Pharmaceutical analysis is analytical chemistry that deals with which process or series of process or series to identify and quantify the drug or formulation and purification of substances, separation of the components from mixture or solutions and determination of structure of chemical compound.

Techniques of Analysis

There are mainly two types of chemical analysis:

(i) Qualitative analysis (identification)

(ii) Quantitative analysis (estimation).

(i) Qualitative Analysis

Qualitative analysis gives an indication of the identity of the chemical species of the sample.

This method is perform to establish composition of natural or synthetic substances. It gives the information whether the substance or compound is present in the sample or not.

Qualitative analysis includes detection of evolved gas, formation of precipitate, limit test, colour change reaction, melting point and boiling point, taste etc.

1. Melting point.

The temperature at which a solid melts is known as the melting point.

It is a physical property of solid substances. This method is used to identify substances.

Melting point determination is a simple, fast and economic method used to obtain a first impression of the purity of a substance.

Pure crystalline substance gives a clear sharp melting point.

This method can identify purity of compound as small amount of impurities present in sample can change the melting or enlarge its melting range.

2. Boiling point

Boiling point is the temperature at which the vapour pressure of a liquid equal to the atmospheric pressure ~~of~~ or some other applied pressure.

Boiling point is physical property of liquids for indicating the purity of solvent or liquids.

The boiling point of a liquid varies depending upon the surrounding, environmental pressure. A liquid in a partial vaccum has a lower boiling point than when that liquid is at atmospheric pressure.

Refractive Index.

Refractive index also called index of refraction is specific property of light. It gives information regarding behaviour of light.

The refractive index is measure of the bending of a ray of light when passing from one medium into another.

When light passes through any substance its velocity decreases and refractive index increases due to the effect of interaction between molecules of substance on light.

Refractometer is a device which is use to measure the refractive index of substance.

8/12/21

Optical Rotation

Optical rotation or optical activity is the rotation of the plane of polarisation of linearly polarised light as it travels through certain materials. Optical activity occurs only in chiral materials, those lacking microscopic mirror symmetry. Optical activity can be observed in fluids. This can include gases or solutions of chiral molecule such as sugars, some proteins and also chiral liquid crystals.

The substance which rotates plane of polarisation of light towards right or in clockwise direction are called **dextrorotatory**.

The substance which rotates plane of polarisation of light towards left or in anti-clockwise direction are called **leavorotatory**.

Polarimeter is used to measure the optical activity.

Quantitative Analysis.

These techniques are mainly used to quantify any compound or substance in the sample or to determine the amount of each compound present in the sample.

Types of Quantitative analysis:

1. Chemical Methods
    a). Volumetric or titrimetric methods.
    b). Gravimetric methods.
    c). Gasometric analysis.

2. Electrical methods.
3. Instrumental methods.
4. Biological and Microbiological methods.

1. Chemical Method.

a). Volumetric or titrametric methods:-

This methods involves the measurement of volume of a solution of known concentration which is used to determine the concentration of the analyte.

Volumetric method is a simple method and requires less apparatus and they are susceptible of high accuracy.

Basic terms involves in Titrimetric or volumetric method.

1. Titrate :- A substance is to be titrated is called titrate.

2. Titrant :- A solution of known concentration is called titrant.

3. Indicator :-

Indicator is a substance that show colour change after completion of chemical reaction between titrate and titrant.

It depends upon pH of solution.

• End point or Equivalence point.

The equivalence point is the point in a titration at which the amount of titrant added is completely neutralises analyte in the solution.

• Standard solution.

A solution of known concentration is called standard solution.

Pharmaceutical Analysis - I

Qualitative

Quantitative

It refers to the chemical analysis of drug molecules or medicinal agents and their metabolites. It consist of quality and quantity of drug and fine chemical which are used in pharmaceutical preparations.

☆ Pharmaceutical Analysis is generally involved in two steps.

① Separation of compound of interest.

② Quantification of compound.

Scope :-

The scope of pharmaceutical Analysis can be extended by incorporating during disease states which serves as diagnostic aid in medicine.

The main object and aim of quantitative analysis is to carry out the determination of the quantitative contents of the individual compound or element. +nt in a drug solution.

Importance of Quantitative analysis in quality control.

The various silent features with respect to the quantitative analysis in quality control are as experimented under:-

① Chemical formula of an unknown substances:

Formula of an 'unknown' substances, either synthesized in a laboratory or isolated from natural occuring plant sources is in variable determined and established from the percentage contents of its constituents found by actual analysis.

② Infact the chemical analysis represent the backbone of a Pletbora of most impt. method of investigation and therefore, imployed extensively and profusely impractical all branches of science that use intimatly associated to chemistry.

eg:- It finds it ~~adb~~ ~~ad~~ abdunt utility in pharmaceutical analysis of inorganic and organic chemical substances, microbiology, bio-chemistry, bio-technology, pharmaceutical technology, besides certain highly specific discipline → physiology, Geology, Minerology, Medical and Agricultural sciences.

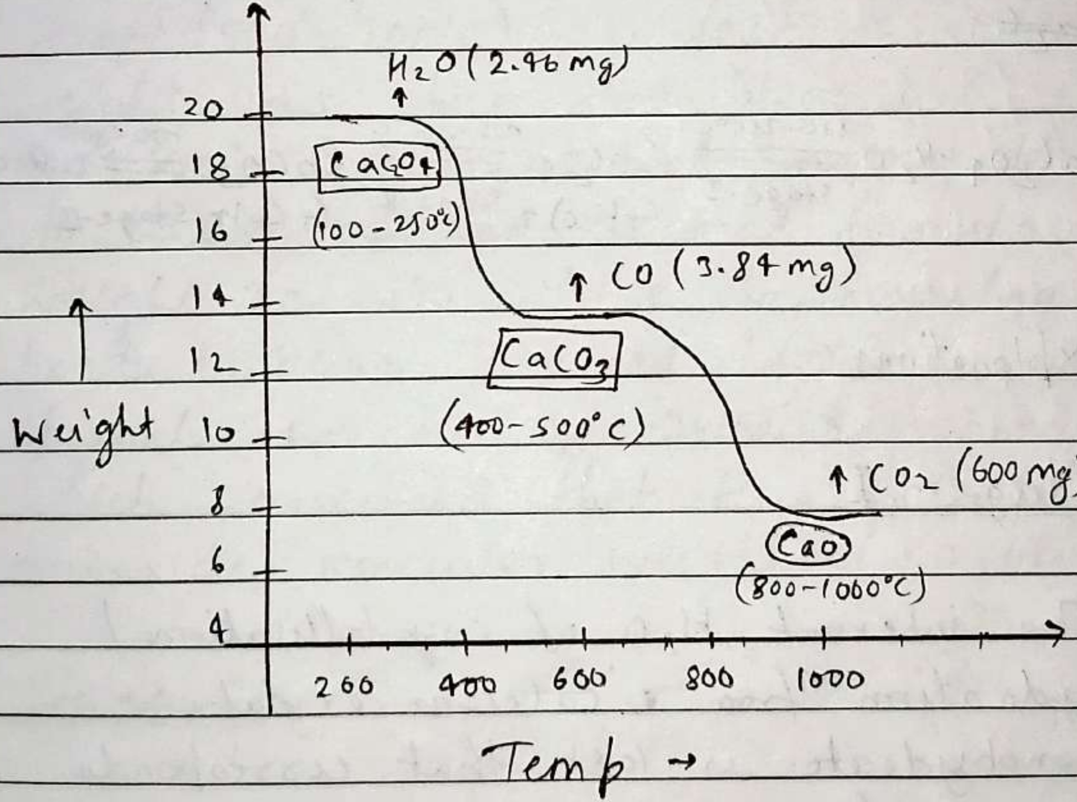
③ The chemical analysis of posses an enormous potential in pharmaceutical industry in particular and others allied industries in general. On a rather more specific note a 'Pharmacist' should be fully aware at each and every steps of adopted production process the qualititative as well as quantitative chemical composition of the materials (substances) that have undergone expected and desired conversion (modification).

eg:-> Thermogravimetric Analysis (TGA) of calcium ~~oxe~~ oxcelate Monohydrate.

It has been duly observed that a large no. of chemical substances usually get decomposed upon heating. Infact this very idea and concept of heating a particular given sample to observe carefully that ensuring weight variations in the underlaying principle of thermogravimetric analysis (TGA). Interestingly, the TGA of Calcium oxalate monohydrate reprents the dynamic TGA. Whereas in the solid sample is specifically subjected to conditions of predetermined and controlled continuous increases in temperature which is mostly observed to be linear with time.

Method:-

The 'thermogram' for calcium oxalate monohydrate $(CaC_2O_4 \cdot H_2O)$ is dully represented in fig. one may however distinctly observe the successive plateous namely.



(i) Correspond to anhydrous oxalate (100-250°C).
(ii) Correspond to calcium carbonate.
(iii) Correpond to Calcium oxide.

In other words, the three observed plateous clearly designate the following vital aspect of the decomposition curve namely.

ⓐ Clear indication of constant weight.

ⓑ Stable phase encounted within a specific temperature interval.

The various distinct chemical reaction that are actually may be summarized as follows :-

~~Ca_2C~~

$$CaC_2O_4 \cdot H_2O \underset{stage\text{-}I}{\overset{100-250^\circ c}{\rightleftharpoons}} \underset{(+H_2O)\uparrow}{CaC_2O_4} \underset{Stage\text{-}II}{\overset{400-500^\circ c}{\rightleftharpoons}} \underset{(+CO)\uparrow}{CaCO_3} \underset{Stage\text{-}III}{\overset{700-800^\circ}{\rightleftharpoons}} Ca(+CO_2)\uparrow$$

Explanations :-

Stage - I

① The inherent H_2O of crystallisation / hydration from calcium oxylate monohydrate is last that corresponds to 2.46 (12.3%) equivalent to 1 mole of H_2O b/w the tempt. range 100°c - 250°c. In actual practice the (12.3%) weight has normally occur between 100° - 250°c must correspond to 12.3% of the original formula weight for $CaC_2O_4 \cdot H_2O$ (146) Therefore the product which get lost eventually has a formula weight of $0.123 \times 146 = 17.958$ ($\simeq 18$) and it definitely correspond to H_2O (water) (Molecular weight of $H_2O = 18$)

Stage -2

One mole carbon monoxide (CO) gets evolved from calcium oxalate (CaC_2O_4) corresponding to 3.84 mg (19.2%) between the temperature varying from (400° - 500°c). In fact the 19.2% weight loss which took place b/w 400 - 500°c must actual correspond to 19.2% of the original formula weight of 146. Hence the resulting product being produced bears a formula weight of $0.192 \times 146 = 28.0$ which correspond that it is CO (carbon monoxide) molecular weight of CO = (12+16=28)

Stage -3:

At the final stage one mole of CO_2 (carbon dioxide get evolved from one mole of $CaCO_3$ which eventually correspond to 6.02mg (3.01%) in the tempt range varying b/w 700° - 800°c. Interestingly the weight loss corresponding to 3.01% which occurs in tempt. range b/w 700°-800° should be equivalent to 3.01% of the original formula weight of 146. Hence the generated product bears a formula weight of 0.301 × 146 = 43.946 (≃ 44) and its correspond to CO_2 (carbon dioxide) (12 + 32 = 44)

Imp

* ④ As to date this is widely accepted practice that no 'drug substances' is either taken into production for actual consumption without proper quality control screening that essentially characterised its overall quality, stability and suitability for various purpose. Importantly those ultimate result serve two major objective namely.

ⓐ To form the fundamental basis of all the processing calculation and.

ⓑ To determine exactly the 'naked cost' of various materials inputs that predominantly serve as core basis of all financial estimates.

⑤ In a broader perspective, the ulmost impt. of adequate and proper control of production is quit evident. Hence it is absolutely necessary each and every pharmaceutical industry should essentially have an well equiped analytical laboratory under the command of a qualified experienced and highly motivated pharmaceutical analysis personally. Now a days these laboratories are called 'Quality Assurance' and 'Quality control' laboratory for the chemical control physical parameters and microbiological screening of a raw material. Intermediates and finite product.

⑥ In actual practice, however pharmaceutical analysis major problem is most commonly implified to a greater extent significantly by vertuië of the fact that the qualititative composition of majority of the investigated product pure drug → substance chemically additives, pharmaceutical intermediate and finished dosage form is well known as

described in official compedia
eg :- (IP, BP, USP, EP, International P.)
Furthermore, the approximately contents of the individual elements are obviously known quite frequently.

Evidently in such particular instances the usual preliminary qualititative analysis become more or less unnecessary absolutely, thereby rendering the proper solution of the most appropriate technique of the qualitative analysis become much more easier and meaningful

Types of Quantitative Analysis :-

① Titrimetry :
Volumetric :- of quantitave method of analysis dealing with volume of solution and their measurement is termed as titrimetric analysis or tritometry. The substance is allow to react with an appropriate reagent added as a standard sol^n^ and the vol. of sol^n^ needed for complex rxn is determined.

The common type of rxn that are used in titrimetry are..

1) Neutrilization rxn (acid, base)

Acid base titration is based on the neutralization rxn b/w the analyte and acidic or basic titrant. Those rxn used at pH indicator, pH meter, as a conductant meter to determine a end point.

2) Precipitate rxn.

A precipitation titration comprises a class of rxn that required a formulation of insoluble precipitate. Provided that the end point at which the precipitation is complete can be determined.

3) Oxidation Reduction rxn :-

ⓐ Redox :-

A redox titration is based on an oxidation - reduction rxn b/w the analyte on oxidant or reductant.

A potentiometer or redox indicator is used to determined the end point. Frequently either the reactants or the titrant have a colour intense enough that an additional indicator is not needed.

ⓑ Complex forming rxn :-

A complexometric titration is based on the formation of a complex b/w the analyte and the titrant the chelating agent EDTA is very commonly used to tritrid metal ions in the soln. This titration generally requires specialised indicators that forms weaker complexes with the analyte. A common examples is Eriochrome. T for the titration of Ca and Mg ions.

★ Non - aquous titration

Non - aquous titration is the titration of substance dissolve in a non - aquous solvent. It is the most common titrimetry procedure used in pharmacopoel assay and serve a double purpose.

① It is suitable for the titration of very weak acid and bases.

② And it provides a solvent in which organic compound are soluble.

Gravimetry :

It involves the separation of the constituents to be estimated in the form of and insoluble precipitate. The insoluble precipitate is vast to free it from all impurities, dried and weighted either as such as ignited to give a residue of some other compound which is the weight. Now from its weighed and no one composition the amount of the constituents in the given sample is calculated.

Determination of chlorine content in common salt (NaCl) the various forms of gravimetry are :-

(i) Electrogravimetry :

It involves at electrolysis and the materials deposited on one of the electrodes is weighed.

(ii) Thermogravity :-

It estimates the change in ~~word~~ weight as a function of temp.

(iii) Differential Thermalanalysis :-

Determine the difference in tempt. b/w a test substance and an inert reference material.

(iv) Differential Scanning colorimetry :-

Records the energy needed to establish at a zero tempt. difference b/w a test substance and a reference materials.

Volumetry.

It is concerned with measuring the vol. of gas evolved and absorb in a chemical method.

★ (II) Physical Method of Analysis :-

It involves the determination of physical properties of liquid like specific gravity, viscosity as surface tension. The common types of measurement that are used in physical method of analysis are.

1) Refractometry:

It involve the measurement of refractive index of liquids using a refractometer.

eg. → Refractive index of arochis against water.

2) Polarimetry:

It is used to measure optical relation of an optically active compound using a polarimeter.
eg. Optical rotation sucrose.

3) Viscometry:

It involves the measurement of viscocity of a liquid using viscometer.

eg. Viscosity of solvent.

III Electrical method of Analysis.

It ~~ino~~ involves the measurement of current voltage as resistance in relation to the concentration of a certain species in solution. The common types of measurements that are used in ~~elem~~ electrical method of analysis includes :-

1. Voltametery :-

It involves the measurement of current at a micro electrode at specified voltage.

2. Carlometery :-

It measures current and time needed to compete an ~~electrode~~ electrochemical rxn. or to generate sufficient materials to react completely with a specified reagent.

③ Potentiometery :-

It is used to measure the potential of an electrode in equilibrium with an ions to be determind.

④ Spectroscopic method of Analysis.

Spectromethod measure the electromagnetic radiation i.e absorbed scattered or emitted by the analyte the methods of measurement of radiation vary from one method to another. The imp. ~~section~~ spectro methods are :-

ⓐ Absorption spectroscopic :-

It depends on measuring the amount of a particular wavelength absorbed by the sample. Absorption method are usually classified according to wavelength involved as visible, ultraviolet or infra-red spectroscopy. The visible spectroscopy or spectroscopy photo-metry is some time called as calorimetry.

ⓑ Turbidimetry and Nephalometric method :-

This process are used to measure the amount of light stolped or scattered by a suspension.

(c) Emission Spectroscopy:-

It determines the amount of radient energy of a particular wavelength emitted by the sample.

(d) Flame photometry:-

It uses a solution of this sample injected into a flame.

⑤ Fluorimetry:-

It takes a suitable substance in solⁿ (commonly a metal fluorescent reagent complex) and excites it using visible or uv radiation.

⑥ Chromatographic methods:-

This methods are used to separate mixture of substances and to identify components of a mixture.
For eg:- Paper chromatography, thin layer chromatography and gas-liquid chromatography.

IV Special technique:

1. X-ray methods:

X-rays are produced when speed $e^{\ominus}$ collide with a solid target (which can be the material under investigation) it is possible to identity certain emission pears that are characteristic of element contain in the target.

2. Radio-activity:-

This procedure measures intensity of the ~~solution~~ radiation from a naturally occuring radioactive material. Measuring radioactivity induced by exposing the sample to a neutron source (activation analysis) or isotope dilution and radioimmunoassay.

③ Kinetic methods:-

This methods are based on increasing the speed of a rxn by adding a small amount of a catalyst, within limits, and the rate of catalyst rxn will be governed by the amount of catalyst ⊕nt.

Volumetry method of Analysis :-

Volumetric analysis is depends on the measurement of the vol. of the solution of the interactive substances. In this analysis a measured vol. of solution of a substance is allowed to react completely with the solⁿ of a given strength of another substance. The end point of the rxn is indicated by sum marked changes such as appear as disappearance of colour or formation of precipitate and the process is termed as titration. The stage during titration at which the rxn is just complete is known as equivalence or end point. Generally end point in a volumetric analysis is detected by the addition of a suitable substance called indicator that changes its colour when the rxn is just completed.

Fundamental of volumetry analysis:-

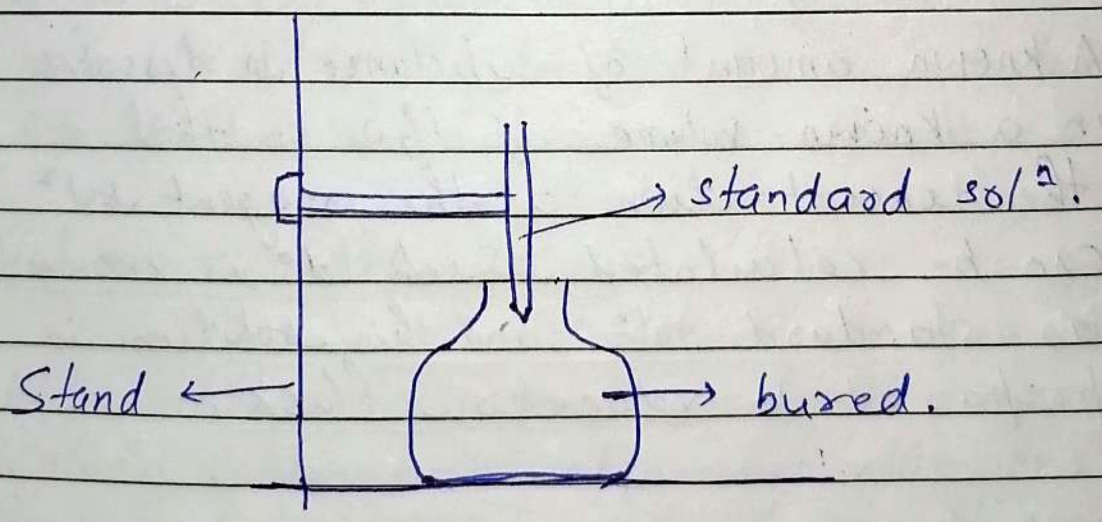
The fundamental requirements to carry out titrimetric or volumetric process are :-

① The rx^n b/w titrate and titrand must be well defined i.e. definite amount of reactants must react to produce definite amount of products.

② The rxn must be rapid so that little time is needed to complete the titration. A catalyst may also be used to increase the rate of rx^n.

③ Titrimetric cal. are based on 100% rx^n b/w the reactants, thus mixing of equivalent amounts of the rx^n must gives a complete rx^n.

④ A standard sol^n of reagent i.e titrand should be taken in a bured and titrate is kept in a conical flask as shown in fig.



⑤ An indicator kept in a conical flask must be available to show the conclusion of the rxn.

⑥ The end point should be well defined

⑦ The vol. of titrand used for completion of a rxn is known as titre volume.

⑧ As the concentration of the reagent solⁿ is known the quantity of reagent ⊕nt in the solⁿ can be calculated.

Step involved in Volumetric Analysis.

→ Volumetric determination of a solⁿ of a given substance (Analyte) with the reagents involves the following steps.

① A known amount of substance is dissolve in a known volume of H_2O so that the concentration of the reagent solⁿ can be calculated. Such solⁿ is known as standard solⁿ. and this solution is prepared in volumetric flask.

② A known vol. of analyte sol^n is taken in a conical flask with the help of a pipette. The analyte sol^n is also called as sample sol^n, test sol^n or titrate sol^n.

③ Few drops of an indicator are added to the titrand sol^n taken in the conical flask. The use of the indicators is to show the colour change when the rxn b/w the analyte and the reagent sol^n is just complete.

④ The objective of titrating and alkaline sol^n with a standard sol^n of an acid is to determine the amount of acid which is exactly equivalent chemically to the amount of the base ⊕nt. This point of neutrilization is termed as equivalence point or theoritical end point due to formation of salt.

Volumetric Apparatus:-

Apparatus used for titrations are called volumetric apparatus due to involvent of measurement of volumes. Acid base titration form part of a group, of laboratory procedures known as volumetric analysis.

Some of the characters are given as:

① Pipette :-

Bulb pipette is designed to deliver an accurately known vol. of solution, after it has been filled exactly to the ~~tank~~ .mark. They are available in volumes of 1, 2, 5, 10 and 20 ml. Also volumetric pipettes are calibrated in units of milimeter (mm). The pipette is held vertically to fix the mark at the same level as the eye.

~~Pipt~~ Pipettes are of two types:-

ⓐ Transfer pipette :-

It has one mark and withdraw a small and constant vol. of sol^n.

ⓑ Measuring / Graduated pipette:

These are graduated used to deliver various small volume. During withdrawal the adhering drops addition are removed by stroking against an inside walls of glass surface as touching to the surface of solⁿ.

② Beaker:-

It is a container having beak like structure. Borosil beaker is used as it with stand with frequent heating and cooling. Beaker's are different capacities.

eg:- 50 ml, 100ml, 500ml and 1000ml are available in market.

The following process are carried out in such containers.

(i) Preparation of solution
(ii) Heating
(iii) Precipitation.

③ Burette :-

A burette consists of a graduated tube fitted with stop cock and used to deliver variable vol. Burettes are normally available in max^{m} capacities of 2,5,10, 25,50 and 100ml. Before using, the burette is thoroughly cleaned with a cleaning agent, rinsed well with a distilled H_2O the stop cock is lubricated and fixed in burette holder. The sol^n^ is filled the help of a small funnel upto zero mark. The liquid is discharged from a burette into a conical flask. The flask is gently rotated with the right hand for mixing of content well. Meniscus is a curve in the surface of a liquid and is produced in response to the surface of the container or another object. It can be either concave or convex.

④. Conical flask:

A conical flask is flat bottom pear shaped apparatus with short ~~neck~~ narrow neck of thin line marked around the neck indicates the volume that it holds at a certain definite tempt. solution to be titrated are usually pipette into a conical flask, also known as an Erlenmayer flask.

⑤ Volumetric flask :-

This flask are used to prepare standard sol^n^ of solutes. In known mass of solute is placed in a flask, dissolved in pure water and then made up a mark etched in the neck of flask. Volumetric flask are normally supplied in volumes of 100ml to 1000ml.

⑥ Measuring Cylinder:-

These are used to measure standard solⁿ of solutes with permanent graduations they are made up of borosilicate glass. The commonly used sized of measuring cylinder are 10 ml, 50 ml, 100ml, 250 ml, 500ml and 1000 ml. Before use the burette is thoroughly cleaned with a cleaning agent and rinsed well with distilled. H_2O. While reading the measuring cylinder you should read the no. i.e. at the bottom of the miniscus.

Some Important terms in volumetric analysis :-

① Titrand or Titrate :-

It is prepared by dissolving a known amount of substance into a known amount of H_2O as solvent. It is prepared in volumetric flask, it has ~~exactly~~ exact purity non-hydroscopic in nature. It is also known primary standard solution, test solution or analyte solution.

Titrant:-

The secondary standard sol^n is known as Titrant. It is used in process of standardization and whose content or concentration of active compound is formed by compassion against primary standard. It is prepared in volumetric flask and taken in burette.

Indicator:-

Indicator is an organic dye which signal the completion of a rxn or titration by the visual change in the colour eg:- methyl orange, phenol red, starch and phenolphthalein etc.

Equivalence point:-

It is a point of a rxn or titration when the no. of titrand molecule reacting with titrate molecule will be equal.

Standardization :- It is the process where the concentration of one solution is determined by the known concentration of the other solution.

End point :

It is exact stage at which an indicator gives its visual colour change and the rxn is just completed.

Standard solution :

A solution whose concentration is accurately known is called standard solution.

Preparation :-

An exactly weight amount of the substance of definite and known volume in composition is dissolve in distilled water and made up to the known vol. in graduated volumetric flask. From the known weight and volume, the concentration of the solution is calculated. These are of the following type of standard sol^n.

① Primary Standard sol^n:-

A primary standard is a compound of efficient purity from which a standard solution can be prepared by direct weighing of a quantity of it and followed by detection to give a definite vol. of sol^n, the sol^n then produced is primary standard sol^n.

A primary standard sol^n should satisfy the following requirements:-

ⓐ It must be easy to purify, to dry (preferably at 110°- 180°C) and to preserve in pure ~~water~~ state.

ⓑ The substance should not be altered in air during weighing.

ⓒ The substance should be capable of being tested for impurities by qualities and other test of known sensitivity.

ⓓ The substance should be readily soluble under each condition in which it is employed.

ⓔ The rxn with standard relationship b/w reactant and products in chemical rxn.

Some ex. of primary standard solⁿ :-

① Arsenic trioxide for standardization of iodine and calcium (IV) sulphate solution.

⑪ Benzoic acid for standardization of TBAH (Tetry-butyl ammonium hydrate) in methanol sol.

⑪ Potassium bromate ($KBrO_3$) for standardization of sodium thiosulphate solⁿ.

Secondary Standard sol^n:-

A secondary standard sol^n is a substance which may be useful for standardization and whose content of the ~~above~~ active substance have been found by comparison against a primary std. sol^n. They are prepared in a laboratory for specific analysis and are usually standardized against primary standard as follows that a secondary standard sol^n is a solution in which the conc^n of dissolve solute has not been determined from the weight of the compound dissolved but by rx^n (titration) of measured vol. of a primary standard sol^n.

eg:-

① Alkali hydroxide → potassium hydroxide (KOH), (NaOH).

② Mineral acids:- HCl, H_2SO_4 (sulphuric acid) and nitric acid (NHO_3).

③ Oxidizing agent:- Potassium permanganate ($KMnO_4$), and potassium dichromate. ($K_2Cr_2O_7$).

The secondary standard component which is not obtain in pure state eg:- Caustic soda (NaOH) and Minerals acids (HCl, H_2SO_4) and (HNO_3) are prepared little more concentrated than required and to dilute it with distilled water until the desired normality is obtained. This sample must be standardized and for standardization they have to be titrated against the solution of pure substances of known concentration (primary standard).

Accuracy :-

The accuracy of determination may be defined as the closeness of a measured value of the true or most probable value for analytical methods there. are 2 possible ways of determining the accuracy absolute method and comparative method.

① Absolute method. :

These test ~~fo~~ of accuracy of the method under consideration is carried out taking varying amounts of the constituents and proceeding

according to specified institution.
The amount of the constituents must be varied be the determinate errors in the procedure may a function of the amount used.
The difference between the mean of an adequate no. of results and the amount of constituents actually ⊕nt is a measure of accuracy of the method in the substance. Here primary std. are used.

Comparative method:-

In this method of accuracy the solid synthetic secondary standard sample of desired composition are prepared. The samples are resorted further as to determine the content of the constituents by one or more accurate method of analysis. This method indicates the absence of appreciable systematic error in the procedure of analysis.

Precision :-

Precision is defined at the agreement of a series of measurement of the same quantity when an analyst is able to reproduce two or more measurement with only slight difference in the result, this work may be reproduced as to be precision.

There are 2 forms of precision:-

① Run Precision Repeatibility :-

If a analyst has marked the determination on the same day in rapid succession, the set of result would be defined as repeatable.

② Run Precision reproductibility :-

If an analyst has made the determination on the separate days when laboratory condition may be rary the set of results would be defined as reproducticible.

(i) Mean or Average :-

Mean or average is obtained by dividing the sum of a set of measurement by the no. of individual measurement in the set.

$$\boxed{\text{Mean} = \frac{Mn}{n}}$$

M = Individual measurement
n = total no. of measurement

(ii) Mean deviation of a single measurements :-

It is the mean of the derivations of all the individuals measurements. It can be calculated as.

ⓐ Determining the arithmetic mean of results.

ⓑ Calculating the deviation of each individuals measurements from the mean.

ⓒ Calculating the deviation by the no. of measurements and.

ⓓ Coefficient of variable.

$$\boxed{(CV) = \frac{S \times 100}{x}}$$

S = Standard deviation, x = mean.

Precipitation ~~method~~ :- Titration :-

Q. Discuss principle of precipitation titration. Discuss Fajan method in detal? [14 marks]

Principle of ppt. titration :-

The main principle of precipitation titration is that the quality of adding precipitating reagent or precipitant is equivalent to the substance been precipitated.

PDF-start

Significant figures :-

The number of digits necessary to express the result of a measurement consistent with measured precision or in other words a significant figure is digit having some practical meaning i.e, it is a figure or digits which denotes the amount of quantity in the place in which it stands or the digit of a number which are needed to express the precision of the measurements from which the number derived are known as significant figures.

The following guidelines indicate whether or not a digit is significant:

(1) All non-zero digits are significant digits

eg. 1, 2, 3, 4, 5, 6, 7, 8, and 9
eg. 345.76 has five significant digit.

(2) Zeros are significant if they :

ⓐ are the last digit of a measurement as long as they are to the right of the decimal point.

Example:- 3.70 has three significant digit. The zero is significant because it is the last digit.

ⓑ Come between two other significant digits.

Example:- 340.61 has five significant digits. The first zero is significant because it falls between 4 and the 6 which are both significant.

③ Zeroes are not significant if they act as placeholder.

eg.. 0.035 has two significant digits. The zeroes are placeholder and are not significant.

④ When the zeroes are on the left of the decimal point then they are not necessarily significant.

Ex → 2100 may have 2, 3 or 4 significant figure.

Ex → 350 may have 2 or 3 significant no.

This ambiguity can be avoided by writing the number in scientific notion.

⑤. In Scientific notation, all digits in the coefficient are significant. The exponent is not considered in terms of significant figure.

eg. → 2.100×10^3 will have with certainty 4 significant figure.

→ 3.50×10^2 will have with certainty 3 significant figure.

→ 3.54×10^5 will have with certainty 4 significant figure.

⑥ Numbers that are known with complete certainty are said to be exact conversion factor, constraints, values that are part of a formula are said to be exact. This exact numbers are considered to have an unlimited number of significant figures and are never used as a limited factor in determining the number of significant figures in the result of an operation.

eg:- 1cm = 10 millimeter. The number 10 Will have an infinity number of significant figure.

Rules for Retaining Significant figures

There are several rules to remember regarding significant figures when manipulating numbers.

(1) When measurements are multiplied or derived, the answer can contain no more significant figures than the ~~last~~ least accurate measurement.

(2) When measurement are added or substracted, the answer can contain no more decimal places than the least accurate measurement.

$$\begin{array}{r} 150.0\ g \\ +\ 0.507\ g \\ \hline 150.5 \end{array}$$

(using significant figures)

(3) In a quotient of experimental members, the final rebuilt has only as many significant figures as the factor with the smallest number of significant no.

eg. In the calculation =

$$= \frac{(0.0181057)(0197.15)(0.218)}{0.9970} = 1.568$$

$= 1.57$

least no. of significant figures is in number 0.218. Thus the answer should also be ~~experiment~~ expressed in three significant figures.

④ Two rules are given for rejecting superflouous digits:

i) When the last digit dropped is greater than 5, the last digit retained is increased by one. It is called rounding

8.492 → New value will be 8.49 as 2 is smaller than 5.

4.863 g → New value will be 4.9 as 8 is greater than 5.

ii) When the last digit disconded is less than 5, the last digit retained is decreased by one. It is called rounding about.

Errors :

It is observed that the numerical data obtained in quantitative analysis or determination differ to greater or lesser extent. Sometimes. It is difficult to obtain the same measurement when performed under identical conditions. So, the reliability of the results depends upon the magnite of the difference between the average value and the true value or more probable value. Under such conditions the determination is subjected to errors. Error ~~then~~ often denote the estimated uncertaintly in a measurement or experiment.

Classification of errors :-

1. Systematic / determination or constant error.

ⓐ Person error.
ⓑ Operational error.
ⓒ Instrument of reagent error.
ⓓ Methodic error.

2. Random or Indeterminate error.

③ Errors in measurement

④ Gross error.

Systematic / determinate or constant error:-

The determinate errors are the errors that remain in a constant way and to a fixed degree in each of the determinations or affect the series of determination to the same degree. These errors can be avoided or their magnitude can be determined, thereby correct.

ⓐ Personal error :-

These errors depend on the personal characteristics of an analyst himself. They may occur due to constitutional inability of the individual to certain observations accurately.

eg:-

① Inability in judging color change sharply in a visual titration.

(ii) The estimation of value between two scales devision of the burette.

(iii) Inability to detect end point in the titration.

(iv) Error in calculation i.e. induplicate weighing and titration.

(v) Mechanical loss of material in various steps of analysis during bumping.

(b) Operational error:-

These errors are physical in nature and occur when sound analytical technique is not followed. They are easy to detect and eliminate.

eg.

(i) Incomplete drying of analytical samples before weighing.

(ii) Under washing of the precipitate which gives consistent excessive results.

(iii) Over-washing of the precipitate resulting in systematic losses.

(iv) Incorrect draining of the solution from the precipitate.

(c) Instrument and reagent error :-

These errors arise from the comperfections in the measuring device and quality of reagent used. eg :-

(i) Inequality of the length of the balance arm.

(ii) Incorrectly graduated burette.

(iii) Using impure reagent.

(iv) Incorrect technique involving in the transfer of solution.

NEW CHAPTER

ACID BASE TITRATION:-

Chemical reaction between and an acid and a base (alkaline) take place the reaction is based on the principle of neutralization.

$$\underset{\text{(from acid)}}{H^+} + \underset{\text{(from alkaline)}}{OH^-} \rightleftharpoons \underset{\text{(Neutralization of ions)}}{H_2O}$$

- Acidimetry :-

A substance acid sol^n is used for quantitative determination of the base / alkali.

- Alkalimetry :-

A standard sol^n of base is used for quantitative determination of acid.

This acid base titration method is used for various volumetric determinations, which involves neutralization one another way.

eg. - Determination of salt like
- Na_2CO_3
- $Na_2B_4O_7$ etc.

- These salt have strongly alkaline reaction that's why they are titrated with acid solution.

☆ Advantages of acid and base titration :-

ⓐ The reaction between acid and base is quite fast and practically instantaneous.

ⓑ The reaction is acid base titrations will be single without the side reaction.

ⓒ The reaction will always reach to completion.

ⓓ The reaction will always stoichiometric.

★ Acid - base concepts (Theories)

There are four theories proposed to understand the concept of acid-base titrimetric reaction :

① Arrhenius Theory [H^+ and OH^-]

Arrhenius in 1984, first and foremost introduced a radical theory which rightly expatiates an adequate quantitative in an aquous medium specifically.

According to arrhenius acid is any substance that ionizes (partially completely) in water or aquous medium to give hydrogen ions $[H^+]$

$$HCl + H_2O \rightleftharpoons H^+ + Cl^- (aq)$$

$$H_2SO_4 + H_2O \rightleftharpoons 2H^+ + SO_2^- (aq)$$

Base is any substance that ions (partically or completely) in water or aquous medium to give hydroxyl ion $[OH^-]$.

$$NaOH + H_2O \rightleftharpoons Na^+ + OH^+ (aq)$$

$$NH_4OH + H_2O \rightleftharpoons NH_4^+ + OH^- (aq)$$

$$KOH + H_2O \rightleftharpoons K^+ + OH^- (aq)$$

Advantage :-

The concept explain the behaviour of an acid and base practically.

Limitation :-

ⓐ In this concept acid and base is defined in aquous medium only.

ⓑ This concept fails to explain the stability of H^+ ions (s)

(c) It does not explain the conjugate acid-base theory.

ⓓ It does not able to define those acid and base O_2 and SO_2 (aq) which does not contain H^+ / OH^- ion eg.→ NH_3 and Na_2CO_3 (base).

2. Bronsted - Lowry theory (Taking and giving proton).

In 1923 Bronsted and Lowry separately described a theory known as Bronsted lowry concept.

A/c to this theory :-

Acids are those compounds or species which have tendency to donate the proton (H^+) in any type of solvent by any method.

eg. H_2SO_4, HCl, $HClO_4$, CH_3COOH etc.

Bases are those compounds or species, which have tendency to accept the protons (H^+) in any type of solvent by any method.

eg :- NaOH, KOH, $H_2SO_4^-$ etc

Conjugate pairs :-

A pair of substance which can be formed from one another by the gain or loss of proton are called as conjugate base and every base has its conjugate acid.

(i) $\underset{\text{(Acid)}}{HCl} \rightleftharpoons \underset{\text{(proton)}}{H^+} + \underset{\text{(conjugate base)}}{Cl^-}$

(ii) $\underset{\text{(acid)}}{NH_4^+} \rightleftharpoons \underset{\text{(Conjugate base)}}{NH_3} + \underset{\text{(proton)}}{H^+}$

i.e. - $Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$

where, $Base_1$ = Conjugate base of Acid 1
$Acid_2$ = Conjugate acid of base 2

$$\underset{acid_1}{HCl} + \underset{base_2}{H_2O} \rightleftharpoons \underset{acid_2}{H_3O^+} + \underset{Base_1}{Cl^-}$$

Advantage :-

This concept explain the acid base in any type of solvent.

This concept is able to explain the stability of proton.

Limitation:-

1. Behaviours of SO_2, SO_3 and CO_2 as acids and behaviour of CaO and BaO_2 as bases.
2. Donating and accepting a proton is must for showing acidic behaviours.
3. Acid/base behaviour depends upon the ~~pref~~ pressure or ~~above~~ absence of solvent.
4. It cannot explain the acid-base reaction taking place in non-protic solvent, like BrF_2 and $AlCl_3$.

★ Lewis theory [Taking and giving electrons] (lone pair of e-)

- 1923, G.N. Lewis Introduced the electronic theory of acid and base
- In this concept he was defined an acid and base according to the electron proton donar - accept concept.

Acids :-

Those species which have self tendency to accept the lone pair of electrons.

Lewis acids are electrophils.

eg. $AlCl_3$, BCl_3, $SnCl_2$, CO_2, SO_2 etc.

Bases:-

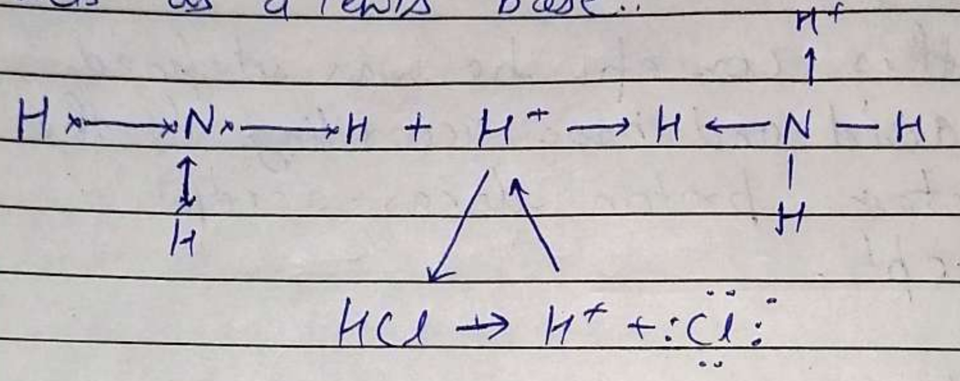
Those species which have ~~of~~ tendency to donate the lone pair of electron

lewis bases nucleophils.

eg. - NH_3, $C_2H_5NH_2$, H_2O, SO_4^{--}, F^-, Cl^- etc.

Details of lewis concept

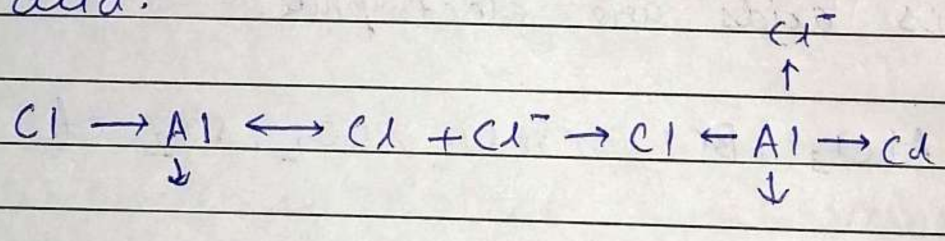
If octate of bases is complete and molecules / ion is still having lone pair of e^- base can donate the electrons acts as a lewis base..



$$H \times\!\!\longrightarrow \underset{\underset{H}{\updownarrow}}{N} \times\!\!\longrightarrow H + H^+ \rightarrow H \leftarrow \overset{\overset{H^+}{\uparrow}}{\underset{\underset{H}{|}}{N}} - H$$

$$HCl \rightarrow H^+ + :\ddot{\underset{..}{Cl}}:$$

If octate of any molecules/ions is incomplete so that will accept the lone pair of e^- and acts as lewis acid.



$$Cl \rightarrow \underset{\downarrow}{Al} \longleftrightarrow Cl + Cl^- \rightarrow Cl \leftarrow \overset{\overset{Cl^-}{\uparrow}}{\underset{\downarrow}{Al}} \rightarrow Cl$$

Advantage :-

It defines acid and base without any types of solvent.

Limitations :-

The relative strength of acids and base cannot be explained by this concept.

★ Hard and Soft acid Base concept:-

Hard Acid.	Soft Acid.
① High +ve charge	① Low +ve charge
② Relative small size	(ii) Relative large size..
③ Unfilled valance orbitals	③ Filled valance orbitals.
④ eg - H^+, L^+, Mg^+, K^+ etc	④ Cu^{2+}, Ag^+, Au^+, Hg^+, I^-.

Hard Base.	Soft Base.
① High electronegative	① Low electronegative
② easily reduces	② easily oxidized.
③ low polarizability.	③ high polarizability.
④ Stable valence shell.	④ Unstable valance shell.
⑤ eg:- H_2O, OH^-, F^-, PO_4^{3-}	⑤ eg - Br^-, SO_3^-

◉ Ionic product of water :-

Kohlrausch and Heydrouiller found in 1894 that the most highly purified water passesses a small and definite conductivity. So water must be highly ionized as per the equation :-

$$H_2O \rightleftharpoons H^+ + OH^-$$

As per the law of mass action, the following equation is obtained at any given temp.

$$\frac{{}^{a}H^+ \times {}^{a}OH^-}{{}^{a}H_2O} = \frac{[H^-]\cdot[OH]}{[H_2O]} \times \frac{{}^{\gamma}H \cdot {}^{\gamma}OH^-}{{}^{\gamma}H_2O}$$

Water is only slightly ionized. so the ionic concentration is small and their activity coefficient is unity. The activity of the unionised molecules is also taken as unity.

So the expression is :-

$$\frac{[H^+][OH^-]}{H_2O} = \text{a constant.}$$

In pure water or in dilute solⁿ, the concentration of the undissociated water is considered constant.

$\therefore [H^+] \times [OH^-] = k_w$

k_w = Ionic product of water.

The ionic product of water varies with the temperature. At 25° c, its value is taken as 1×10^{-14}. The value is constant in dilute solⁿ. If the product of $[H^+]$ and $[OH^-]$ in aquous solution exceeds the value, the excess ions will immediately combine to form water. On the contrary, if the product of two ionic concentrations is less than 10^{-14} more water molecules will dissociate until the equilibrium value is obtained.

☆ Henderson - Hasselbalch Equation :-

The change in pH upon the addition of an acid or base and the pH of a buffer solution is calculated by buffer equation The buffer equation is calculated by considering the effect of a salt on the ionization of a weak acid if the salt and the acid have an ion in common.

Handerson - Hasselbalch equation :-

The pH of an acidic/basic buffer solution can be calculated from the dissociation constant k, of all acids/ bases, concentration of the acid/base and salt used. The dissociation expression of weak acid may be represented as:-

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

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \ldots ①$$

$$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+ \quad — (ii)$$

According to law of mass action:-

$$K_a = [H^+][A^-]/[HA] \quad \text{or} \quad [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

Where, $[CH_3COOH]$ = representing the total concentration of an acid in solution and $[CH_3COO^-]$ = representing the total concentration of acetate ion as most of them are entirely contributed by salt (CH_3COONH_4).

$$H^+ = Ka \frac{(Acid)}{(Salt)}$$

Expressing of negative logarithm on both side.

$$-\log[H^+] = -\log ka - \log \frac{(Acid)}{(Salt)}$$

But, $-\log[H^+] = pH$ and

$$-\log ka = pk_a.$$

$$pH = pka - \log \frac{(Acid)}{(Salt)}$$

$$pH = pka + \log \frac{(salt)}{(Acid)}$$ (inverting the sign)

The relationship is called Henderson's Hasselbalch equation for acidic buffer Similarly the Henderson's Hasselbalch equation for a basic buffer can be derived as;

$$\boxed{pH = pk_b + \log \frac{(salt)}{(Base)}}$$

Significance:

1. The pH of the buffer solution can be calculated from the initial concentration of the weak acid and the salt provided Ka is given.

2. It allows calculation of the ~~ratio~~ ratio in which the weak acid and its salt must be mixed in order to get a buffer solution of known pH

☆ Strength of acids and bases:-

An acid is a substance which ionizes to yield hydrogen ions or protons. Base is a substance which combines with hydrogen ions so, an acid is a proton donor and a base is a proton acceptor.

$$\underset{\text{(Acid)}}{A} \rightleftharpoons H^+ + \underset{\text{(Base)}}{B}$$

Strength of an acid is related to the concentration of hydrogen ions which it yield upon ionization and will depend upon the value of the degree of dissociation

α at any given concentration.

The acid dissociation content K_a provides a relationship between α and the concentration. It is a measure of the acid strength.

Similarly, the strength of a base is related to its dissociation constant.

$$\underset{\text{(Acid)}}{HA} \rightleftharpoons H^+ + \underset{\text{(conjugate base)}}{A^-}$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_a = \frac{[H^+].[A^-]}{[HA]} \text{ and } K_b = \frac{[HA].[OH^-]}{[A^-]}$$

$$K_aK_b = \frac{[H^+].[A^-]}{[HA]} . \frac{[HA].[OH^-]}{[A^-]}$$

$$\therefore K_a.K_b = [H^+][OH]^-$$

$$\therefore K_aK_b = K_w.$$

Stronger acid the weaker its conjugated base.

★ Law of mass action :-

This was first ~~coind~~ coined by Guldberg and wage in 1867. The law is expressed as:-

The rate of a chemical reaction is proportional to the active masses of the reacting substance. In dil. sol^n, the active mass is the concentration of the ~~reading~~ reacting species i.e. gram-molecules or gram-ions per litre. The constant of proportionality is the velocity constant. Here,

$A \longrightarrow B$ is a reaction.

Rate of reaction $= K[A]$

$[A]$ = Concentrate of A

K = Velocity constant

A homogeneous reversible reaction is considered.

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

A/c to the law of mass action

$$V_f = k_1 [A].[B]$$

$$V_b = k_2 [C].[D]$$

V_f = velocity of forward recⁿ

V_b = velocity of backward rxⁿ.

At equilibrium, $V_f = V_b$

$$k_2 [C].[D] = k_1 [A].[B]$$

$$\frac{k_1}{k_2} = \frac{[C].[D]}{[A].[B]}$$

Since k_1 and k_2 are both constant the fraction k_1/k_2 must also be a constant.

$$\therefore \ k = \frac{[C].[D]}{[A].[B]}$$

k = Equilibrium constant of the reaction.

The equilibrium constant for the general reversible recⁿ is.

$aA + bB + cC + \ldots \rightleftharpoons pP + qQ + rR + \ldots$ is

$$K = \frac{[P]^p \cdot [Q]^q \cdot [R]^r}{[A]^a \cdot [B]^b \cdot [C]^c}$$

Where, a, b, c and p, q, r are the no. of molecules of the reacting species.

Application of the law of mass action to solution of weak electrolytes :-

Strong electrolytes get completely dissociated ever in less concentrated solution, so they do not constitute equilibrium system.

Weak electrolyte are only incompletely dissociated ever in favourable ionization condition of dil. sol^n - so an equilibrium is considered in terms of the law of mass action which occurs b/w undissociated molecules and ions.

☆ Common ion effect:-

The concentration of a particular ion in an ionic reaction is increased by the addiation of a compound which gives that ion on dissociation. This means that the particular ion is thus obtained from the compound present in solution and is also obtained from the added reagent. that is why the name 'common ion' is given',

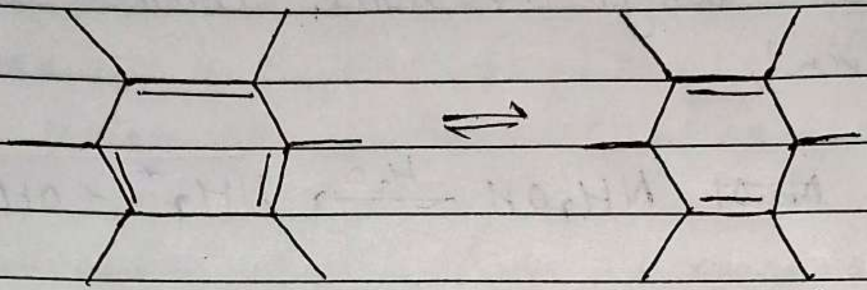
eg :- ~~NaOH~~ $NH_4OH \xrightarrow{H_2O} NH_4^+ + OH^-$

$$H_2O \longrightarrow H^+ + OH^-$$

Here excess of OH^- ions is present. This system has excess of hydroxyl ion some of the hydroxyl ion combines with NH_4^+ ion to form ammonium hydroxide. OH^- ion is the common ion. This is the common ion effect.

★ Theory of indicators :-

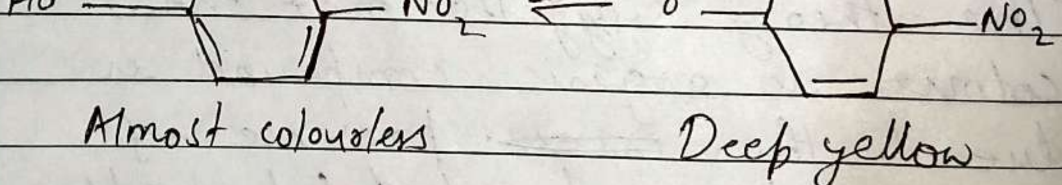
The theory suggests that the colour is organic compound is due to the ~~excess~~ presence of some ~~unsatu~~ unsaturated 'chromophones' like $C=O$, $C=C$, $N=$ ... and $N=N$. These chromophones are intensified by 'auxochromes' like NH_2 and OH group. The colour change of many indicators is due to the transformation of a benzoid structure into a quinonoid and vice versa, along with the change in H^+ concentrate of the solutions.



Benzonoid form (colourless) Quinonoid form (Coloured)

H.E Armstrong explained this case by taking the examples of nitrophenols

In alkaline solution p-nitrophenol is present as the yellow ion. But in acid solution, it is found as colourless nitrocompound.



Almost colourless Deep yellow

☆ Choice of Acid-Base indicators:-

Methyl orange is used in the assay of strong acids and in reactions where CO_2 is evolved. CO_2 does not affect this indicator. Methyl red is used in the assay of weak bases.

Eg. - Ammonia ~~am~~ and amines.

Phenolphthalein is used in the assay of weak acids.

The choice of some well known indicators along with their pH range, colours changes are summarized below.

1. Congo red :-

It is sodium salt of an azo compound. Its pH range is 3-5 causes blue colour to became red.

2. Dimethyl red:-

It is 4-dimethylamino azobenzene. its pH range is 2-8 - 4.0 it turns red to yellow. It gives latter end point is~~sto~~ strongly alcoholic solution. It is used in the determination of carvone.

3. Methyl orange :-

It is the sodium salt of 4-dimethyl-amino azobenzene - 4-sulphanic acid.

Its pH range is 2.8 - 4.0 it turns red colour to yellow.
A 0.04 %. aquous ~~solution~~ .alcoholic solution is used.

4. Methyl red :-

It is 4-dimethyl amino azobenzene-2-carboxylic acid. Its pH range is 4.2 - 6.3 . It turns red colour to yellow colour. The preparation of this indicator is described in pharmacopoeia. This methyl red indicator is used in place of methyl orange in the titration of NH_3 and other weak bases where it gives a better end-point.

5. Phenolphthalein :-

It turns colourless to red. It acts in the pH b/w 8.3-10.3 . The colour limit of red varies with the concentration of the indicator Generally a 1% solution in alcohol is used in titration.

★ Mixed indicators :-

In some cases it is required to have a sharp colour change in a narrow and ~~soluted~~ selected range of pH. This does not occur with an ordinary acid base indicator as the colour change extends over two units of pH. This condition is achieved by a mixture of indicators. Mixed indicators are selected so that their pKin value are close together and the overlapping colours are complementary at an intermediate pH value. The examples are given below.

① A mixture of equal parts of neutral red (0.1 %) solution in ethanol) and methylene blue (0.1 % solution in ethanol) provides a sharp colour change from violet-blue to green. This occurs from acid to alkaline sol^n at pH 7. This indicator is used to titrate acetic acid with NH_3 solution and vice-versa.

(ii) A mixture of thymol Blue (3 part of a 0.1 % aquous sol^n of the sodium salt) and cresol red (1 part of a 0.1 % aquous sol^n of the sodium salt) changes its colour from yellow to violet at pH 8.3. This indicator is used for the titration of carbonate to hydrogen carbonate stage.

Buffer action in a solution of a weak acid and its salt is due ~~the~~ to the fact that H⁺ ions are removed by the anions of a weak acid to form unionized molecules.

Guess Question and Answer

Q1. Discuss principle of precipitation titration. Discuss Fajan method in detal. - ⑭ marks.

→ Principle of precipitation titration:-

The main principle of precipitation titrations is that the quality of added precipitationg reagent or precipitant is equivalent to the substance being precipitated.

Fajan's Method:-

This method was given by K. Fajan in 1924. The method employs adsorption indicators for the detection of end point in precipitation titration.

The principle of fajan's method of precipitation titration is based on the fact that at the end point, the indicator get adsorbed by the precipitate resulting in a substance of different colour. commonly used indicator in Fajan's method for the titration of halide and isocyanates silver nitrate are :

(2 marks)
① Fluorescein
② Dichlorofluorecein
③ Eosin (Tetrabromo fluroesech)
④ Erythrosine

Choice of adsorption Indicator

ⓐ The indicator ion (Fluorescinate ion) must be on opposite charge to the ion of precipitating agent.

ⓑ It should be strongly adsorbed immediately after the end point.

ⓒ The indicator should not be adsorbed before the precipitate formation.

Principle of adsorption Indicator:

The principle of adsorption Indicator is based upon the phenomenon of adsorption. The phenomenon of concentration of molecules of gas or liquid at a solid surface is termed as adsorption. The substance that concentrates at the surface is called adsorbate and solid surface on which concentration occur is known as adsorbent.

eg. Silver nitrate ($AgNO_3$) is titrated against sodium chloride ($NaCl$) solution.

In solution the ions present are.

$NaCl \longrightarrow Na^+ + Cl^-$ (In flask)

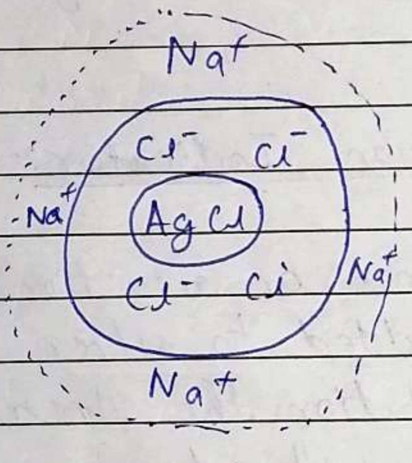
$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$ (In burette)

$AgNO_3 + NaCl \longrightarrow \underset{\text{White precipitate}}{AgCl^-} + \underset{\text{Sodium nitrate}}{NaNO_3}$

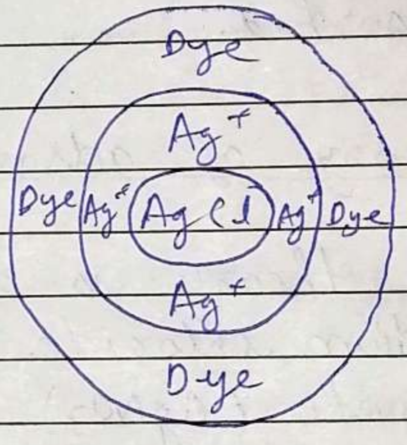
The precipitates of silver chloride (AgCl) adsorbs chlorides ion (Cl^-) to form a primary adsorbed layer. It will hold secondary adsorbed positevely charged ions as Na^+ form. solution present in the flask. At the end point Ag^+ ions are added from the burette which are not primary adsorbed and oppositively charged NO_3^- ions will form the secondary adsorbed layer. Now on the surface of first traces of Ag^+ ions the modified fluoresinate ions of indicator get adsorbed.

Theory of adsorption Indicator:-

The theory is based on reaction of sodium chloride added to silver nitrate ($AgNO_3$) solution the silver chloride precipitate will adsorb Chloride ions which are initially in excess. Thus the chloride ions form the primary adsorbed layer. which is turn will hold the secondary adsorbed layer of oppositely charged Na^+ ions. Immediately after the equivalence point. Ag^+ ions are in excess and hence silver Chloride ions now adsorb Ag^+ ions as primary adsorbed layer and NO_3^- as secondary adsorbed layer. Now if the sodium salt of fluorscein is also present in the solution then negatively charged fluoride ions would be adsorbed instead of NO_3^- as secondary adsorbed layer and ~~their~~ this adsorption occurs along with a charge to pink colour due to the formation of a pink coloured complex of Ag^+ and modified florescence ions.



ⓐ AgCl precipitated in presence of excess of Cl^-.



ⓑ AgCl precipitated in presence of excess of Ag^+.

Q.2. Discuss Valhard's method of precipitation titration :-

→ (Indirect method or residual titration)

This method was given by Vahlard in 1874. In this method the excess of silver nitrate ($AgNO_3$) is added to the solution of halide acidified with nitric acid. The unreacted silver nitrate ($AgNO_3$) is treated against standard ammonium thiocynate (NH_4SCN) solution using ferric salt as indicator.

eg :- Assay of Ammonium chloride.

NH_4Cl + H_2O + Nitric acid + Nitrobenzene + AgN

Shake vigrously for one minute and add ferric salt indicator → Titrate with 0.1N ammonium thiocynate (NH_4SCN) till redish brown color is obtained.

When standard solution as NH_4SCN is added to a solution of silver salt a precipitate of silver thiocynate (AgCNS) continues to be formed till the Ag^+ ions are not completely precipitated.

$$Ag^+ + CNS^- \longrightarrow AgCNS$$

The addition of further drop of thiocynate react with the ferric ions to form a reddish brown ferric thiocyanate complex.

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

(Red/reddish brown.)

When the end point is approached the solution of silver thiocynate (Ag(NS) should be vigorously agitated because a large amount of the Ag^{+} ions are absorbed on the surface of AgCNS precipitate which get removed only very slowly when thiocyanate is added.

Application :-

It is employed in the determinator of iodides, chlorides and thiocyanate ion.

Solubility product :- $\boxed{4 \text{ marks}}$

The process of gravimetric precipitation is completely based on the ~~complex~~ concepts of stability product let us consider a dissociation of slightly soluble salt AB.

$$AB \rightleftharpoons A^+ + B^-$$

Applying law of mass action.

$$k = \frac{[A^+][B^-]}{[AB]}$$

The concentration of the AB in the solution remains constant in presence of undissolved AB i.e)

$$K_{sp} = \frac{[A^+][B^-]}{AB}$$

$$K_{sp} = [A^+][B^-]$$

Where KSP is constant at constant temp and is called solubility product of salt [AB] and is defined as maximum product of concentration of its constituent ion solution.

$[A^+]$ and $[B^-]$ = Ionic concentration is standard solution.

If ionic product or ~~conc~~ concentration is ~~standard sol~~ greater than KSP. precipitation will occur..

PDF-end.

If the Ionic product or concentration is equal to KSP solution remains ~~constant~~. consistent.

If the ionic product or concentration is less than KSP precipitation do not occur.

Types of Acid - Base Titration / Neutralization Titration curves :

A titration curve is the plot of the pH of the analyte solution versus the volume of the titrant added as the titration progresses.

A. Aqueous Acid - Base Titration

These are normal titration between acids and base dissolved in water. Hence, the called aqueous acid-base titration.

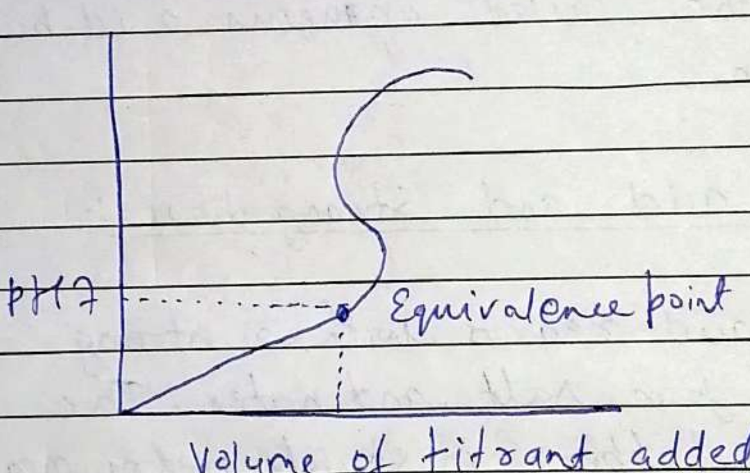
1. Strong acid and Strong base :-

Strong acid reacts with a strong base to form salt and water. The reaction happens in stoichiometry means i.e. each molecule of acid reacts with corresponding molecule of base. At the end of reaction acid and base are completely reacted to form salt. Hence the end point or equivalence point is precise and sharp.

eg. HCl as strong acid and NaOH strong base.

$$HCl + NaOH \rightarrow NaCl + H_2O.$$

Initially, due to HCl, the pH of Solution is less. As the NaOH added slowly, the dissociation of NaOH takes place and pH of solution increases. At the equivalence point, HCl is completely reacted with NaOH to form water and salt. The pH of Solution is 7. After the equivalence point the addition of NaOH, increases the concentration of OH^- ions as HCl is completely react. The pH of solution increases.



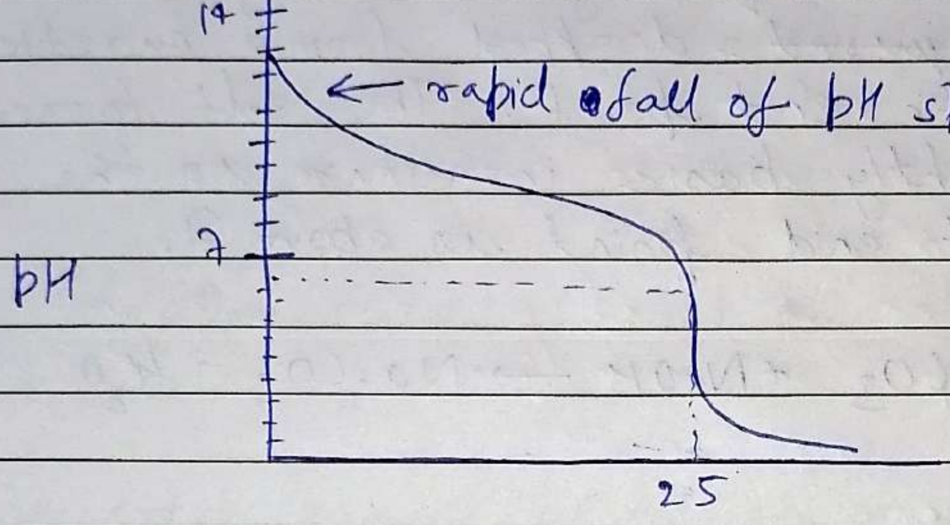
Volume of titrant added

Titration curve for strong acid vs strong base.

(2) Strong acid vs Weak base :-

Here a strong acids reacts with weak base to form salt and water. But since, the reaction uses strong acid, the pH at end point will be towards acidic i.e. below 7.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$



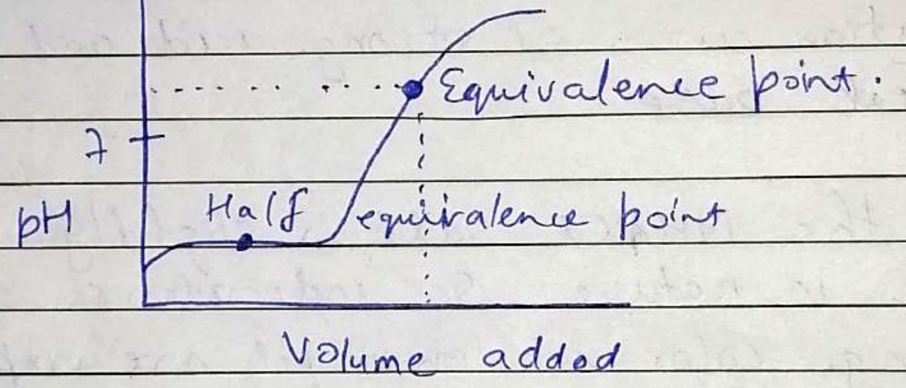
Titration curve of strong acid and weak base.

Here the NH_4Cl salt is slightly acidic in nature. So indicators chaning color at lower pH are employed. During reaction known concentration of strong acid is taken in burette and allowed to react drop by drop with the base in beaker. Initialy the pH of solution is high due to ammonia. After end point, further addition of HCl decreases pH of solution as there is no ammonia present in solution to react.

3. Weak acid vs Strong base.

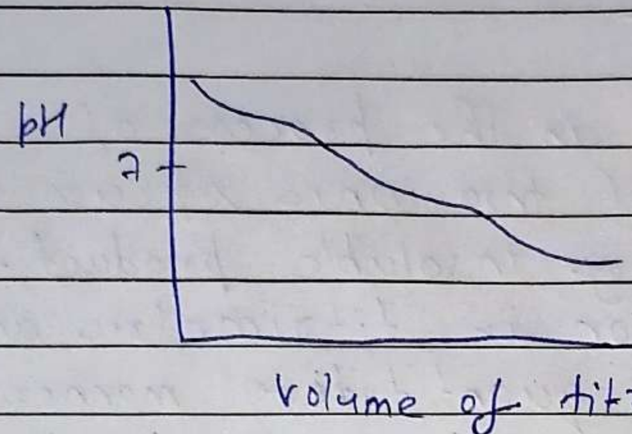
The weak acid is taken in a beaker and known quantity of strong base is ~~required~~. dropped from a burette till the end point. The salt formed is slightly basic in nature so the pH at end point is above 7.

$$H_2CO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$



4. Weak acid vs Weak base. :

Here both acid and base are weak. So mostly they are avoided due to Imprecise end point. At the end point, the pH will 7 theoretically but cannot be measured precisely as that is strong acid and strong base case.



Titration curve of weak acid and weak base.

An extra amount of titrant is needed to reach the end point due to imprecise reaction.

$$H_2CO_3 + NH_4OH \rightarrow NH_4OH + H_2O$$

The end point is neutral as the salt is neutral but due to excess titrant added the pH can be in favour of it.

Class

Precipitation

Precipitation is the process of combination of two ionic species to form a very insoluble product. The reaction in titrimetric analysis occurs in a quantitative manner. It must proceed completely to form the product of the reaction. This type of reaction is neutralization redox, completion and of precipitation reaction.

The reaction in titrimetric analysis must include the following requirements:

i) The precipitate must be practically insoluble.

ii) Precipitation reaction must occur in quantitative manner.

iii) The reaction should be rapid.

iv) The titration results must not be damage due to absorption or any kind of co-precipitation effect.

v) Determination of equivalence point during the titration must be detectable.

Principle of precipitation

Solubility depends on the solvent and temperature. It is the concentration of dissolved solute in moles per litre when the solution is in equilibrium with a solid solute.

In order to dissolve a solid the intermolecular forces of attraction must be overcome i.e. solute - solute attraction is ~~replied~~ replaced by solute - solvent.

Here the solvent completes with crystal forces and overcome them. This means that the solvent environment must be similar to that provided by the crystal structure. i.e. like dissolves like but during precipitation opposite things happen here in precipitation, intermolecular forces between the molecules of product are high. so Solute - solute forces replace the solute - solvent forces.

Solubility Product:

The process of precipitation titration is completely based on the concept of solubility ~~prod~~ product. Let us consider a dissociation of slightly soluble salt AB. In solution it will exist in equilibrium with its dissociation ions are.

$$AB \rightleftharpoons A^+ + B^-$$

Applying law of mass action

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$Ksp = [A^+][B^-]$$

The concentration of the AB in the solution remains constant in the presence of undisolved AB i.e.

$$Ksp = \frac{[A^+][B^-]}{[AB]}$$

Where K_{sp} is unchanged at constant temperature and is called solubility product of salt AB and is defined as the maximum product of the concentration of its constituent ion in saturated solution.

If the ionic product or conc. is greater than Ksp, precipitation will occur.

If the ionic product or concentration is ~~greater than~~ lesser than Ksp, precipitation don't occur.

If ionic concentration is equal to Ksp then solution remains saturated.

Fundamental of precipitation titration

For precipitation titration following condition must be satisfied by a ~~ppt~~ precipitation reaction to act as a titrimatric analysis.

i) The rate of the reaction between the precipitant and the analyte or the substance to be precipated must be fast.

ii) The reaction between the analyte and the reagent should proceed according to a definite stoichiometric relationship

eg. $AgNO_3 + KCN \rightarrow AgCNS\downarrow + KNO_3$

169.89 gm of silver nitrate ($AgNO_3$) reacts with 97.18 gm of potassium thiocyanate to give 165.96 gm of silver thiocyanate ($AgCNS$) and 101.11 gm of potassium nitrate (KNO_3).

iii) A suitable indicator should be available to locate the end point of the titration.

iv) The end point should be well defined.

Argentometric titration.

The precipitation process in titrimetoric analysis using silver nitrate ($AgNO_3$) as a reagent is called Argentometric titration. In other word we can say the part of titrimetric analysis in which precipitation of compound occurs by titrating against the standard silver nitrate sol^n is called argentometoric titration.

Mohr's method.

The Mohr's method was first published in 1855. The Mohr's method involves the use of a silver nitrate as the titrant for the determination of chloride and bromide in the presence of potassium chromate indicator. when a chloride containing solution reacts with a standard solution of silver nitrate it results in the formation of silver chloride. when all the existed chloride is precipitated completely then the next excess drop of the silver nitrate solution reacts with potassium chromate indicator ions and silver chromate is formed, the colour of the solution changes from yellow to red.

$$\underset{\text{Silver ion}}{2Ag^+} + \underset{\text{chromate ion.}}{CrO_4^{2-}} \rightleftharpoons Ag_2CrO_4 \text{ (red)}$$

Determination of NaCl by Mohr's method

Principle:

It depends on the titration of NaCl sample with standard $AgNO_3$ using potassium chromate (K_2CrO_4) and indicator.

Titration reaction

$$Cl^- + Ag^+ \rightarrow \underset{\text{(White ppt)}}{AgCl \downarrow}$$

End point

$$2Ag^+ + \underset{\substack{\text{Titrant} \\ \text{indicator.}}}{CrO_4^-} \rightarrow \underset{\text{(Brick red ppt)}}{Ag_2CrO_4 \downarrow}$$

In this experiment Cl^- sample is titrated with Ag^+ in the presence of CrO_4^- indicator where AgCl is ~~ppt~~ precipitated as a white precipitates before Ag_2CrO_4. Then at the end point the first slight excess of Ag^+ will react with CrO_4^- indicator giving Ag_2CrO_4 leading to darkening of yellow of the solution.

Mohr's method should be done in neutral or slightly alkaline medium.

If pH is more than 9 then Ag^+ will be precipitated as $AgOH \downarrow$ (brown to black ppt) and therefore end point will not be obtained.

$Ag^+ + OH \longrightarrow AgOH \downarrow$
(Brown to black ppt)

If the pH is less than 6.5 then formation of dichromate compound through acid chromate intermediate takes place and again making of end point happen.

$2CrO_4^- + 2H^+ \rightarrow 2HCrO_4^- \rightarrow Cr_2O_7^{-} + H_2O$

12/03/22

Volhard's method

(Ammonium thiocyanate - silver nitrate titration process)

This reaction is based on following eq^n. i.e.

$NH_4SCN + AgNO_3 \rightarrow AgSCN \downarrow + NH_4NO_3$

Ammonium thiocyanate — Silver Nitrate — Silver thiocyanate — Ammonium Nitrate.

Here Ammonium thiocyanate solution is always taken in the burette. This is added dropwise into the silver nitrate solution which is in conical flask.

The silver Nitrate solution must be acidified with nitric acid. Here ferric ammonium sulphate used as indicator. End point is the formation of deep red color of ferric thiocyanate.

Ferric thiocyanate forms due to the interaction b/w Fe^{2+} and SCN^- ions with a trace of SCN^- ions.

Nitric acid used in this method must be free nitrous acid as the presence of nitrous acid because thiocyanic acid to give an instant red color.

Titration is to be carried out at a temp. below 25°c since as elevated temp. is the red color. of ferric thiocyanate complex fades away rapidly.

The excess of silver nitrate solution is estimated by residual tit. with standardised ammonium thiocyanate sol^n.

Preparation of 0.1N ammonium thiocyanate standard solution

→ Take 8 gm of ammonium thiocyanate weighed and volume is made upto 1000ml in volumetric flask.

09/03/22

Gay-lussac method.
(without indicator method)

Gay-lussac method is the method for determining end point in argentometric titration without the use of Indicator.

~~It is also preferred as turbidity method. The end point is marked by cessation of the precipitation. The following reaction takes place when sodium bromide (NaBr) solution is titrated with silver nitrate ($AgNO_3$)~~

$NaBr$	+	$AgNO_3$	→	$AgBr$	+	$NaNO_3$
Sodium Bromide		Silver nitrate		Silver Bromide		Sodium Nitrate

It is evident that the precipitation of silver bromide occurs only as long as an excess of bromide ion (Br^- ion) is present in solution. Therefore, we can detect accurately the point at which precipitation creates by taking small portion of the titrated solution at the end of the titrations and adding a single drug of silver nitrate ($AgNO_3$) sol^n diluted and fold.

In this instance detection of end point is may much easier by the fact that near the equivalence point the AgBr precipitate coagulate and collect at the bottom of the vessel in the form of the large curdy flakes. The small quantity of pure barium nitrate may be added to assist the coagulation of the ppt. It is advisable to carry out titration twice the first titration is used to take appropriate reading. In the second determination silver nitrate added drop wise near end point to have the exact end point.

——x——x——x——

Oxidation - Reduction Titration

NEW CH

Theory of redox titrations or redox titrations.

Every titrations doesn't require an indicator. In some cases either the reactants or the products are strongly coloured and serve as the indicator.

For ex:- An oxidation reduction titration using potassium permanganate (pink/purple) as the titrant does not require any indicator.

Diphenyl amine is used as redox indicator in dichromate titration for determining Fe^{++} from $FeCl_2$.

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl$$
$$\downarrow$$
$$2CrCl_3 + 6FeCl_3 + 2KCl + 7H_2O.$$

In acidic solⁿ the reduction of $K_2Cr_2O_7$ may be represent as

Reduction

$$Cr_2O_7 + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O.$$

Oxidation

$$6Fe^{2+} \rightleftharpoons 6Fe^{3+} + 6e^+$$

When all the Fe^{2+} ion are oxidised to Fe^{3+} ions excess of dichromate ions oxidized diphenyl amine to diphenyl benzezine.

In redox titration a sharp ~~odour~~ colour change in indicator occurs only in its E_0 (standard Electrode potential) lies between standard potential of oxidation reduction when titrated against each other.

0.76 → ε° (V) of diphenyl amine indicator

0.77 → ε° (V) of ferrous ferric system.

In order to overcome the variation of +0.01 phosphoric acid is added in the sol^n in order to take sharp colour change at the end point.

Redox Potential

Strength of an oxidising agent or reducing agent is expressed in terms of normal or standard potential.

Oxidising (oxident) + ne → Reducing (Reductant)

$$[Ox] + ne \rightarrow [Red]$$

Redox titration

It is based on the redox reaction (oxidation - reduction) between analyte and titrate. In oxidation-reduction titration method a reducing substance is titrated with a std sol^n of an oxidising agent or an oxidising substance is titrated with a std. sol^n of a reducing agent.

Such a system the [illegible] nerst equation takes place that is.

$$E = E^\circ + \frac{2.303\ RT}{nF} \times \log_{10} \frac{[ox]}{[Red]}$$

Where,

E is the formal potential at the specify $conc^n$.

n is no. of electron involved in the half reaction,

R is gas constant that is 8.314 J/mol/K.

T is the absolute temp,

F is Faraday constant i.e. 96500.

and E° is the standard electrode potential and is characteristic of a particular system.

Rahman
16/6/22

→ At 25°C

$$\boxed{\frac{2.303\ RT}{F} = 0.05915}$$

Then eqⁿ (i) will be.

$$E = E^\circ + \frac{0.05915}{n} \log_{10} \frac{[ox]}{[Red]}$$

The solution potential can be calulated if we know the concⁿ of the two forms [ox] (oxidising agent) and [Red] (Reducing agent).

Also knowing the chemical reaction involved and the potential of the solution, we can use nerst equation to evaluate the relative conc. of oxidised and reduced forms. Some of the redox system with their standard reduction potential are below.

Oxidised from	Reduced from	E° volt.
MnO_4^-	Mn^{2+}	1.51
$Cr_2O_7^{2-}$	Cr^{3+}	1.33
Fe^{3+}	Fe^{2+}	0.76
Sn^{4+}	Sn^{2+}	0.15

★ Redox Indicator :-

In the redox titration we need a chemical species that can change colour in potential range corresponding to the sharp change at the end point.

A chemical substance which changes colour when the potential of the solution reaches a definite value is termed oxidation-reduction or redox indicator. It is necessary while choosing a redox indicator for particular titration to ensure that its redox potential lies within that of the system.

A redox indicator may be defined as a substance whose oxidised form is of different colour from that of its reduced form. The oxidation and reduction of ~~this~~ the indicator is readily reversible.

The Indicators which is use in redox titration are of three types:-

i) Self indicator :-

In permagnetic titration potassium ($KMnO_4$) change colour at the end point is called self indicator.

ii) External Indicator :-

These indicator are not added internally to the reaction medium but are used externally in the form of small ~~particles~~ dropletson a white tile i.e. Potassium ferric cyanide ($K_3Fe(CN)_6$) is used as an external indicator in the chromatometry. Howerer, the method of using external indicator has become absolute as it introduces errors in quantitative volumetric analysis.

iii) Internal Indicator.

These are the substances which are added in the flask. In case of chromatometry the indicators such as 1% diphenylamine is added in the reaction mixture such indicator are called internal indicator.

Types of redox indicators :-

1) Permagnet indicators :-

A large no. of reducing agent may be determined directly by titration with standard potassium permagnet.

Oxidation - Reduction Curve.

In acid - base titration curves are plotted in terms of pH or ~~both~~ poH vs the concentration of standard by in redox titration the titration curves are plotted in terms of cell potential vs the percent titration of the standard for each redox titration there are 5 significant reasons :-

① The start zero percent titration

It is the point at which titration starts.

(ii) Buffering reason :-

Greater than 0% and less than equivalence point. It is a region where the reducing agent takes small amount of time to lose all the electrons and substituting the electrons ~~and substituting the reactions~~ are gained by an oxidizing agent to reach the equivalence point.

(iii) The equivalence point :-

It is the region where the percentage of oxidized and reduced form are equivalent to each other at this point there is a ~~point~~ sharp increase in curve till the end point is reached.

(iv) Inflection point:-

A point on a curve at which tangent crosses the curve itself. A point on a curve at which a curvature changes sign. The curve changes from being concave upward (positive curvature) to concave downwards (negative curvature).

(v) Over titration

It is the region showing the constant curve or potential and colour showing by these indicator at a significant region.

☆ Equivalence weight of $KMnO_4$.

1.) In acidic medium (H_2SO_4)

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe(SO_4) + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Ionic form :-

$$5Fe^{2+} + MnO_4^- + 8H^- \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Half reaction :-

$5Fe^{2+} \rightleftharpoons 5Fe^{3+} + 5e^-$ (oxidation)

$MnO_4^- + 2H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ (Reduction)

2) In alkaline medium [KOH]

$$Cr_2(SO_4)_3 + 2KMNO_4 + 8KOH \rightarrow 2K_2(CrO_4) + MnO_2 + 2K_2SO_4 + 2H_2O$$

Ionic Form.

$$MnO_4 + 2H_2O + \cancel{2H_2O} + 3e^- \rightarrow MnO_2 + 2H_2O$$

$$\text{Equivalent weight} = \frac{158.03}{3} = 52.68$$

Preparation of 0.1 KMnO$_4$.

Eq Wt = Mol. Wt/gain of electrons

$$= \frac{158.03}{5} = 31.61 \text{ g}$$

Weight accurately 31.61 g of KMnO$_4$. dissolve it in 1000 ml of distilled water to give 1N solution and 3.161 g of KMnO$_4$ in 1000 ml of distilled water to give 0.1 KMnO$_4$

Standardization of 0.1 KMnO$_4$ by oxalic acid / sodium oxalate.

V.V.I

1) Iodometric and Iodimetric titration.

Iodine is a mild oxidizing agent. Iodine is reduced according to the half reaction as.

$$I_2 (s) + 2e^- \rightleftharpoons 2I^-$$

A solution of iodine is aquous iodide and has an intense yellow colour to brown colour. One drop of 0.05 M iodine solution imports a perceptible yellow to 100 ml water.

In colourless sol^n iodine can serve its own ~~character~~ indicator. The taste is made much more sensitive by causing a solution of starch as indicator.

Starch reacts with iodine in the presence of iodide to form an intensly blue colored complex which is visible at very low conc. of iodine

Starch should be added near the ~~experience~~ equivalence point in iodometric titr^n because it gives water insoluble complex with iodine and indicates release of iodine from KI (Potassium iodide) (reducing agent).

Direct iodometric titration turned iodimetric refers the first titration with standard sol^n of iodine.

In direct iodometric titration turned iodometry deals with the titration of iodine liberated in conical flask reaction

1) Iodimetry :

Standard solⁿ of I_2 may be prepared from accurately weigh the pure reagent. It is simpler to make up the solution from the reagent grade product and then to standardize it. It is slightly soluble in H_2O but it forms a soluble triodide ion in solⁿ of iodide.

$$I_2 + I \rightarrow I_3$$

The use of iodide in solution both increase the solubility of the iodine and decreases its volatility. Thus controlling to the stability of the iodide solution. The arsenic trioxide is oxidized by iodine according.

The position of equilibrium depends upon the pH.

11) Iodometric

The formation of iodine takes place as a result of hydrogen iodide with an oxidizing agent. The HI is open directly in the reaction flask by the action of dilute HCl or H_2SO_4 on the sol^n of potassium iodide.

Free iodine is liberated as a result of oxidation of KI in acidic sol^n. The liberated iodine is treated with standard sol^n of sodium thiosulphate.

$$\underset{\text{Potassium iodide}}{2KI} + H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{Hydrogen iodide.}}{2HI}$$

Starch mucilage acts as an indicatorr which gives blue color with free iodine.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6.$$

Titration of ceric ammonium sulphate the titration involves the use of ceric salt which is a powerful oxidizing agent. Ceric salt as intense yellow color. The oxidizing power of ceric salts depends upon the conc. and the type of acid used in the assay.

eg Ce^{+4} (iv) in HNO_3 and $HClO_4$.

The fluorides and phosphate have tendency to interfare with concerned ions because they form precipitate with them as ceric fluoride and ceric phosphate.

The end point of cerimetric titration is indicated by using redox indicator as ferroin, diphenyl sulfonate and N-phenylanthrallic acid.

Sulphuric acid solution of ceric sulphate is stable even at boiling point but HCl acid solution is unstable due to its reduction resulting in the liberation of 3 chlorine.

Preparation of 0.1N cerric sulfate:

$$\underset{IV}{Ce^{4+}} + e \rightleftharpoons \underset{III}{Ce^{+5}}$$

~~Eg~~ Eq. Wt. $= \frac{333.25}{1} = 333.25$

Weight accurately 333.25 gm of cerric sulfate and dissolve it in 1000 ml of distilled water to give 1N solution and 33.325 gm of cerric sulfate in 1000 ml of distilled water to give 0.1N cerric sulfate solution.

$FeSO_4$ the acidic constituent of Mohr's salt $FeSO_4 (NH_4) SO_4 . 6H_2O$ reduced Ce (IV) to Ce (III) itself getting ~~reduced~~ oxidised to $FeSO_4$.

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

Procedure

Pippette out 25 ml ferrous ammonium sulphate sol^n into a conical flask.

Add 25 ml H_2SO_4 and two drops of ferrous indicator,

Titrate it against cerric sulphate solution till the orange changes to blue.

Gravimetric Analysis

Gravimetric Analysis or quantitative analysis by weight is the process of isolating and weighing an element or definite compound.

Ex :- Progesteron injection.

The content of progesteron quantitatively determine by this method, in other option when other component in a sample are difficult to separate by physical method chemical reaction is employed to convert the substance to be analysed to chemically equivalent omount of some other substance which can be separated, purified and weigh.

Advantage :-

i) It is accurate and precise when using analytical balances.

ii) Positive sources of errors are readily checked, since filterate can be tested for completeness of the precipitation and precipitate may be examined for the presence of impurities.

iii) It is absolute method.

iv) Relative inexpensive apparatus is required.

☆ Disadvantage:

1) Measure disadvantage is that the procedure is time consuming.

ii) It consist of following steps.

a) Precipitation
b) Digestion
c) Filteration
d) Washing of dried ppt.
e) Drying and ignition of ppt.
f) Weighing of ppt.

☆ Gravimetric consists of following steps:

1) Precipitation

It is an important step in which the anion or cation to be determined is precipitated from a solution of the substance in the form of insoluble compound consisting of either definite composition itself on leaves a residue of definite composition on ignition. For precipitation a slight exess of precipitating agent is added to achieve complete precipitation.

Precipitation step is the most critical step for successful gravimetric analysis. The desire constituent which is to be analyzed, must be precipitated quantitatively. The precipitate must be pure.

2) Digestion

To increase the coarseness of the precipitate for easy filteration, the contents are either left for sometimes to settle or they are boiled. The procedure is termed as definition of the precipitate.

3) Filteration

These are two methods for separating a precipitate from the mother ~~liqo~~ liquor for the purpose of drying or ignition to constant weight. Suspension of solid is filtered through the filter paper or other means such as Gooch and sintered silica crucible. Gooch crucible is particularly -

suitable where traces of precipitate can never be separated from ordinary paper.

Sintered glass crucible have porous bottom of growl glass. Sintered glass disk is available in various porosity grade ranging from 0 to 5. The 0 is maximum pore size of 150 to 250 micrometer while 5 size has pore size of 1-2 micrometer. It is used for bacteriological filteration grade 3 is used but fine precipitate such as barium sulphate grade 4 is used.

4) Washing of dried precipitate.

Most precipitate are produced in presence of one or more soluble compounds. Since the soluble compounds are frequently non-volatile at the drying temperature of the ppt., it is necessary to wash the ppt. to remove impurities as completely as possible. The ideal washing solution should comply following conditions.

a). It should have not solvent action on the ppt. but dissolve foreign substance easily.

b) It should have no dispersive action on a ppt.

c) It should contain no substance which is likely to interfare with substituent determination in the filterate.

d). It should be easily volatile at the drying temp. of the ppt.

e) It should not form any volatile or insoluble product with the ppt.

5) Drying and ignition of ppt.

To remove the extra amount of water drying is required after washing and drying of precipitate is done by using whatmann filter paper dried in an oven at about 110°c -120°c. After drying the crucible is allow to coOl in a ~~deter~~ dessicator and then weigh with the ~~pt~~ ppt. Heating, cooling and weighing is ~~repitate~~ repeat it ~~un~~till constant wt. is obtained.

Ignition

The ignition of precipitate can be described under following two conditions :

a) Ignition and the incarnation of filter paper. The filter paper having ppt. is taken out of the funnel carefully and open in such a way that the fingers don't touch the ppt. Alternatively the precipitate may also be collected over a clean and dried glazed paper. Take the help of feather or camel brush to collect the fine particles of the precipitate. Now cover the precipitate with a funnel and keep it safe.

Fold the filter paper several times so that it looks like a long small cone. Catch the top side of the cone with a pair of tong by one hand and ignite the cone by means of a plate by a burner in other hand horizontally.

Collect the ash in previously weighed crucible placed on a glazed paper. The crucible is the heated strongly to brush off all the carbon to a white ash.

During ignition the smart ignition of ppt may kept reduced by the carbon of the paper into a compound (or metal) altogether different from the compound in which determination is sought.

The ash is treated with suitable reagents to get back to form (compounds) in which it is finally to be weigh. The step is called the ash treatment.

6) Weighing of precipitate.

Crucible containing the ppt. is weight and the weight of ppt. may be obtained as.

a) Weight of empty crucible = x grams.

b) Weight of crucible of ppt = y grams

c) Wt of precipitate = $(y-x) = z$ gms

Mechanism of precipitate.

The formation of ppt. involves two steps:

a) **Nucleatation:**

It is a process in which a minimum number of atoms ions and molecules joined together to give a stable solid. It also involves the formation of nucleus and is further classification into two types.

i) **Spontaneous:-**

Sometimes it is possible in supersaturated solution ions will joints together to form nucleus. It is called spontaneous nucleation and it will occur its own.

ii) **Induced:**

If a small crystal of solid is added to the supersaturated sol^n, it will act as a nucleus for growth of a crystal. It is called induced nucleation and require a seed particle to get things started.

b) Crystal growth:

It is achieved after nucleation. It is absorbed in two cases.

i) Diffusion of ion to the surface of growing crystal.

ii) Diffusion deposition of these diffused ion on crystal surface. Once a nucleation site is formed the other ion are attracted to the site and will result in the formation of large filterate particles.

Impurities and purity of precipitate.

Purity of precipitate

Co-precipitation

Co-precipitation is a state in which impurities are precipitate with analyte. It is a major problem. Concerned to the purity of analyte. Co-precipitation results into excess mass production. This problem can be overcome by digestion process to achieve pure analyte.

There are four types of co-precipitation.

i) Surface Adsorption
ii) Mixed-crystal formation
iii) Occlusion
iv) Mechanical entrapment.

Surface adsorpent and mixed crystal formation are equilibrium processes, whereas occlusion and mechanicals entrapment arise from the kinetics of crystal growth.

1) Surface adsorption

Surface adsorption is common sources of co-precipitation where contaminants or impurities are get adsorbed on the surface of precipitation, It is common co-precipitation source.

The co-precipitated contaminant on the coagulated colloid consists of the lattice ion originally absorbed on the surface before coagulation and the counter ion of opposite charge held in the film of solution immediately adjacent to the particle. The net effect of surface adsorption is the carrying down surface contaminant soluble form with ~~adsorption~~ precipitation.

The purity of many coagulated colloids is improved by digestion.

ii) Mixed crystal Formation

In mixed - crystal formation, one of the ions gets replaced by another ion having same charge and size in the crystal class. For example $MgKPO_4$ in $MgNH_4PO_4$, $SrSO_4$ in $BaSO_4$. This problem can be solved by using more selective precepitating agent or reprecipitation of analyte can resolved this problem.

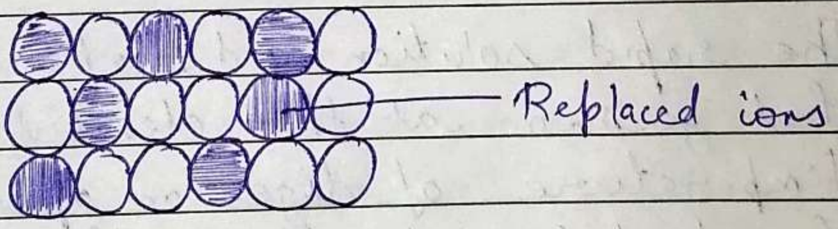


Fig :-> Mixed crystal formation.

iii) Occlusion and Mechanical Entrapment

Occlusion is a process where impurities are trapped within the pocket of crystal lattice. This process happens when rapid precipitation occurs.

Mechanical entrapment occurs when crystals lie close together during growth. Crystals grow together and in ~~so~~ · so doing trap a portion of the solution in a tiny pocket. Digestion process can solve this ~~portion~~ problem by forming large pure crystals. Digestion is often remarkably helpful in reducing these types of co-precipitation.

The rapid solution and reprecipitation that goes on at the elevated temperature of digestion opens up the pockets and allows the impurities to escape into the solution. If the precipitation rate is slow then occlusion and mechanical entrapment is minimum.

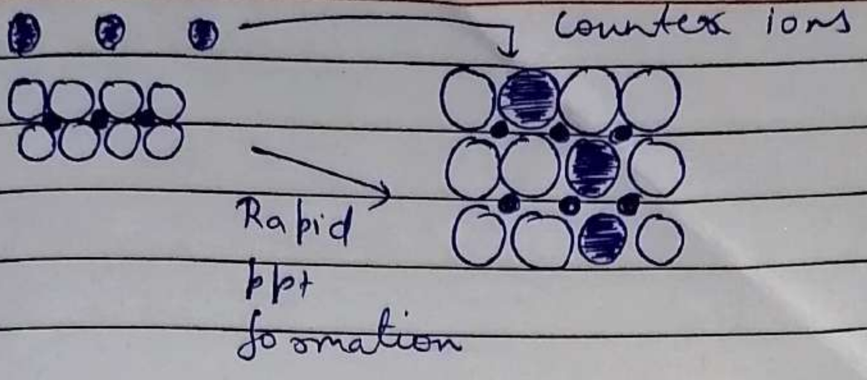


Fig → Occlusion

Post - Precipitation

Post-precipitation is the process by which impurities are deposited after the formation of desired ppt. when ppt stands in contact with the mother liquor long period it becomes contaminated by an impurity on surface of the desired ppt. For ex:- calcium oxalate precipitated as analyte and magnesium is also present in solution of oxalate then slowly magnesium oxalate gets precipitated over desired calcium oxalate due to post-precipitation.