Date

Expt. No. Page No. 1

Pharmaceutical Analysis (BP - 102)

B. Pharmacy Semester - I

(UNIT - 1)

1. **Pharmaceutical analysis** –

Pharmaceutical analysis is branch of practical chemistry that involves a series of process for identification, determination, quantification and the purification of a substance, seperation of the components of solution or mixture, or the determination of structure of the chemical compounds.

The substance may be single compound or a mixture of compounds and it may be in any of the dosage form. The substance used as pharmaceuticals are animals, plants, micro organisms, minerals & various synthetic pro-ducts.

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- **Scope** ⟹ The object of analysis is determination of the quantitative contents of individual elements or compounds present in substance. Pharmaceutical anaylsis has enormous importance in science & industries.

Analysis is a most important method of investigation & is widely used in all branches of science which are related to chemistry.

Therefore, in almost every factor one of the most important sections is the analytical laboratory for chemical control of production.

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- 2. Techniques of analysis –

a) Chemical method – In chemical method, for analysis of any element or compound, we use different types of chemicals for testing its limits, organoleptic properties, physical properties and biological properties.

Different techniques used in chemical method are below –

1. Volumetric or titrimetric
2. Gravimetric
3. Gasometric

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b) Instrumental methods – In instrumental method for analysis of any compound, we use different types of laboratory instruments or glasswares.

Some examples of this analytical instruments or glasswares are –

1. Spectrophotometry, 2. Fluorimetry,
3. Polarimetry, 4. Potentiometry, 5. Polarography.

c) Microbiological method – In this method, we use different types of microbes such as bacteria, virus, fungi, algae

Two general methods are usely employed –

1. cylindrical plate method
2. Tube assay method.

d) Biological method – In this method of bio assays the procedure by which potency or the nature of the substance is estimated by studying its effect on living matter.

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3. Primary and secondary standards

i) Primary standard – The primary standard should be readily solube under the conditions in which it is employed. It must be easy to obtain, to purify, to dry and to pre-serve in a pure state.

It should have a high equivalent so that the weighing errors may be negligible.

The titration error should be negligible or easy to determine accurately by experiment.

ii) Secondary standard – A substance which is not primary standard in nature is called a secondary standard.

Examples may include most of the alkali hydroxides some inorganic acids, various deliquescent substances.

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4. Preparation and standardization of molar and normal solution.

i) Oxalic acid, 0.1 N :

$H_2C_2O_4, 2H_2O$ = 126.07; (6.303 g in 1000 ml).

Dissolve 6.45 g of oxalic acid in sufficient water to produce 1000 ml and standardise the solution as follows :

Pipette 30 ml of the solution into a beaker, add 150 ml of water, 1 ml of sulphuric acid and heat to about 70°, Add slowly from a burette freshly standardised 0.1 N potassium permanganate with constand stirring, until a pale pink colour, which persists for fifteen seconds, is produced. The temperature at the conclusion of titration should not be less than 60°. Each ml of 0.1 N potassium permanganate is equivalent to 0.006303 g of $H_2C_2O_4 \cdot 2H_2O$.

ii) Sodium Hydroxide, N :

NaOH = 40.1 K); (40.00 g in 1000 ml).

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Dissolve 40 g of sodium hydroxide in 150 ml of carbon dioxide free water, cool solution to room temperature, and filter through handened filter paper. Transfer 54.5 ml of the clear filtrate to a tightly-closed polythene container, and dilute with carbon dioxide free water to 1000 ml.

Standardise the solution as follows -

Weigh accurately about 5 g of potassium hydrogen pbthalate P.S., previously powdered & dried at 120° for two hours, and dissolve in 75 ml of carbon dioxide free water. Add two drops of phenolphthalein solution & titrate with the sodium hydroxide solution until a permanent pink colour is produced. Each 0.0242 g of potassium hydrogen phthalate is equivalent to 1 ml of N sodium hydroxide.

iii) Hydrochloric Acid, N:

HCl = 36.46; (36.46 g in 1000 ml). Dilute 85 ml of hydrochloric acid with water to 1000 ml & standardise the solution as follows -

Weigh accurately about 1.5 g of anhydrous sodium carbonate P.S., previously heated at about 270° for one hour.

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Dissolve it in 100 ml of water & add two drops of methyl red solution. Add the acid slowly, from burette, with constant stirring, until the solution becomes faintly pink. Heat the solution to boiling, and titrate further as necessary until the faint pink colour is no longer affected by continued boiling.

Each 0.05299 g of anhydrous sodium carbonate is equivalent to 1 ml of N hydrochloric acid.

5. Pharmacopoeia – A pharmacopoeia is a book of standards applicable to drug substances and their dosage forms used in a country or region, which accepts it as such. It is prepared by a recognized authority appointed by & Government of the the concerned country. A knowledge of the history of pharmacy would help us better to understand the development of pharmacopoeias.

6. Impurity – Impurity is undesirable foreign material which may be toxic or may not be toxic, present in the pharmaceutical

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substances. Impurity is the substance or the matter which does not form the part of medicinal or pharmaceutical substances or drugs.

- **Sources of impurities -**

1. Raw materials used in the manufacture.
2. Reagents used in the manufacturing process.
3. Method used in manufacture.
4. Intermediate Products in the manufacturing Process.
5. Solvents
6. Action of Solvents and Reagents on Reaction Vessels.
7. Atmospheric contamination during the manufac-turing process.
8. Storage condition
9. Adulteration

- **Effect of impurities -**

1. Impurities having a toxic effect, can be injurious when present above certain limits.
2. Impurities may sometimes harmless. However, if these are present in large such proportions that active strength of the substance gets lowered, its therapeutic effect gets decreased.

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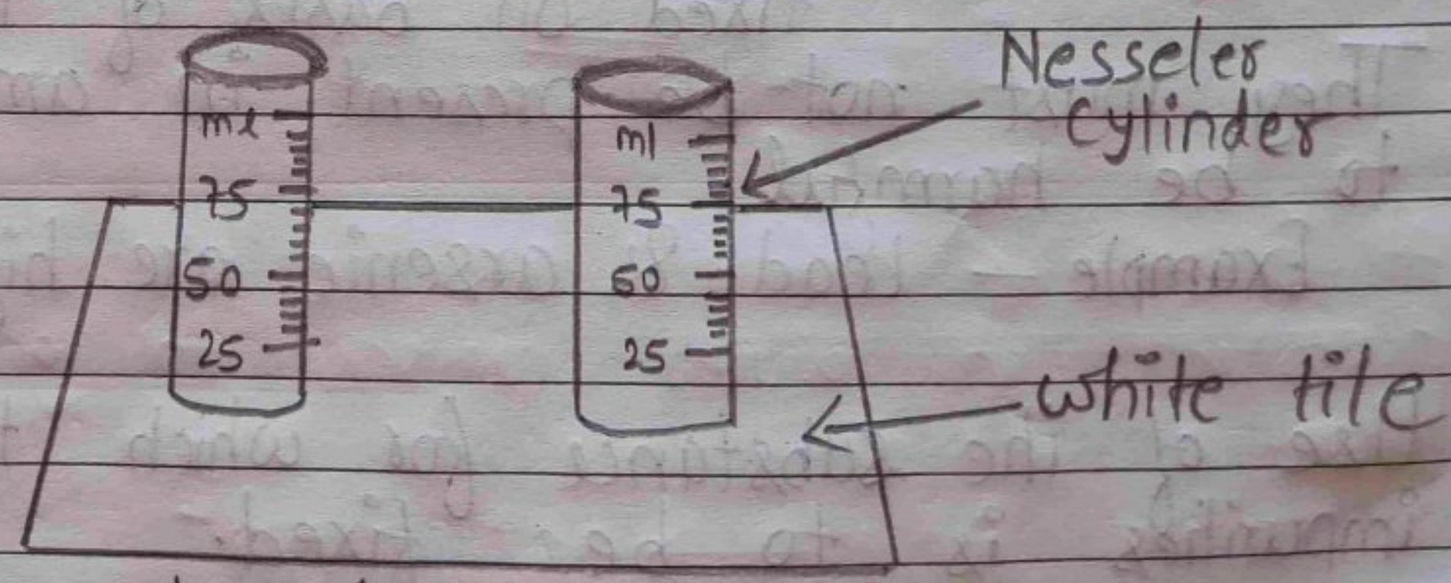
3. Impurities may cause a change in the physical and chemical properties of the substance, there by making it medically useless.

4. Impurities may cause an incompatibility with other substances.

5. Impurities may decrease the shelf life of the substance.

7. <u>Limit Test</u> – Limit test are the quanta-tive or semi-quantitative test designed to identify & control small quality of impurity, which are likely to be present in the substance.

Examples – a. Limit test of sulphates
b. Limit test for iron
c. for Arsenic etc.



Nessler's cylinder

Limit test are generally carried out in Apparatus known as Nessler cylinder which is made up of colourless glass.

- Factors responsible for designing limit test.

1. Specificity of the tests
2. Sensitivity
3. Control of personal Errors.

- Factors Considered While fixing the limit test.

1. Incompatibilities
2. Practicability of getting the particular limit or particular standard of purity.
3. Harmful effect – Limit of some impurities is fixed on basis of their toxic effect. They must not be present in amounts likely to be harmful.
   Example – Lead & arsenic are highly toxic.
4. Use of the substance for which the limit of impurities is to be fixed.

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- **Importance of limit test.**

a) They are used for quantitative determination of impurity.
b) They provide visible appearance to test the appearance.
c) To test moisture volatile matter and residual solvents.
d) For the specificity of test and to control the senitivity of test.
e) To test and detect various in soluble and soluble matter.

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UNIT ⇒ 2

1. Acid Base Titration

Neutralization or aqueous acid base titrations are usually reactions in which H_3O^+ in solution is titrated by OH^-. The reaction basically involved is :

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

2. Acid Base Theories

i) Arrhenius theory – Arrhenius defined acid as substance that when dissolved in water gives rise to hydrogen ions which in association with solvent form hydronium ions.

$$HA \rightleftharpoons H^+ + A^-$$

$$H^+ + H_2O \rightleftharpoons H_3O$$

A base is defined as the substance which when dissolved in water ionises to give hydroxyl ions.

$$BOH \rightleftharpoons B^+ + OH^-$$

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ii) Bronsted theory — Bronsted defined an acid as species that can donate protons and a base as a species that can accept protons.

$$HA \rightleftharpoons H^+ + A^-$$
$$B + H^+ \rightleftharpoons BH^+$$

In Bronsted theory, an acid donates proton. It is independent of solvent, this theory differs from Arrhenius theory in their con-cept of the base. In the system.

$$HA \rightleftharpoons H^+ + A^-$$

The anion A acts as base as it accepts a proton. Also in other system,

$$B + H^+ \rightleftharpoons BH^+$$

iii) Lewis theory — Lewis proposed that an acid as a species that can accept an electron pair & a base as a species that can donate an electron pair. There is no change in the concept of acid-base as every proton acceptor is an electron-pair donor.

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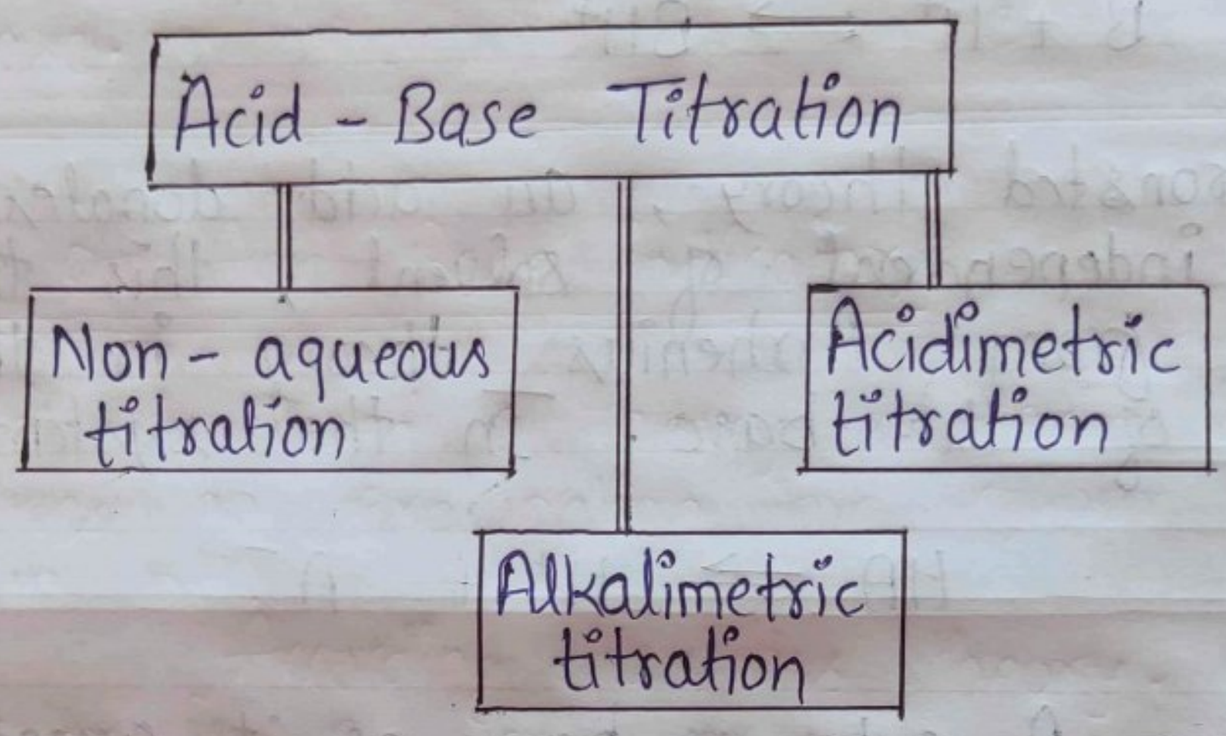
3. Classification of Acid - Base Titration -

Acid base titration is based on reaction of acid and base to form salt & water. In this titration, neutralization reaction is involved so it is also called as neutralization titration.



i) Non - aqueous titration – Substance which cannot be titrated satisfactorily either by acidimetry or alkalimetry in aqueous solution are titrated by non-aqeous solvents and known as non-aqueous titration.

ii) Acidimetric titration – Alkaline substance is titrated with standard acid is known as acidimetric titration.

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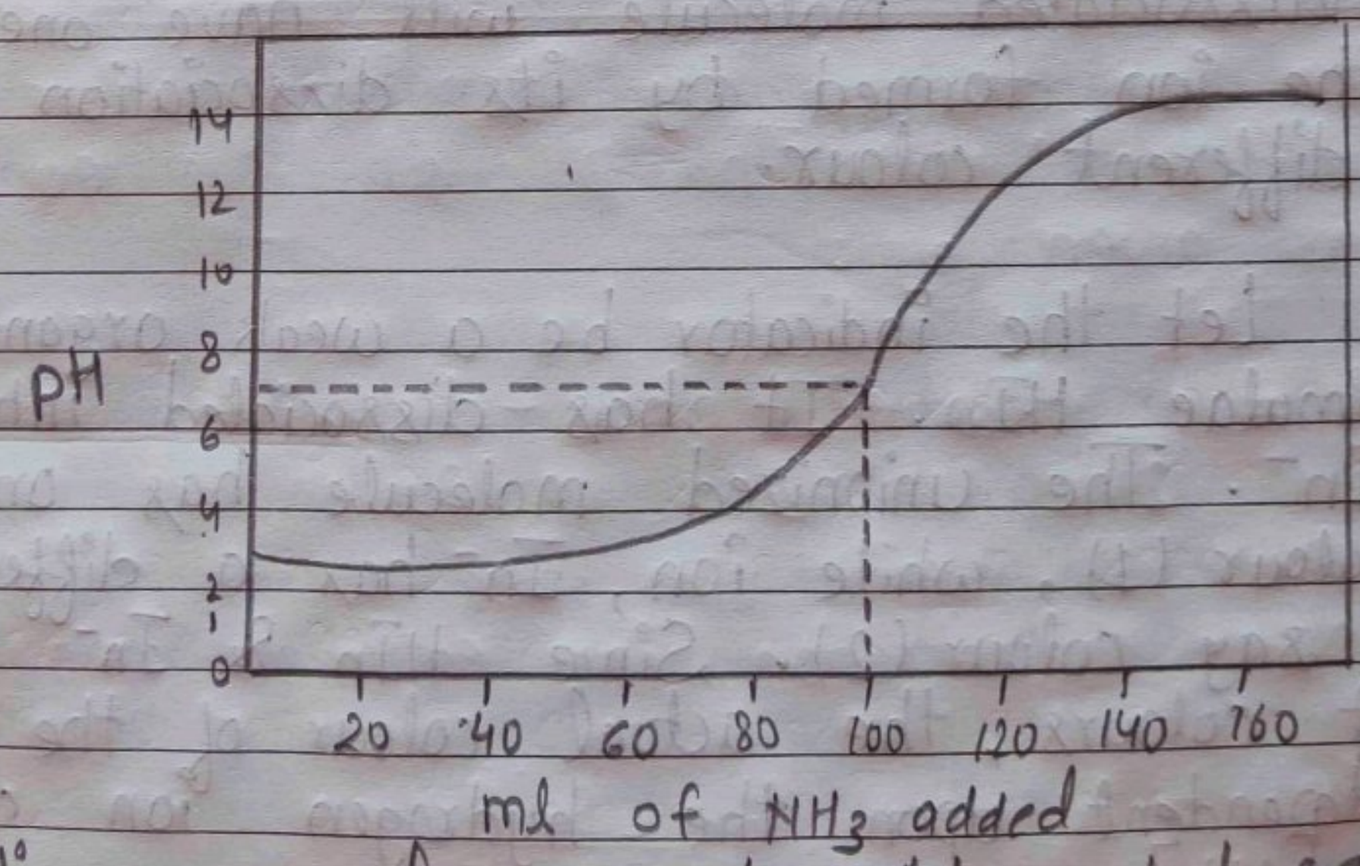
iii) Alkalimetric titration – Acidic substance is titrated with standard base is called as alkalimetric titration.

4. Weak acid and Weak Base Titration –

Let us consider titration of 100 ml, 0.1 N acetic acid with 0.1 N ammonia. pH at equivalence point is

$$pH = pK_w + \frac{1}{2} pK_a - pK_b$$
$$= 7.0 + 2.37 - 2.37$$
$$= 7.0$$



Titration curve for weak acid-weak base

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The chief feature of the curve is that change of pH near equivalence point & during whole neutra-lisation is very gradual. Hence, the end point cannot be detected by ordinary indicator. Hence, mixed indicator is often used.

On the whole, It is best to avoid titration involving both weak acid and weak base.

5. Theory of Acid Base indicators

Ostwald, developed a theory of acid base indicator which gives an explanation for 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 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 ion, In^- has a different colour, say colour (2). Since HIn & In^- have different colours, the actual colour of the indicator, will dependent upon the hydrogen ion concentra-tion $[H^+]$.

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6. Indicators used in Acid-Base titrations -

Indicators are the substances or solutions which show various colours changes in accordance with titration. The indicators are useful for determination of end-point.

pH is negative logarithm of hydrogen ion concentration, $pH = -\log[H^+]$

Indicators are the weak acids or weak bases which have different colour in their conjugate bases & acid forms. Most of the indicators are used in dilute form.

Selection of indicators -

i) When a weak acid is titrated against a strong base phenolphthalein should be used as an indicator.
ii) Three drops of indicator test solution should be used unless otherwise directed.
iii) In a titration between a weak alkali and a strong acid, methyl orange can be used as the indicator.
iv) In titration, it is advisable to titrate wherever possible to the appearance of colour rather than to disappearance.

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7. **Neutralization curve** — The curve obtained by plotting pH as ordinate against the percentage of acid [neutralised for number of ml of alkali (titrant) added] as the abscissa during titration, is called as neutralisation or more generally titration curve.

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Types of Neutralization curve

1. Neutralisation of strong Acid - strong Base
2. Neutralisation of weak Acid - strong Base
3. Neutralisation of weak Base - strong Acid
4. Neutralisation of weak Acid - Weak Base.

☆. Neutralization of Weak Acid – Strong Base.

Consider the titration of 100 ml of acetic acid with 0.1 N NaOH. The pH at the equivalence point is given by:

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} P_c$$

for other concentration, the equation employed as -

$$pH = pKa + \log \frac{[Salt]}{[Acid]}$$

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the initial pH of 0.1 N acetic acid is

$$[H^+] = \sqrt{Ka \cdot c}$$
$$pH = 2.87$$

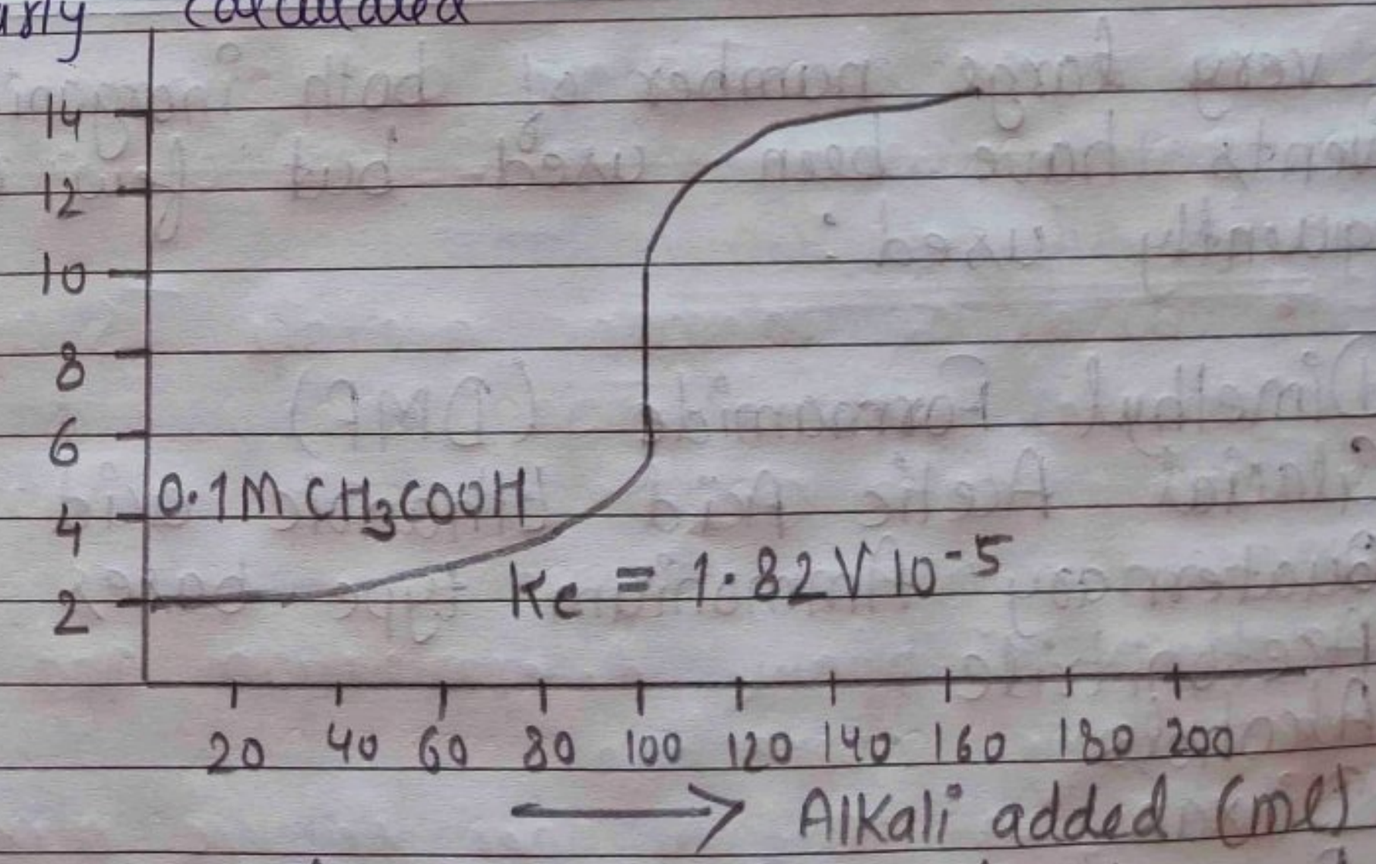
When 50 ml of 0.1 N alkali is added,

$$[Salt] = \frac{50 \times 0.1}{150} = 3.33 \times 10^{-2}$$

$$[Acid] = \frac{50 \times 0.1}{150} = 3.33 \times 10^{-2}$$

$$pH = 4.74 + \log \frac{(3.33 \times 10^{-2})}{(3.33 \times 10^{-2})} = 4.74$$

The pH values at other points on titration curve are similarly calculated.



Neutralising curve for weak acid and strong base.

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Unit - 2
(Topic - 2)

1. **Non - aqueous titration** – Non - aqueous titration are those in which the titration of "weakly acidic or basic substance are carried out using non - aqueous solvents so as to get sharp end point.

Principle – Principle & technique of this method is simple. It is based upon the Bronsted - Lowry and Lewis theory of acids and bases and the nature & influence of leveling effect of non - aqueous solvents on substances.

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☆. Solvents for Non - aqueous titrations

A very large number of both inorganic and organic solvents have been used but few are more frequently used:

i) Dimethyl Formamide (DMF)
ii) Glacial Acetic Acid Ethanoic acid
iii) Quaternary Ammonium type bases
iv) Acetonitrile
v) Alcohols
vi) Dioxan
vii) Benzoic acid and phenyl Cinchonic Acid

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a) **Solvents** – The solvents used in non-aqueous titration plays an important role. Generally, solvent should be non-toxic for its wide use in analysis, it must be liquid at the time of analysis. These organic solvents are used but it is mainly dependent on their properties. Such as:

i) Capability of self-dissociation
ii) Dielectric constant
iii) Acid-base character of solvent

Types of solvents –

(i) Protogenic Solvents
(ii) Protophilic Solvents
(iii) Amphiprotic Solvents
(iv) Aprotic Solvents

b) **Acidimetry** – The determination of the strength of a solution of an acid by titration with standard solution of a base is called the acidimetry.

c) **Alkalimetry** – When the strength of a solution of an alkali is determined by means of the titration with standard solution of an acid, it is termed as alkalimetry.

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2. Estimation of sodium Benzoate

i) Wash the burette with the D.W and the titrant (HCl).
ii) Fill the burette with N/2 HCl to a level.
iii) Put 10 ml of an unknown sodium benzoate solution in a clean conical flask.
iv) Add 25 ml of D.W and 15 ml of ether.
v) Add 6 drops of bromophenol blue.
vi) Start titration by adding HCl drop wise with shaking the aqueous and ethereal layers until a light green colour persists in the aqueous layer.
vii) Record the volume of HCl used.

3. Ephedrine HCl

i) Dissolve about 500 mg of Ephedrine Hydrochloride accurately weighed in 25 ml of glacial acetic acid.
ii) Add 10 ml of mercuric acetate TS and 2 drops of crystal violet TS.
iii) Titrate with 0.1 N per chloric acid VS to an emerald - green endpoint.
iv) Perform a blank determination, and make any neccessary correction.
v) Each mL of 0.1 N per chloric acid is equivalent to 20.17 mg of $C_{10}H_{15}NO.HCl$

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UNIT - 3

(topic - 1)

1. **Precipitation titration** — In precipitation titration, the stoichiometric reaction is reaction which produces in solution slightly sol-ble salt that precipitates out.

a) **Mohrs Method** —

This is one of the important methods of precipita-tion and for first time it was developed by Mohr in 1856. Potassium chromate is used as indicator in this titration.

Principle —

This method involves the titration of silver nitrate against halides in neutral solution using 2% solution of Potassium chromate as an indicator. The end point is marked by appearance of a brick red precipitate or colouration due to the formation of silver chromate with an excess of silver nitrate.

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Reactions –

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \downarrow \text{ (Brick red)}$$

This method is based on fact that silver halide is more insoluble than silver chromatic. Hence so long as there is any halide left in the solution, no silver chromate is formed.

In fact silver chromate, even if formed, will immediately change to the silver chloride or bromide by interaction with chloride or bromide.

Ex: $Ag_2CrO_4 + 2Cl^- \rightarrow 2AgCl + CrO_4^{2-}$

When the whole of chloride has been used up, silver chromate will be formed & brick red coloration or precipitate will appear.

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b) Volhard's Method –

The method was designed by Volhard (1874) for the estimation of silver in dilute nitric acid solution by titrating against a standard thiocyanate solution in presence of ferric salt as indicator.

Principle – In this method, a standard solution of ammonium or potassiumthiocyanate is

added from burette to a solution of silver salt in the presence of nitric acid & ferric indicator. In the titration flask a precipitate of silver thio-cyanate continues to be formed till the silver gets completely precipitated.

$$Ag^+ + CNS^- \rightarrow AgCNS \downarrow$$

The addition of further drop of thiocyanate reacts with the ferric ion to form a red colored ferric thiocyanate complex.

$$Fe^{3+} + 3CNS^- \rightarrow Fe(CNS)_3 \text{ (Red)}$$

Pharmaceutical Applications - of volhard Method-

The following is the list of some important drugs-

1. Aminophylline
2. Chloributon
3. Aminophylline tablets
4. Dimenhydrinate
5. Chlorophenothane
6. Sodium chloride injection
7. Phenyl mercuric acetate
8. Ethionamide
9. Oxyphenoium bromide

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c) Fajan's method –

This method was introduced by Fajan in 1923-1924. This method employs adsorption indicators for detection of end point.

Principle – The action of these indicator is based upon the simple fact that at end point, the indicator gets adsorbed by precipitate and during the process of adsorption, a change in colour of the indicator will take place which may result in a substance of different colour. These are termed as the adsorption indicators.

Indicator used –

Commonly used indicators for titration of chloride against silver nitrate are :

1. Dichlorofluorescein
2. Di-iodo diethyl fluorescein
3. Fluorescein
4. Eosin.

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Unit - III (topic - 2)

1. Complexometric titration -

Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of mixture of different metal ions in solution.

(i) **Complex** :- The term complex in chemistry, also called a "coordination compound" or "metal complex", a structure consisting of a central atom or molecule connected to surrounding atoms or the molecules.

Example : Metal - EDTA complex

ii) **Ligand** :- A ligand is either an atom, ion, or molecule that bonds to a central metal, generally involving formal donation of 1 or more of its electron.

Ligands are viewed as lewis bases, although rare cases are called involving lewis acidic ligands.

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2. Classification of titrations :-

(i) **Direct titrations** – In this method metal ion solution in a suitable buffer is titrated with standard disodium edetate solution using metal indicator that changes color at equivalence point. Magnesium salts are titrated by the direct titrated method.

ii) **Back titration** – When direct titration is not possible because of insolubility of substance, or instability of complex or precipitation of metal hydroxide in alkaline solution of buffer, then back titration method adopted.

iii) **Replacement titrations** – When direct titration or back titration is not possible for various reasons, metal ions are estimated by replacement technique.

iv) **Alkali metric titration of metals** – It is clear from the metal-EDTA complex formation reaction that protons from di-sodium edetate are liberated resulting in formation of acid.

$$M^+ + H_4Y = MY + 4H^+$$

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v) Indirect titration method (Miscellaneous methods) –
Exchange reactions between the nickelocyanide ion $[Ni(CN)_4]^{-2}$ and element to be analyzed is carried out so as to set free the nickel ions. This can be applied for estimation of silver, palladium, gold which are not titrated complexometrically.

This method can also be used for estimation of halide and thiocyanate ion.

3. Masking Agent – A masking agent is called as auxiliary chelating agent or the complexing agent. It is a substance that will form complex more strongly with the metal than titrant under the conditions of titration.

Example :-

(1) Ammonium fluoride
(2) Potassium cyanide
(3) Triethanolamine
(4) Ascorbic acid
(5) Potassium iodide
(6) Dimercaprol

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Demasking Agent –

It is the substance which releases the masked metal ion. The cyanide complexes of zinc and cadmium can be demasked by formaldehyde - acetic acid solution. Demasking can also be possible by use of chloral hydrate.

$$[Zn(CN)_4]^{--} + 4H^+ + 4HCHO \rightarrow Zn^{++} + 4HO.CH_2-CN$$

4. Metal ion indicators –

These are dyes which show one colour in the presence of metal ion and no colour or different colour in absence of metal ion.

Properties :-

(i) Metal ion indicator should be sufficiently stable. It should not dissociate otherwise colour change is not observed.

ii) The indicator must be sensitive to metal ion concentration.

iii) The colour reaction should be specific or atleast selective.

iv) All above requirements, must be fulfilled within the pH range at which titration is performed.

v) The colour reaction should be such that before the end point the solution is strongly coloured.

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Indicators commonly used & official in Indian Pharmacopoeia are :

i) Murexide (Ammonium purpurate).
ii) Modrant Red 7
iii) Calcon
iv) Pridylazonapthol (PAN)
v) Catechol violet
vi) Mordant Blue 3 (Solochrome cyanne R)
vii) Xylenol orange
viii) Erichrome black T (Mordant Black-11)

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Topic - 3

GRAVIMETRY

1. Definition / Principle –

The quantitative determination of substance by precipitation followed by isolation & weighing of the precipitate is called gravimetric analysis.

Method –

i) A weighed sample is dissolved after which an excess of precipitating agent is added.

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ii) The precipitate which forms is filterated, dried or ignited & weighed.

iii) From the mass and known composition of the precipitate, amount of the original ion can be determined.

2. Gravimetry Analysis — The operations of gravim-etric analysis consist of a number of important techniques in order to get accurate, quantita-tive estimation. It includes :

i) Sampling
ii) Preparation of solution or dissolution
iii) Precipitation
iv) Testing the completeness of precipitation
v) Digestion of Ageing of precipitate
vi) Filtration
vii) Washing of precipitate
viii) Drying or ignition of precipitate
ix) Weighing
x) Calculations.

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3. Purity of Precipitate :- When the precipitate separates out from the solution, it is always not perfectly pure i.e the precipitate is contaminated with varying amounts of impuri-ties even after the extensive washing. These amounts of impurities depend upon nature of precipitate and condition of precipitation.

4. Co-Precipitation :- The contamination of the precipitate by substances which are normally soluble in mother liquid is termed as co-precipitation.

Examples -

To a mixture of barium chloride and the potassium permangnate solution, excess of the sulphuric acid is added slowly in small portions & then potassium permangnate is reduced by the addition of some - reducing agent. After the rea-ction, the solution becomes colourless but the precipitation appears to be of violet colour.

This indicates that some potassium permangnate is co-precipitated together with barium sulphate.

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5. Post Precipitation :-

Sometimes when the precipitate is allowed to stand in presence of mother liquor the second substance will form the precipitate with the precipitating reagent, this is called post-precipitation.

They usually have an ion in common with the primary precipitate.

Examples -

When calcium oxalate is precipitated in presence of magnesium ions, magnesium oxalate does not precipitate immediately.

Longer the precipitate remain in solution greater will be the error due to post precipitation.

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UNIT = 4

REDOX TITRATION

1. Oxidation - Reduction Titrations (Redox titration).

In oxidation - reduction (redox) titrations the indica-
-tor action is analogous to other types of visual
colour titrations. In the immediate vicinity of the
end point, the indicator undergoes oxidation
or reduction, depending upon whether the
titrant is an oxidizing agent or a reducing
agent. The oxidized & reduced forms of the
indicator have distinctly different colours.

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Example –

Example of redox titration is tre-
ating a solution of iodine with a reducing
agent and using starch as indicator.

Iodine forms an intensely blue comp-
-lex with the strach. Iodine (I_2) can be
reduced to iodine (I^-) by e.g. thiosulfate
($S_2O_3^{2-}$), and when all iodine is spent
blue colour disappears.

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2. Oxidation Reduction Reaction –

Oxidation - reduction reactions are the chemical processes in which a change in valency of reacting elements or ions takes place.

Oxidation – It can be defined to involve any of the following:

(i) Addition of oxygen to any substance
e.g. $SO_2 + O \rightarrow SO_3$

ii) Removal of hydrogen from any substance or species.
e.g. $H_2S + OH \rightarrow H_2O + S$

iii) Loss of electrons from a species
e.g. $Fe^{+2} \rightarrow Fe^{+3} + e$

Reduction – It can be involve any of following-

(i) Addition of ~~oxygen~~ hydrogen to any substance.
e.g. $C_2H_2 + 2H \rightarrow C_2H_4$

(ii) Removal of oxygen from any substance or species.
e.g. $CuO + 2H \rightarrow Cu + H_2O$

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(iii) Gain of electrons by a species.

e.g. $Cl_2 + 2C \rightarrow 2Cl$

A reactant which loses electrons in an oxidation-reduction reaction is known the reducing agent or reductant.

$$Fe^{+2} \rightarrow Fe^{3+} + e$$

The electrons lost by the reducing agent are gained by the oxidising agent (oxidant).

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

Therefore, a combination of oxidising and reducing agents forms chemical reaction.

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e$$
$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$
$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

- Types of Redox titration

(i) Titrations involving potassium permanganate (Permanganametry).

(ii) Titrations involving Ceric Sulphate (cerimetry)

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(iii) Titrations involving iodine General

(iv) Redox methods involving Bromine theory

(v) Redox method involving KIO_3

(i) Titrations involving potassium permanganate (Permanganametry) :-

Potassium permanganate is a valuable and powerful oxidising agent. When potassium permangante is used as an oxidising agent under acidic conditions to following equations are involved:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

(ii) Titrations involving ceric Sulphate (cerimetry)

Ceric sulphate in the presence of dil H_2SO_4 (1.8N) is a powerful oxidising agent. The acidic should present in sufficient amount to prevent the hydrolysis & precipitation of basic salts.

Ceric has only one oxidation state as follows:

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

Ceric sulphate is bright yellow in colour both

in solid state and in solution & the cerous salt formed on reduction is colourless.

(iii) Titrations involving iodine General :-

Iodimetry covers the titrations with a standard solution of iodine. Iodometry deals with titration of iodine liberated in a chemical reaction.

This method of analysis is based upon inter-conversion of elemental I, and Iodide ion.

$$I_2 + 2e \rightarrow 2I^-$$

This method is employed for quantitative determination of oxidising and reducing agents. Standard Solution of sodium thiosulphate and iodine are used in this method with starch as indicator. With free iodine it gives blue colour.

(iv) Redox methods involving Bromine theory

In the determination of substances like phenol, resorcinol, aniline etc. in place of iodine, bromine is used as an oxidising agent.

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The reason being that bromine is easily reduced by the organic substances.

(v) Redox method involving KIO_3

This method is employed for determination of the percentage purity of the following compounds-

1. Weak iodine solution
2. Iothalamic acid
3. Semicarbazide HCl
4. Aq. Iodine solution
5. Stannous chloride
6. Phenyl hydrazine HCl

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3. Ceriometry :-

Oxidation - reduction titrations involving ceric sulfate as an oxidising agent are called as ceriometric titrations.

End point detection can be possible without any indicator in hot solutions.

4. Iodimetry and Iodometry -

(i) Iodimetry - Iodimetry which describes titrations in which a standard iodine soln is used.

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(ii) Iodometry – Iodometry deals with titrations in which the iodine liberated during chemical reactions is titrated.

5. Bromatometry :-
$KBrO_3$ is a strong oxidizing agent in addle solution. In most of the cases, potassium - bromate is used as titrant in the pren presence of bromide. In this case:

$$BrO_3 + 5Br + 6H^+ \rightarrow Br_2 + 3H_2O$$

so the oxidizing power is determined by the Br_2/Br system ($E_0 = +1.08V$)

6. Dichrometry – Dichromate titrations or titration with potassium dichromate in acidic solution are based on conversion of dichromate ion- containing sexivalent chromium into trivalent chromium ions.

$$Cr_2O_7^{-2} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O$$

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Unit - 5

Electrochemical methods of Analysis

1. Conductometry —

The determination of end point of titration by means of conductivity

It is the method in which the capability of analyte to conduct an electric-al current is monitored. From ohm's law ($E = IR$) it is apparent that electric current (I) is inversely proportional to the resistance (R); where E represents potential difference. The inverse of resistance is the conductance ($G = I/R$) Determination of the quantity of a material present in mixture by measurement of its effect on the electrical conductivity of the mixture.

2. Conductometer / conductivity cell —

Principle —

The conductometer works on principle of wheat stone bridge circuit.

To measure the conductance of a solution, solution is placed in the suitable of

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conductivity cell & then connected to the terminals of the conductivity bridge or Conductometer.

Working –

(1) The wec wheat stone bridge circuit consists of standard resistance in one of its arm and other arm contains a conductivity cell (platium electrode) dipped in the solution whose conductivity is to be determined.

(2) The sliding contact with a galvanometer can be moved on a wire of standard dimensions which balances the resistance of unknown solution with that of the standard resistance.

When null deflection is obtained,

$$\frac{R_2}{R_1} = \frac{\text{Resistance of unknown solution}}{\text{Resistance of standard solution}}$$

3. Conductometric titration –

The determination of end point of a titration by means of conductivity measurements is called as the conductometric titration.

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Principle :-

The principle of conductometric titration is based upon the substitution of ions of one mobility (conductance) by ions of another mobility.

Thus:

$$A^+B^- + C^+D^- = A^+D^- + C^+B^-$$

Construction :-

(i) Titration vessel (Beaker)
(ii) Stirrer for mixing
(iii) Automatic (or) manual burette
(iv) Conductivity meter with conductivity cell.

Procedure :-

(1) Initially the titrant is added in small increments like 0.5 ml and 1 ml

(2) The solution is mixed properly and the conductivity readings are taken.

(3) Several readings are taken, few before and few after the approximate end point.

(4) A graph of conductivity vs the volume of titrant is drawn and point of intersection of lines is found out.

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(5) This point of intersection of lines represents the end point (or) volume of titrant required to neutralise the reactants and sample present in the titration vessel.

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