Republic of Iraq
Ministry of Higher Education & Scientific research
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Analytical Chemistry

For

First Year Student

Lecture 2

By

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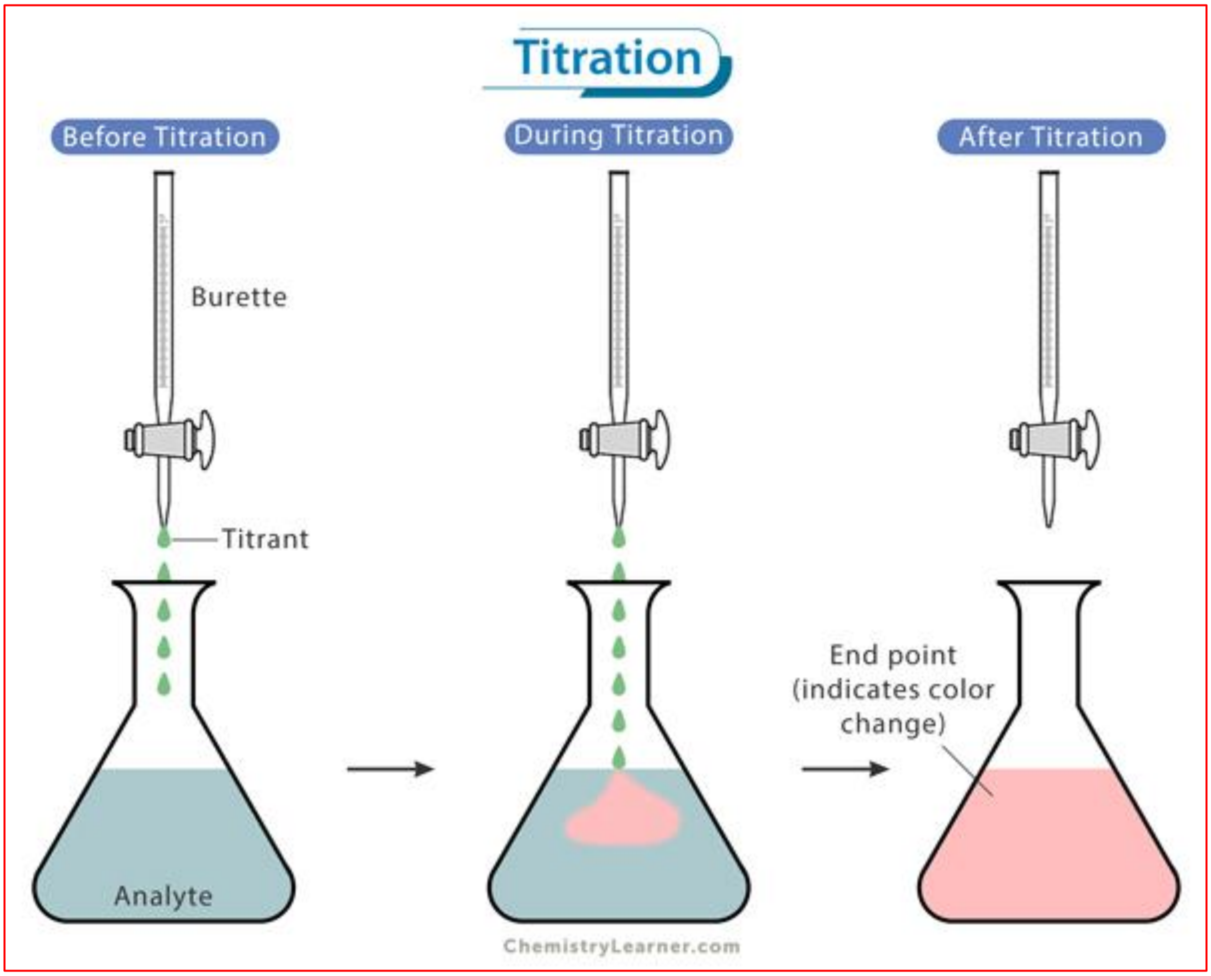
Volumetric analysis (titration analysis)

Titration :

Is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant. Because volume measurements play a key role in titration, it is also known as **volumetric analysis**.



Some Terms Used In Titration

Equivalence point (Veq):

The point in a titration where stoichiometrically equivalent amounts of analyte and titrant react (theoritical end of titration).

End point (Vep):

The point of titration at which the completion of a reaction is practically observed Unfortunately, the endpoint and the equivalence point are not exactly the same. The difference between the two is called the titration error.

Titration error:

The difference between the end point and the equivalence point

Et = Vep – Veq

Titrant:

The standard solution of known concentration added from the burette.

Analyte:

An unknown solution which is to be determined .

Indicator:

A colored compound reagent added to the analyte solution to produce an observable physical change (usually change in color) at or near the equivalence point when the titration reaction is complete, and so mark the endpoint e.g: Phenolphthalein, Methyl Orange, Methyl red, etc.

Indicator	Acidic Colour	pH Range of Colour Change	Basic Colour
Phenolphthalein	Colourless	8.3-10.0	Pink
Bromothymol Blue	Yellow	6.0-7.6	Blue
Phenol Red	Yellow	6.8-8.0	Red
Methyl Orange	Red	3.2-4.4	Yellow

Back titration :

A technique used to determine the excess of a reagent used in the neutralization of the sample by a titration with a second reagent.

The requirements of a titration are as follows:

(1) The reaction must be stoichiometric: That is, there must be a well-defined and known reaction between the analyte and the titrant..

$CH_3COOH+NaOH \longrightarrow CH_3COONa+H_2O$

(2) The reaction should be rapid. Most ionic reactions.

(3) There should be no side reaction, and the reaction should be specific.

(4) There should be a marked change in some property of the solution when the reaction is complete. This may be a change in color of the solution or in some electrical.

or other physical property of the solution (by used indicator or pH meter).

(5) The point at which an equivalent or stoichiometric amount of titrant is added is called the equivalence point. The point at which the reaction is observed to be complete is called the end point, that is, when a change in some property of the solution.

(6) The reaction should be quantitative. That is, the equilibrium of the reaction should be far to the right so that a sufficiently sharp change will occur at the end point to obtain the desired accuracy. The equivalence point is the theoretical end of the titration where the number of moles of titrant = number of moles of analyte. The end point is the observed end of the titration.

Standard solution:

A reagent of known concentration used to carry out a titrimetric analysis (titration).

The properties of standard solution are:

1 – Be sufficiently stable so that it is only necessary to determine its concentration once.

2 – React rapidly with the analyte so that the time required to complete the analysis is minimized.

3 – React completely with the analyte so that satisfactory end point is realized.

4 – Undergo a selective reaction with the analyte.

5 – The reaction with the analyte can be described by a balanced equation.

Primary standard:

Is a pure compound from which a standard solution of accurately known concentration can be prepared directly, without any need for standardization.

Secondary standard:

Is a solution that its concentration is not accurately known so it is to be standardized by “Primary Standard” before use in titration.

Standardization:

The process of finding the actual concentration of the secondary standard solution by titrating it with a suitable primary standard solution.

Requirements for the Primary Standard Material

1. Highest purity.
2. Atmospheric stability.
3. High solubility.
4. High formula weight.
5. Easily available at reasonable cost.

6. Free from hydrated water so that the composition of the solid does not change with variations in humidity.

Types of volumetric titrations

i. Acid-base (Neutralization) titration.

ii. Precipitation titration.

iii. Compleximetric titration.

iv. Oxidation-reduction (redox) titration.

1.Acid- Base titrations:

Many compounds, both inorganic and organic, are either acids or bases and can be titrated with a standard solution of a strong base or a strong acid. The end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH using a pH meter.

$$\mathbf{NaOH + HCl \longrightarrow NaCl + H_2O}$$

2.Precipitation titrations:

In this type of titration, the titrant forms a precipitate with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate. Again, indicators can be used to detect the end point,...

$$\mathbf{AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3}$$

3.Complexometric titrations:

In complexometric titrations, The titrant is often a chelating agent(Ligand) that forms a water-soluble complex with the analyte (metal ion).

Ethylenediaminetetraacetic acid (EDTA) is one of the most useful chelating agents used for titration. It will react with a large number of elements, and the reaction can be controlled by the adjustment of the pH. Indicators can be used to form a highly colored complex with the metal ion.

$$AgNO_3\,(aq) + 2KCN(aq) \rightarrow [Ag(CN)_2]\text{-}(aq) + K^+\,(aq) + NO3^-(aq)$$

4.Reduction-Oxidation (Redox) titrations:

The “redox” titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

$$\mathbf{5Fe^{2+} + Mn^{7+} + 8H^{+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O}$$

Volumetric (Titration) Calculations

$$\textbf{No. of moles A} = \frac{\textbf{mass A g}}{\textbf{molar mass A}\left(\frac{\textbf{g}}{\textbf{mol}}\right)}$$

No. of moles A = volume(L) x Molarity of A (mol / L)

No. of mmoles A = volume(mL) x Molarity of A (mmol /mL)

mass of A(g) = No. of moles x Molar mass (g/mol)

Example 1:

Calculate the concentration of 100.0 mL of NaOH solution titrated to the end point with 75.8 mL of a 0.100 M standard solution of HCl.

Solution:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

na = 1 nb = 1 (stiochiometric mole ratios of acid and base)

No of moles = Molarity (M) x volume(L)

No of mmoles = Molarity (M) x volume(mL)

$$\frac{Ma\,Va}{na} = \frac{Mb\,Vb}{nb}$$

$$\frac{75.8 \times 0.1}{1} = \frac{M \times 100}{1}$$

$$Mb = \frac{75.8 \times 0.1}{100} = 0.758\,M$$

Example 2:

20 mL of H_2SO_4 (98 g/mol) was neutralized with 25mL of 0.1M sodium hydroxide solution. The equation of reaction is $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Calculate (i) molar conc. of acid (M) (ii) acid content of the solution in grams.

Solution:

$$\frac{Ma\,Va}{na} = \frac{Mb\,Vb}{nb}$$

$$\frac{Ma\,20}{1} = \frac{0.1 \times 25}{2}$$

Concentration of H_2SO_4 (Ma) =$\frac{\mathbf{0.1\times25\times1}}{\mathbf{2}}$ **= 0.0625 M**

ii) mass of the acid in the solution(g)

mass (g) = Molar conc.(Molarity) x Volume (L)x Molar mass

mass (g) = 0.0625 x(20×10^{-3}) Lx 98 = 0.1225 g

Example 3 :

A 18.50 mL of hydrochloric acid were neutralized by 25 mL of potassium hydroxide solution(56 g/mol) containing 7g/liter. what is the molar concentration of the acid? $HCl + KOH \rightarrow KCl + H_2O$

Solution:

Given:

Molarity of KOH= $\frac{\boldsymbol{wt}}{\boldsymbol{m.wt \times V\ L}}$=$\frac{\boldsymbol{7g}}{\boldsymbol{56 \times 1L}}$ **=0.125M**

$$\frac{Ma\ Va}{na} = \frac{Mb\ Vb}{nb}$$

$$\frac{Ma \times 18.5}{1} = \frac{0.125 \times 25}{1}$$

Concentration of HCl (Ma) = 0.169M

Example 4:

50.0 mL portion of HCl solution required 29.71 mL of (0.019M) $Ba(OH)_2$ to reach an end point with bromocresol green indicator , Calculate the molarity of HCl .

Solution:

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$

1mole 2 mole 1mole

$$\frac{M\mathrm{Ba(OH)_2} \times V\mathrm{Ba(OH)_2}}{1} = \frac{M\mathrm{HCl} \times V\mathrm{HCl}}{1}$$

$$M\ HCl = \frac{2[0.019 \times 29.71}{50} = 0.023\ M$$