence point is a stage in which the amount of reagent added is exactly and stoichiometrically equivalent to the amount of the reacting substance in the titrated solution. The end point is detected by some physical change produced by the solution, by itself or more usually by the addition of an auxiliary reagent known as an 'indicator'. The end point and the equivalence point may not be identical. End point is usually detected only after adding a slight excess of the titrant. In many cases, the difference between these two will fall within the experimental error.

Indicator:

It is a chemical reagent used to recognize the attainment of end point in a titration. After the reaction between the substance and the standard solution is complete, the indicator should give a clear colour change.

When a titration is carried out, the free energy change for the reaction is always negative.

That is, during the initial stages of the reaction between A & B, when the titrant A is added to B the following reaction takes place.

$$A + B \rightleftharpoons C + D$$

Equilibrium constant,

$$K = \frac{a_C . a_D}{a_A . a_B} = \frac{[C].[D]}{[A].[B]}$$

a = activity co-efficient.

Large values of the equilibrium constant K implies that the equilibrium concentration of A & B are very small at the equivalence point. It also indicates that the reverse reaction is negligible and the product C & D are very much more stable than the reactants A & B. Greater the value of K the larger the magnitude of the negative free energy change for the reaction between A & B. Since,

$$\text{Free Energy Change} = \Delta G = -RT \ln K$$

Where,

R = Universal gas Constant = 8.314 $JK^{-1}mol^{-1}$,
T = Absolute Temperature.

The reaction of the concentration of A & B leads to the reduction of the total free energy change. If the concentrations of A & B are too low the magnitude of the total free energy change becomes so small and the use of the reaction for titration will not be feasible.

Expressions of Concentration of Solutions:

The concentration or strength of solution means the amount of solute present in a given amount of the solution. The concentration may be expressed in physical or chemical units.

1. **Normality (N):** It is defined as number of gram equivalents of the solute present in 1 litre (1000mL.) of the solution. If W g of solute of equivalent

weight E is present in V mL of the solution, the normality of the solution is given by:

$$\text{Normality} = \frac{W \times 1000}{E \times V}$$

2. **Molarity (M):** It is defined as the number of moles of the solute present in 1 litre (or 1000 mL) of the solution. A one molar solution contains 1 mole of the solute dissolved in 1 litre of the solution.

3. **Molality (m):** It is defined as the number of moles of solute dissolved in 1000 g of the solvent. One molal solution contains one mole of the solute dissolved in 1000 g of the solvent.

Normal solution:

A solution containing one gram equivalent weight of the solute dissolved per litre is called a normal solution; e.g. when 40 g of NaOH are present in one litre of NaOH solution, the solution is known as normal (N) solution of NaOH. Similarly, a solution containing a fraction of gram equivalent weight of the solute dissolved per litre is known as subnormal solution. For example, a solution of NaOH containing 20 g (1/2 of g eq. wt.) of NaOH dissolved per litre is a sub-normal solution. It is written as N/2 or 0.5 N solution.

Formulae used in solving numerical problems on volumetric analysis;

1. Strength of solution = Amount of substance in g litre^{-1}.

2. Strength of solution = Amount of substance in g moles litre^{-1}.

3. Strength of solution = Normality × Eq. wt. of the solute = molarity × Mol. wt. of solute.

4. Molarity = Moles of solute/Volume in litre.
5. Number of moles = Wt.in g/Mol. wt = M × V (initial) = Volume in litres/22.4 at NTP (only for gases).

6. Number of milli moles = Wt. in g × 1000/mol. wt. = Molarity × Volume in mL.
7. Number of equivalents= Wt. in g/Eq. wt = x × No. of moles × Normality × Volume in litre (Where x = Mol. wt/Eq. wt).

8. Number of mill equivalents (meq.) = Wt. in g × 1000 / Eq. wt = normality × volume in mL.

9. Normality = x × No. of mill moles (Where x = valency or change in oxi. number).

10. Normality formula, $N_1V_1 = N_2V_2$, (Where N_1, $N_2 \rightarrow$ Normality of titrant and titrate respectively, V_1, $V_2 \rightarrow$ Volume of titrant and titrate respectively).

11. % by weight = Wt. of solvent/Wt. of solution × 100 .

A solution is a homogeneous mixture of two or more components, the composition of which may be changed. The substance which is present in smaller proportion is called the solute, while the substance present in large proportion is called the solvent.

Acid base titration:

The chemical reaction involved in acid-base titration is known as neutralisation reaction. It involves the combination of H_3O^+ ions with OH^- ions to form water. In acid-base titrations, solutions of alkali are titrated against standard acid solutions. The estimation of an alkali solution using a standard acid solution is called *acidimetry*. Similarly, the estimation of an acid solution using a standard alkali solution is called *alkalimetry*.

The Theory of Acid–Base Indicators:

Ostwald, developed a theory of acid base indicators which gives an explanation for the colour change with change in pH. According to this theory, a hydrogen ion indicator is a weak organic acid or base. The undissociated molecule will have one colour and the ion formed by its dissociation will have a different colour.

Let the indicator be a weak organic acid of formulae HIn. It has dissociated into H^+ and In^- . The unionized molecule has one colour, say colour (1), while the ion, In^- has a different colour, say colour (2). Since HIn and In^- have different colours, the actual colour of the indicator will dependent upon the hydrogen ion concentration $[H^+]$. When the solution is acidic, that is the H^+ ions present in excess, the indicator will show predominantly colour (1). On other hand, when the solution is alkaline, that is, when OH^- ions present in excess, the H^+ ions furnished by the indicator will be taken out to form undissociated water. Therefore there will be larger concentration of the ions, In^-. thus the indicator will show predominantly colour (2).

Some indicators can be used to determine pH because of their colour changes somewhere along the change in pH range. Some common indicators and their respective colour changes are given below.

Indicator	Colour on Acidic Side	Range of Colour Change	Colour on Basic Side
Methyl Violet	Yellow	0.0 - 1.6	Violet
Bromophenol Blue	Yellow	3.0 - 4.6	Blue
Methyl Orange	Red	3.1 - 4.4	Yellow
Methyl Red	Red	4.4 - 6.2	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol Blue	Yellow	6.0 - 7.6	Blue
Phenolphthalein	Colourless	8.3 - 10.0	Pink
Alizarin Yellow	Yellow	10.1 - 12.0	Red

i.e., at pH value below 5, litmus is red; above 8 it is blue. Between these values, it is a mixture of two colours.

Indicators Used for Various Titrations:

1. Strong Acid against a Strong Base:

Let us consider the titration of HCl and NaOH. The pH values of different stages of titration shows that, at first the pH changes very slowly and rise to only about 4. Further addition of such a small amount as 0.01 mL of the alkali raises the pH value by about 3 units to pH 7. Now the acid is completely neutralized. Further of about 0.01 mL of 0.1 M NaOH will amount to adding hydrogen ions and the pH value will jump to about 9. Thus, near the end point, there is a rapid increase of pH from about 4 to 9.

An indicator is suitable only if it undergoes a change of colour at the pH near the end point. Thus the indicators like ***methyl orange, methyl red and***

phenolphthalein can show the colour change in the pH range of 4 to 10. Thus, in strong acid- strong base titrations, any one of the above indicators can be used.

2. Weak Acid against Strong Base:

Let us consider the titration of acetic acid against NaOH. The titration shows the end point lies between pH 8 and 10. This is due to the hydrolysis of sodium acetate formed. Hence ***phenolphthalein*** is a suitable indicator as its pH range is 8-9.8. However, methyl orange is not suitable as its pH range is 3.1 to 4.5.

3. Strong Acid against Weak Base:

Let us consider the titration ammonium hydroxide against HCl. Due to the hydrolysis of the salt, NH_4Cl, formed during the reaction, the pH lies in the acid range. Thus, the pH at end point lies in the range of 6 to 4. Thus ***methyl orange*** is a suitable indicator while phenolphthalein is not suitable.

StrongAcids	StrongBases	WeakAcids	WeakBases
HCl	NaOH	Acetic acid	Ammonia
HNO_3	KOH	Hydrocyanic acid	Magnesium hydroxide
HBr	etc	HF	Pyridine
H_2SO_4		Oxalic acid	Sodium carbonate
HI		Ethanoic acid	Potassium carbonate
$HClO_4$		etc	etc

For acid base titration (procedure), Please go through the following link:

https://www.youtube.com/watch?v=XD5GZYjtGek

Object: To determine the strength of oxalic acid solution (gm/lit) by titrating it against approx. N/10 NaOH solution.