JRG College of Pharmacy

JRG COLLEGE OF PHARMACY

UNIVERSITY SOLVED QUESTION

WITH ANSWER

Year : 2024-25

Subject : Ph.Analysis

Subject Code : BP102T

Subject In-Charge : MS.Kiranmayee Bhatra & Mr. Jyotiprasanna Nanda

Registration No: | | | | | | | | | | |

Total Number of Pages:02 **Course: B. Pharm**

SUBJECT: Pharmaceutical Analysis - I **Sub Code: BPT102T**

1st Semester Regular/Back Examination: 2024-25

BRANCH(S): B. Pharm **Q. Code: A219**

Time: 3 Hours **Max Marks: 75**

Answer Question No.1 (Part-I) which is compulsory, any seven from Part-II, and any two from Part-III.

The figures in the right-hand margin indicate marks.

Part-I

Q1		**Answer the following questions mentioning the answer with correct option (MCQs)**								**(20 x 1)**
	1)	The quantity of chemical in each litre of solution is known as								
		a	Normality	b	Strength	c	Molecular weight	d	Equivalent weight	
	2)	The pH at which an indicator changes colour is known as the								
		a	Standard point	b	Transition point	c	Equivalence point	d	Stoichiometric point	
	3)	Non aqueous titration is carried out for								
		a	Water insoluble drug	b	Weakly acidic drug	c	Weakly basic drug	d	All	
	4)	Protogenic solvent is								
		a	Sulphuric acid	b	Hydrochloric acid	c	Nitric acid	d	All	
	5)	Titration based on the use of silver nitrate are called-------titration								
		a	Argentometric	b	Complexometric	c	Amperometric	d	Conductometric	
	6)	Which one of the following is an example of adsorption indicator?								
		a	Eosin	b	Phenophthalein	c	Methyl red	d	Ninhydrin	
	7)	Which is used as masking agent for lead in complexometric titration?								
		a	Sod.Sulphide	b	Oxalate	c	Thiocetamide	d	All	
	8)	The endpoint for an EDTA titration is usually found by using a ---------indicator								
		a	Metallochromic	b	Redox	c	Acid base	d	All	
	9)	External indicator used in diazotization titration is								
		a	Starch solution	b	Phenolphtalein	c	Iodine solution	d	None	
	10)	SI unit of conductance is								
		a	Mho	b	Seimens	c	Volt	d	None	
	11)	The hydrogen and hydroxyl ions are potent								
		a	Conductivity	b	Molar conductance	c	Conductance enhancers	d	None	
	12)	--------is the product of specific conductance and volume of electrolyte								
		a	Conductivity	b	Molar conductance	c	Conductance Enhancers	d	None	
	13)	Which method is used in water analysis								
		a	Fajan's method	b	Mohr's method	c	Volhard's method	d	None	
	14)	Protophilic solvent is								
		a	Sodium hydroxide	b	Lithium methoxide	c	Sodium methoxide	d	All	
	15)	An electrode, whose electrode potential is well known and stable is a----------								
		a	Indicator electrode	b	Reference electrode	c	Both A & B	d	None	

	16)	Each electrochemical cell is composed of								
		a	Two half cells	b	Half cells	c	Both A & B	d	None	
	17)	The D and L isomeric forms can be distinguished by								
		a	Polarimetry	b	Refractometry	c	Potentiometry	d	Conductometry	
	18)	Limiting current is sum of diffusion current and								
		a	Residual current	b	Faradic current	c	Migration current	d	Additional current	
	19)	Oxidizing agents								
		a	Are mostly non-metals	b	Are mostly metals	c	Decrease in oxidation state	d	Are mostly transition metals	
	20)	In a Redox reaction								
		a	Oxidation occurs	b	Reduction occurs	c	Neutralization occurs	d	Both A & B	

Part-II

QII **Focused-Short Answer Type Questions- (Answer Any Seven)** **(7 x 5)**

1) Define and classify error. Explain how errors can be minimized.
2) Briefly mention the theories of neutralisation indicators with examples.
3) Explain the importance of common ion effect in gravimetry?
4) Define and explain the principles of complexometric titrations.
5) Write a brief note on non-aqueous titration and give its applications
6) Explain what is co-precipitation and post precipitation with examples.
7) Give a brief note on the construction and working of DME.
8) Classify the various EDTA titrations with example.
9) Give the principle involved in barium sulphate estimation.

Part-III

QIII **Long Answer Type Questions (Answer Any Two)** **(2 x 10)**

1) Differentiate between alkalimetry and acidimetry with an example. Explain the selection of indicators in the titration between weak acid with a strong base using neutralization curve.
2) Explain Mohrs method of determination of halides.
3) What is gravimetric analysis? Explain the precautions during washing of a precipitate.

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Part-I:-

Q.I) (1) The quantity of chemical in each litre of Solution is known as
a) Normality

(2) The pH at which an indicator changes colour is known as the
b) Transiton point

(3) Non-aqueous titration is carried out For
d) All

(4) Protogenic Solvent is
d) All

(5) Titration based on the use of Silver Nitrate are Called —— titration
a) Angentometric

(6) Which of the Following is an ex. OF adsorption Indicator
a) Eosin

(7) Which is used as Marking agent For Lead in Compluxometric titration
b) Oxalate

(8) The end point For EDTA titration is usually Found by using —— Indicator
a) Mutallochromic

(9) External indicator used in diazatization titration is
c) Iodine Solution

(10) SI unit of Conductance is
b) Siemens

(11) The hydrogen and hydroxyl ions are patent ——
a) Conductivity

(12) —— is the product of Specific Conductance and Volume OF electrolyte
b) Molar Conductance

(13) Which method is used in Water analysis?
b) Mohrs method

(14) protophillic Solvent is
d) All

(15) An electrode whose electrode potential Well known and Stable is a
b) Reference electrode.

(16) Each electrochemical cell is composed of
a) Two half cells
(17) The D and L Isomeric form can be distinguished by
a) polarimetry
(18) Limiting current is the sum of diffusion current and
a) Residual current
(19) Oxidising Agent
a) Are mostly transition Metal
(20) In a redox reaction
d) Both A & B

Part-II:-

II) (i) Error denotes difference betn measured and true Value.

Classification

It is of two types
(i) Systematic Error
(ii) Random Error

(i) Systematic Error

- Cause of Error is known as constant.
- Identification & correction is possible
- It can prevented & removed.

(ii) Random Error

- Cause of error is unknown & difficult to identify.
- Error can't be prevented & removed.
- Can be minimised by repeating Exp. may take time main Value of reading.

Minimizing of Error →

Errors can be minimised by;

a) Calibration Calibrative all instrument (Weighing machine, burette, pipette) and applying appropriate correction Error.

b) Independent Method This method perform analysis for a particular substances by 2 or more different method and compare result.

c) Running a blank determination

By carrying out Separate determination without Sample under same condition for actual analysis. We can find out errors occurs due to presence of the impurities in the reagents.

d) Running a control determination

In this determination we use a standard and perform analysis in the identical condition comparing with actual Analysis.

e) Running a parallel determination

In this basically perform the analysis for the particular analyte. More than 2 or 3 times for that. we can given.

② Indicators are weak organic acids or bases that changes colour based on the pH of the soln. Their Func is explained by two primary theories. The ostwald theory & quanonoid theory.

① Ostwald theory Theory is based on the Ionisation of indicator which is weak acid or weak base.

- The colour change is due to a Structural difference between ionised and unionised form of the indicator.
- The equillibrium of indicator's ionisation is shifted depending on whether an acid or base is added.
- Ex; phenolphthelein (in weak acid)

In it is a weak organic acid represented as HPH

$$HPh\ (colourless) \rightleftharpoons H^+ + Ph^-\ (pink)$$

② Quanonoid theory

- This theory focuses on tautomeric form of indicator molecules and provides a more detailed explanation of colour change.
- Indicator exist in two tautomeric form, the benzenoid Form and quanonoid Form which having diff. Str. and Colour.
- The two form are in equillibrium and change in Medium (Ex; an acidic to alkaline) converts one form into Other, causing Colour change.
- The quanonoid Form generally more intensely colored that than the benzoid Form.
- Ex; phenolpthlein

in acidic medium → the molecule exist in its benzenoid form which is colourless.
on alkaline medium → the medium's pH change causes a rearrangement of molecule into its quinonoid form. resulting in pink colour.

(3)/ Importance of common ion effect in gravimetry are as follows;
The common ion effect is a crucial concept in gravimetry, playing a significant role in quantitative analysis of Ions By adding a common ion to the solution the solubility of precipitate decreases, enabling the effect of Efficient precipitation of the desired ion.

Increasing precipitation Efficiency
- Common ion effect enhances the precipitation reaction ensuring the desired ion is precipitated out of the soln efficiently.

Improved Selectively
- By controlling conc. of common ion, the precipitation of specific ion can be achieved reducing interference from other ions.

Quantitative analysis
- The common ion effect enables accurate quantitative analysis by ensuring that the precipitation reaction goes to completion.

Reducing Solubility
- The common ion effect reduces solubility of precipitation allowing for Efficient separation of desired Ions.

Application
- The common ion effect is widely used in gravimetric analysis to determine the conc. of ion such as chloride, sulphate, phosphate.
- By adding a common Ion, such as silver or Barium, the precipitation reaction can be controlled & desired ion can be accurately quantified.

Advantages →
- Accurate results by enabling effecient precipitation of desired Ions.
- Improved precision.

(4)/ — Complexometric titration is a type of titration in which the formulation of colored complex is used to indicates the end point

- In this, it is particularly used for the determination of mixture of different metal ions in a solution.
- The principle of the complexometric titration is based in this titration the metal Ions are titrated with a complexing agent (Ligands) or Chelating agent or EDTA.
- It involves the transformation of simple metal Ion into the complex ion and the metal Ion indicator is used for the determination OF end point by changing the colour.
- It is also called as the chelometric titration / EDTA titration.

$$\text{Metal Ion} + \text{Ligand} \xrightarrow[\text{Indicator}]{\text{metal Ion}} \text{Metal Complex}$$

(5)/ — Non-aq. titrations are those titrations in which analyte substances is dissolved in non-aq solvents other than Water.

- The Non-aq. titrations are mainly are used for weak acid and weak base because weak acid and weak base are partially dissociate in aq. (H_2O) solvents.
- In non-aq. titration strong acid & strong base are used as the solvents in which weak acid and weak bases are dissolved.

Mechanism →

According to Bronsted Lowry theory,.

- Those substance which donate H+ ions are acids.
- & those substance which accept H+ ions are called base.

Ex; $HCl + NH_3 \rightarrow NH_4^+ + Cl^-$

(Acid) (Base)

- Now, For weak acid we use strong base and For strong acid we use weak base.

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

- For weak base BA concept that accept H+ ions during strong acid to donate H+ ions helpin dissociate completely.

Application

- Analyzing weak acids & weak base.
- Used in pharmaceutical Industry For purity & conc. of Certain drug.
- Used For analysis of organic compounds
- Used to determine water content in sample.

(6)

Co-precipitation	post-precipitation
- precipitation of impurities at time of sample prepn.	- precipitation of impurity after some time of sample prepan.
- decrease with increase in time	- increase with increase in time.
- Increase with agitation of solution.	- decrease with agitation of soln.
- degree of contamination is high.	- degree of contamination is Low.
- Time of precipitation is during the desirable ppt.	- time of precipitation after the desirable ppt.
- Ex; Calcium oxalate (CaC_2O_4) and magnesium oxalate (MgC_2O_4) during the ppt. of Calcium Ions as CaC_2O_4 Magnesium Ions can co-precipitate with as MgC_2O_4.	- Ex; post ppt of Magnesium Oxalate occurs if a ppt. of Calcium oxalate allows to stand too long before being Filtered.

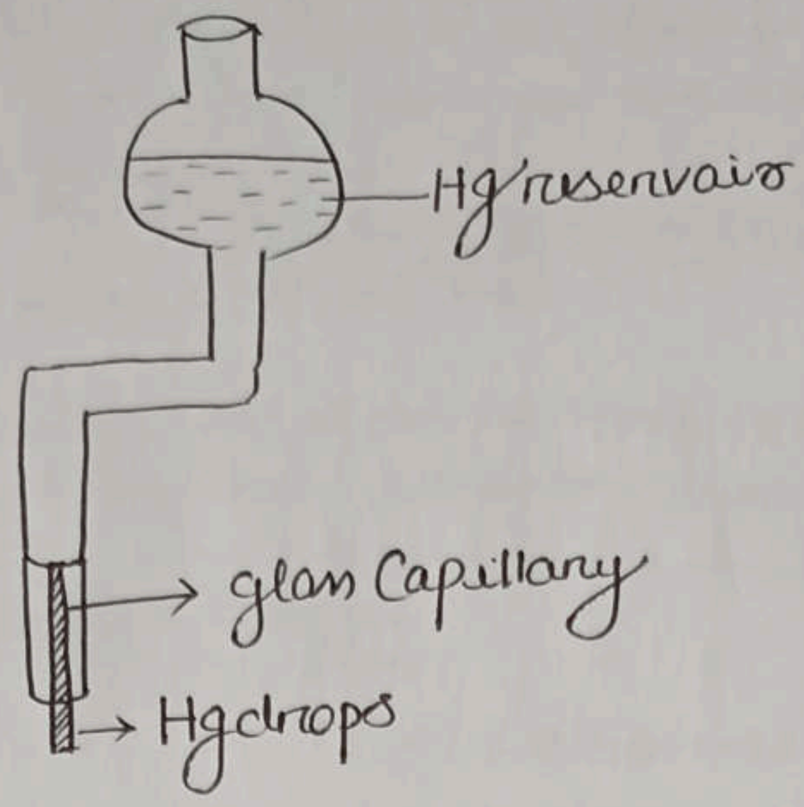
(7) - Dropping mercury electrode is a working electrode which is used in polarography.

- In polarography, it acts as an indicator electrode

Construction — It is made up of 3 components.

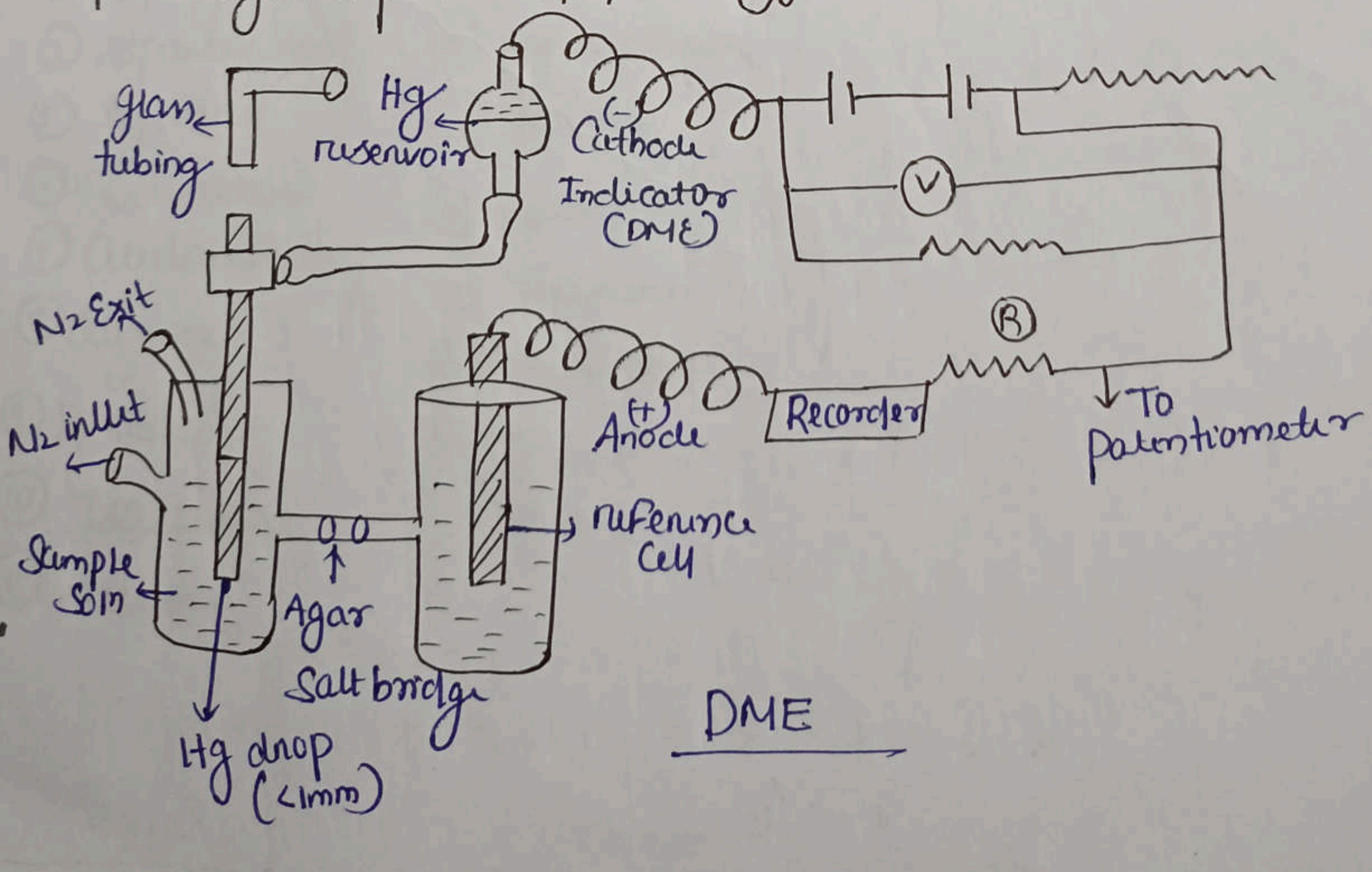
(i) Glass capillary
(ii) Mercury reservoir Vessels
(iii) Standard tube with adjacent stoplock

Capillary Length → 8 to 12 cm
Internal diameter → 0.02 to 0.05 mm
Interval betn drop → 2 to 5 Sec adjusted



Working →

- It is a polarisable and work as indicator electrode.
- In this gradually increasing voltage is applied betwn 2 electrode.
- Due to this, Ionisation of soln takes place which generates the current by flowing the electrons.
- Hg continuously drop from reservoir through capillary tube into soln. The interval betn drops of Hg is 2 to 5 sec adjantied which acts as Cathode (-ve)
- Now current flow betn these electrodes and results are obtained through polarogram in the form of current voltage curve or sigmoid curve.
- Pure N_2 gas is pass to expel out oxygen.



Q.8 Classification of various EDTA Titration with Example are following below :-

1. Direct Titration :- It is similar to acid, base titration which involves the titration of mental ion solution against Chelating agent till the End point.

Example - Titration of hydrochloric acid (HCl) with Sodium hydroxide (NaOH) using phenolphthalein indicator.

Reac^n :- $HCl + NaOH \longrightarrow NaCl + H_2O$

2. Back / indirect titration :- It is similar to Vohland's method in which the Excess amound of EDTA (Ligands) Solution is used for the titration of metal ions solution then this Excess EDTA is titrated with standard solution of a second metal ions.

Example :- Determination of calcium carbonate ($CaCO_3$) in chalk by titrating the Excess HCl with NaOH.

Reac^n :- $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

(Excess HCl is added)

The remaining HCl is titrated with NaOH :-

$HCl + NaOH \longrightarrow NaCl + H_2O$

3. Replacement Titration :- In this titration the mutual ions to be analysed is displaced from the metal ligand Complex.

→ It is used when direct or indirect titrations don't give the sharp End Point.

Example :- Titration of copper sulfate ($CuSO_4$) with $Na_2S_2O_3$ (Sodium thiosulfate) after displacement of iodine.

Reacⁿ :- $CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$

$CuI_2 \longrightarrow CuI + I_2$ (liberation of Iodine)

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

4. Alkalimetric Titration :- It is used for the determination of anions which do not react with EDTA chelate protons (H^+) ion for disodium EDTA are displaced by a heavy Metal and titrated with Sodium alkali

Example :- Titration of hydrochloric acid (HCl) with Sodium hydroxide (NaOH) using phenolphthalein indicator.

Reacⁿ :- $HCl + NaOH \longrightarrow NaCl + H_2O$

Q.9 The Principle involved in barium Sulphate Estimation are Mention below :-

In the gravimetric Analysis the amount of sulphate is Estimated quantitatively as Barium Sulphate.

Chemical formula :- $BaSO_4$

Molecular weight :- 233.4 g/mol

Principle :- In this dilute H_2SO_4 is added to dilute Solution of $BaCl_2$ which forms the white precipitate of $BaSO_4$.

$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HCl$

Procedure :- Take 20.08gm of $BaCl_2$ & dissolved in 1000ml of distilled water.

→ Dil. H_2SO_4 take 3ml & dissolved in 100ml of distilled water.

→ Pipette out 25ml of $BaCl_2$ Solution into 500ml Beaker.

→ Added 0.5 ml Conc. H_2SO_4 in a solution & Make up volume upto 100 ml with distilled water.
→ Now, heat the solution add dilute H_2SO_4 dropwise in a solution untill the precipitate is not separate out.
→ Now filtered, washed & dryed it.

Calculation :-

$$\% \text{ Purity of substance} = \frac{g \times S}{w} \times 100$$

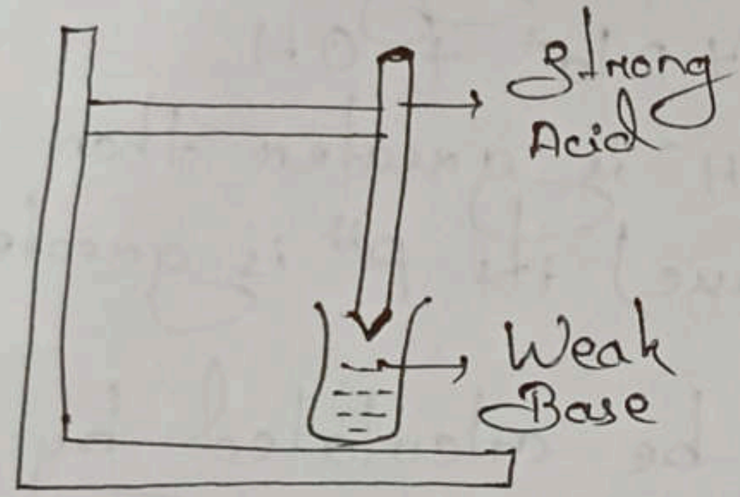
where, g = weigh of residue (precipitate)
S = Gravimetric factor
w = weight of the sample.

PART - III (10 marks)

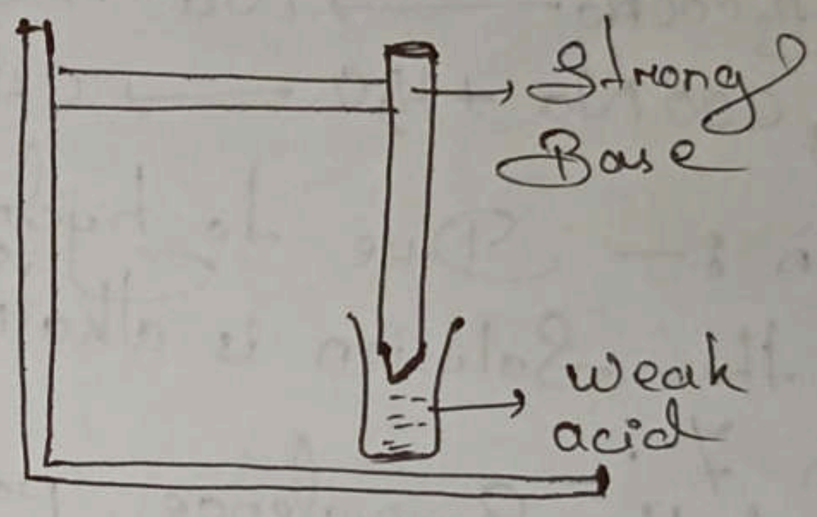
Q.1

Alkalimetry :- It is determination of unknown conc. of acidic solution by using standard Basic solution.
→ Some substance behave as acid under the condition of titration. This determination of acidic substance is categorised as Alkalimetry.
→ In non-aqueous Conc. of weak acid is determined by using strong basic solution.
→ In this samples are Acetazolamide
→ Protophillic Solvents (Base) are used.
Example - DMF (Dimethyl formamide) and Pyridine (C_5
→ Titrant used are Strong Base.
→ Indicator are used in this titration is Thymal Blue which changes colour from Yellow, Pink to Blue.

Acidimetry :— It is determination of unknown conc. of Basic alkaline solution by using standard acidic solution.
→ In Non-aqueous Conc. of Weak Base is determined by using Strong acidic solution.
→ In this Sample are Morphine, Caffine and Adrenaline.
→ Progenic Solvants are used. Ex :— Nitric Acid, Glacial Acetic Acid.
→ Some Substance behave as base under the codition of titration. Thus, determination of Basic Substance is catagorised as Acidimetry.
→ Titrant used are Strong Acid Ex :- $HClO_4$ (Perchloric Acid)
→ Indicator used in this titration is Crystal Violet which Changes Colour from Violet to Blue green.

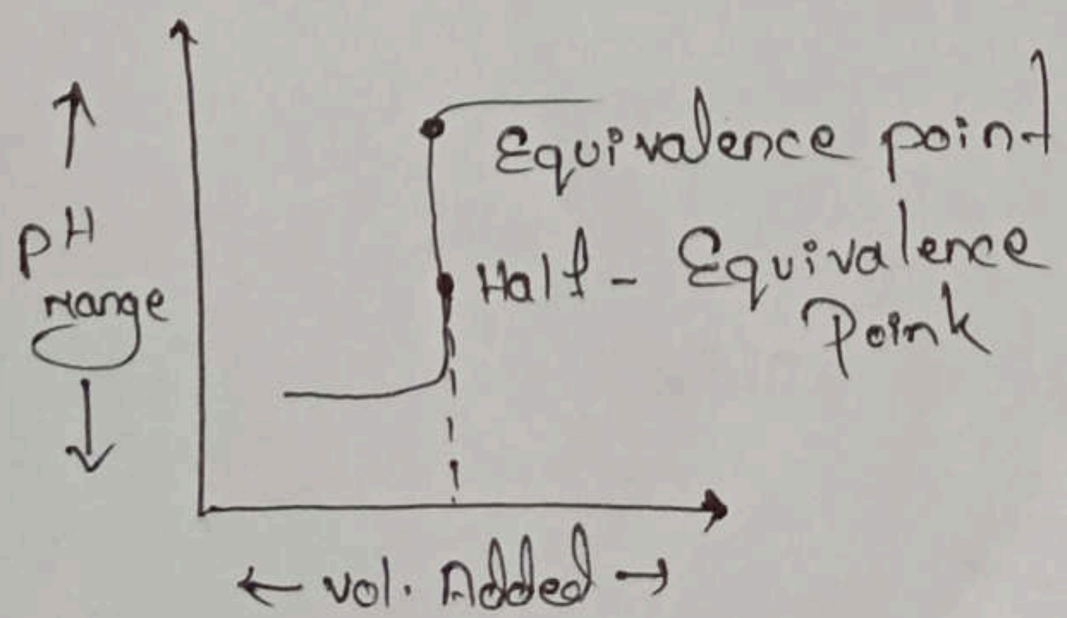


(Acidimetry)



(Alkalimetry)

⟶ The titration between Weak acid with a Strong base using neutralization Curve :—
⇒ In this titration a weak acid such as acetic acid is titrated with Strong base such as NaOH using Suitable indicator to detect the End Point.



→ This type of titration may be represented as

$$HA + OH = H_2O + A$$

→ HA represents the weak acid that is written in the undissociated form.

→ There are three important difference between this titration and a strong Acid and a strong Base.

→ H^+ is small at the start of the titration in 0.1 HCl

→ In 0.1 M CH_3COOH ($H^+ = 1.34 \times 10^{-3}$ & $pH = 2.8729$).

Because CH_3COOH is a weak acid & is poorly dissociated.

Hence, it gives smaller conc. of H^+ ions.

→ In the titration of HCl with NaOH p^H at Equivalence Point is 7 but if a weak acid like CH_3COOH is taken p^H at Complexion of titration is more than 7.

→ Example :- $CH_3COOH \longrightarrow H^+ + CH_3COO^-$ (poorly dissociated)

$CH_3COONa \longrightarrow Na^+ + CH_3COO^-$ (strongly dissociated)

$CH_3COONa + H_2O \longrightarrow CH_3COOH + Na^+ + OH$

Reason :- Due to hydrolysis OH^- is greater than H^+

→ If the solution is alkaline (Basic) its p^H is greater than 7.

→ p^H of the Equivalence point can be calculated by

$$\boxed{p^H = 1/2\ pkw + 1/2\ pka + 1/2 \log c}$$

Example :- Study the neutralise of 100ml, 0.1N acetic acid with 0.1N NaOH.

$$p^H = 1/2\ p^{kw} + 1/2\ p^{ka} + 1/2 \log c$$

$$p^H = 1/2 \times 14 + 1/2 \times 4.74 + 1/2 \times 2.70$$

$$p^H = 8.72$$

Q.2 Mohr's Method :-

It involves determination of the chloride ions conc. of a solution by titration with $AgNO_3$. In this Method the $AgNO_3$ solution is slowly added to chloride solution to produce a ppt. of AgCl.

$$Ag^+ + Cl^- \longrightarrow AgCl$$

→ It is one of the important method of precipitation titration and for 1st time it was development by Mohr's in 1856 (Karl Friedrich Mohr).

→ potassium chromate (K_2CrO_4) used as an Indicator.

Principle :- This Method involves the titration of $AgNO_3$ against halides in neutral solution using 2% of solution of potassium chromate as an Indicator.

→ The End point is Marked by the appreance of brick red coloured precipitate due to formation of Silver chromate and Silver chloride.

→ During titration, $AgNO_3 + NaCl \longrightarrow \underset{(ppt)}{AgCl} + NaNO_3$

→ At the End point,

$$2AgNO_3 + K_2CrO_4 \longrightarrow \underset{(ppt)}{AgCrO_4} + 2KNO_3$$

Procedure :- 1.2 gm of Nacl solution is dissolved in H_2O then add 50ml of this solution into volumetric flask.

→ 2ml of 0.1N K_2CrO_4 indicator is added.

→ A burette is filled with $AgNO_3$ solution and initial reading is noted.

→ During titration, $AgNO_3$ reacts with Nacl and Form AgCl [Silver chloride] precipitate red colour which indicates the End point.

Calculation :- $N_1V_1 = N_2V_2$

OR $M_1V_1 = M_2V_2$

where, V_1 = vol. of $AgNO_3$ solution (burette reading used)

Limitation :- It is not possible to used titration in Basic Solution. otherwise it will produce AgOH.
→ Not possible to use titration in Presence of NH_4 ions & many anions PO_4^{3-}, S^{2-}, etc.

Pharmaceutical Application :-
→ Some of the important drugs are determined by this Methods as;
1. Sodium chloride & dextrose injection
2. chromate ions
3. It is used for determination of chloride, bromide & thiocyanate.

Q.3 Gravimetric analysis is a quantitative method of analysis in which the amount of an analyte (substance to be Measured) is determined by Converting it into a Pure, Stable Compound of known Composition and weighing it.

Principle :- The principle of gravimetric analysis is based on the Measurement of Mass. A Substance is first Converted into an insoluble precipitate. which is then filtered, washed, dried (or ignited) and weighed.
The mass of the precipitate is used to calculate the amount of the analyte Present in the Sample.

$$\text{Amount of analyte} = \frac{\text{weight of precipitate} \times \text{Molecular weight of analyte}}{\text{Molecular weight of precipitate}}$$

Steps involved in Gravimetric Analysis :-
1. Preparation of solution - The analyte is dissolved completely in a Suitable solvent.

2. Precipitation :- A reagent is added to form an insoluble Precipitate.
3. Digestion (Aging) :- The precipitate is heated gently to form larger and purer particles.
4. Filtration - The precipitate is separated from the solution using filter paper or Gooch Crucible.
5. Washing - The precipitate is washed to remove impurities or Soluble salts.
6. Drying or Ignition - The precipitate is dried or heated to a Constant weight.
7. Weighing - The residue is weighed accurately to calculate the amount of analyte.

Washing of the Precipitate :-

→ After filteration, the precipitate is washed several times with small portions of distilled water or with a washing Solution.

→ Purpose of washing :-

(a) To remove adsorbed impurities and soluble salts.
(b) To Prevent Errors in weighing Caused by impurities.

→ Precautions during Washing :-

(a) Use Minimum Quantity of wash liquid to prevent loss of Precipitate.
(b) Washing Solution should not dissolve the precipitate.
(c) Sometimes a volatile electrolyte (like dilute HNO_3 or NH_4NO_3) is added to prevent peptization of Colloidal precipitate.
(d) Continue Washing untill the filterate is free from impurities (tested using appropriate reagents).