JRG COLLEGE OF PHARMACY

UNIVERSITY SOLVED QUESTION WITH ANSWER

Year	:	2019-2020
Subject	:	Pharmaceutical Analysis
Subject Code	:	BP-102T
Subject In-Charge	:	Kiranmayee Bhatra

Registration No: ⬜⬜⬜⬜⬜⬜⬜⬜⬜⬜

Total Number of Pages : 01

B.Pharm
BP102T

1st Semester Regular/Back Examination 2019-20
PHARMACEUTICAL ANALYSIS I
BRANCH : B.Pharma
Max Marks: 75
Time : 3 Hours
Q.CODE : HRB628

Answer Question No.1 (Part-A) and 02 (Part-B) which are compulsory and any TWO from Part-C.

The figures in the right hand margin indicate marks.

Part-A

Q1	Only Short Answer Type Questions (Answer All-10)	(2 x 10)
a)	State Acid and Base according to Bronsted-Lowry Theorem with examples.	
b)	Why nitrobenzene is used in precipitation titration?	
c)	Define titrant and titrand.	
d)	What is self indicator? Give an example of it.	
e)	Give examples of masking and demasking agent.	
f)	Differentiate between qualitative and quantitative analysis.	
g)	State Equivalent conductivity.	
h)	Why acetic anhydride is used for preparation of 0.1N perchloric acid?	
i)	Calculate the pH of 100 ml of 0.1 N Hydrochloric acid.	
j)	How to calculate percentage of analyte in gravimetric analysis.	

Part-B

Q2	Only Focused-Short Answer Type Questions- (Answer Any SEVEN out of NINE)	(7 x 5)
a)	Illustrate iodimetric titration for iodine.	
b)	Prepare and standardize 0.1 N Sodium Hydroxide solution.	
c)	Explain Ostwald theory of acidic and basic indicators.	
d)	Discuss different types solvents used in Non-aqueous titration.	
e)	Write principle and applications of Diazotization titration.	
f)	Describe the principle behind Mohr's method of precipitation titration.	
g)	Explain the various types of EDTA titrations.	
h)	Give the design and working of glass electrode.	
i)	Write in brief about limit test for chlorides.	

Part-C

Only Long Answer Type Questions (Answer Any TWO out of FOUR)

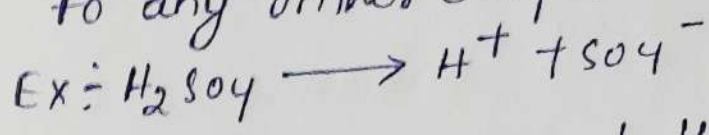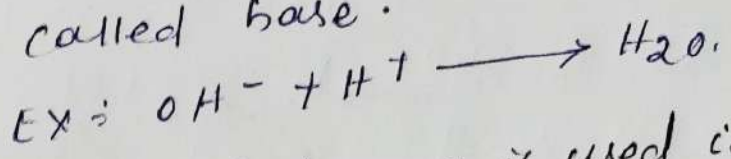| Q3	Define Errors. Classify it. Discuss the methods to minimize the error.	(10)
Q4	Discuss the different types of conductometric titrations involved in pharmaceutical analysis. Mention its advantages and disadvantages.	(10)
Q5	Explain the construction and working of dropping mercury electrode with neat labeled diagram.	(10)
Q6	Describe the neutralization curve of Strong acid when titrated against strong base. Mention its significance.	(10)

(5)

(A)

1) State acid and base according to Bronsterd lowry theorm with Example?

1) According to the bronsted lowry theory
acid - any compound that can transfer proton to any onther compound is called acid.

Ex: $H_2SO_4 \longrightarrow H^+ + SO_4^-$

Base - The compound that accept the proton is called base.

Ex: $OH^- + H^+ \longrightarrow H_2O$.

2) Why netrobenzene is used in precipitation titration?

A) The nitrobenzene is used in precipitation titration because if a little nitrobenzene is added, it will add to agcl (silver chloride) protect it form reaction with thiocyanate how ever, nitrobenzene slows down the realtion.

3) Define titrant and titrand?

Titrant - Titrant indicates of the solution of known concentration, always taken in beaker.

Titrand - The solution of unknown concentration always taken in Flask also known as analyte.

4) What is self indicator? give an example of it?

A) We can define self indicator as a chemical substance which could spot the end point of a titration. It is act as a self participation of the realtion.

(ii) Example: Pottasium dichromate $(K_2Cr_2O_7)$ paper which changes from orange to green in presence of sulphur dioxide.

(5) Give Example of masking agent and demasking agents?

(A) masking agents :- masking agents are the reagents that forms a complex with some components or the analyte and protect them from reaction with EDTA.

(ii) masking agents are mainly used when the analyte solution contains two or more metal ions.

EX :- EDTA serves as a masking agent in spectrophotometric determination.

Demasking agents :- Demasking agent are the reagent that release the metal ions from masking agent

ii) They break the complex fromed beetween metal ion and masking agent.

EX :- for the selective demasking of aluminium triethanolamine is added which also realt with iron.

(6) Difference beetween Quautative and Quantitative analysis?

A) Qualitative analysis :- It basically deals with the identification presence or absence of various components in the given sample on the basis of physical and chemical properties.

Quantitative analysis :- It basically deals with the determination of quantity of various substance that are present in the given sample.

(7) State Equivalent Conductivity?

(A) When one gram equivalent of an electrolyte is dissolved in a solution then conducting power of all ions produced is called equivalent conductivety

Equivalent conductivity formula $= \lambda = \dfrac{K \times 1000}{C}$

where Λ = Equivalent conductivity in sm^{-2} (gram equi valent^{-1})

K = specific conductance in sm^{-1}

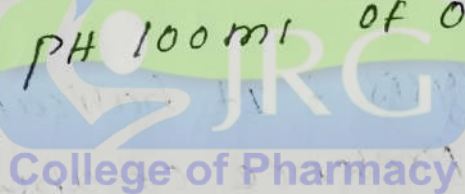C = concentration of 1 gram equivalent in gram equivalent $\times m^{-3}$

3) Why acetic ^an hydride is used for preparation 0.1N perchloric acid?

A) The perchloric acid solution is prepared from 70 percent aqueous solution.

— Acetic anhydride is added after dilution to eleminate the water - so acetic an-hydroxide is used for preparation 0.1N perchloric acid.

9) calculate the pH 100ml of 0.1N hydrochloric acid?

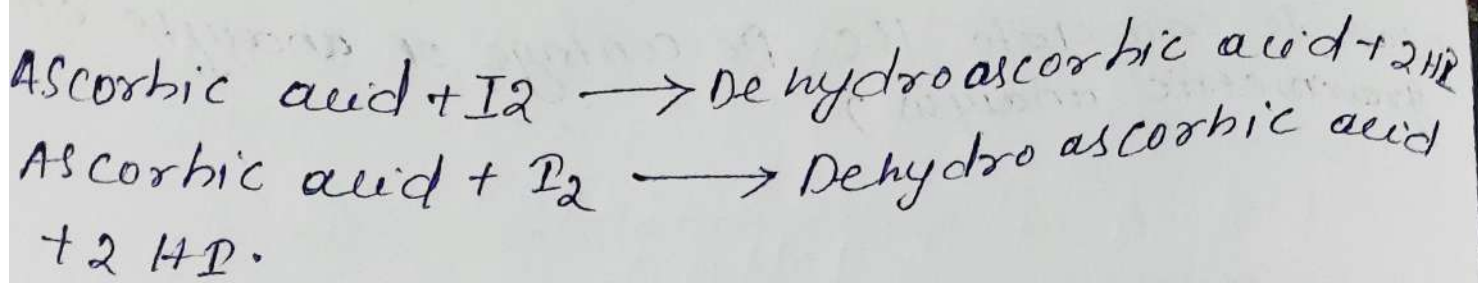(2) How to calculate the percentage of analyte in gravimetric analysis?

Part-B   5marks

(a) illustrate iodimetric titration of iodine?

(A) iodimetry titration involves the use of iodine as a titrant to determine the concentration of oxidizing agents

Example: Determination of vitamin C (Ascorbic acid) in a pharmaceutical formulation

- In this titration a known volume of ascorbic acid solution is titrated with iodine solution untill the colour changes form colourless to faint yellow.

- The reaction is involved as

Ascorbic acid + I2 ⟶ Dehydro ascorbic acid + 2HI

Ascorbic acid + I2 ⟶ Dehydro ascorbic acid + 2 HI.

The amount of iodine solution used is then used to calculate the concentration of ascorbic acid in the sample.

b) prepare and standardize 0.1N sodium hydroxide solution?

A) Preparation of sodium hydroxide

calculate the molecular weight

NaOH :

Na = 22.9 gm/mol

O = 16 gm/mol

H = 1.01gm/mol

molecular weight of the NaOH = 40 gm/mol

Determine the normality of the solution =

Normality = molarity × Equivalent factor NaOH is a monoprotic base, so its equivalent factor 1

Therefore $N = 0.1 m \times 1 = 0.1 N$

calculate the molarity of the solution ÷

$$molarity = Normality \times Equivalent \ weight = \frac{molecular \ weight}{Equivalent \ factor \ NaOH}$$

= 40 Equivalent weight = 40.00 g/mol

= 40.00 gm/mol

$m = 0.1N \times 40.00 \ gm/mol = 4.00 \ g/L$

Preparation of the solution

- weighed about 4 grams of NaOH pellets (small hard ball like structure)
- Dissolved the pellets in distilled water.
- transferred the solution to a 1-litre volumetric flask.
- mixed thoroughly to ensure the NaOH is completely dissolved and the solution homogeneous.

Standardize of the solution :

- use a primary standard acid (pottasium. hydrogen phthalate) to titrate against the NaOH solution.
- Record the volume of acid is used to neutralize the NaOH solution.
- calculate the exact molarity of the NaOH solution based on the volume of acid used

C) Explain ostwald theory of acidic and basic indicators

A) According to ostwald theory, acid base indicator weak and strong base. substances give different colours in different medium.

- The formation of colour in different medium depends upon dissociative or non dissociative state of indicator.
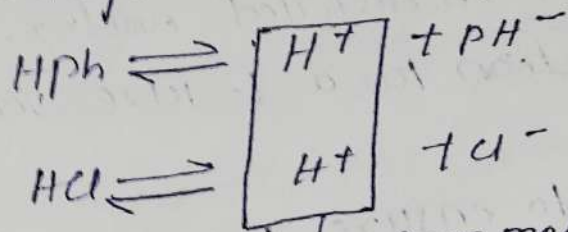
Example := ⓐ phenopthalin
ⓑ methyl orange

Phenopthalein (HPh)

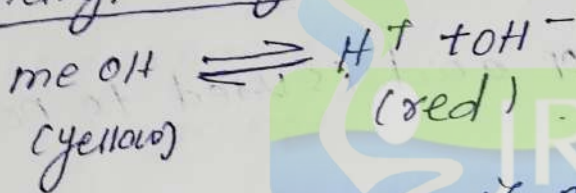$$HPh \rightleftharpoons H^+ + PH^-$$

(colourless)   (pink)

when phenopthalin is added acidic medium.

$$HPh \rightleftharpoons \boxed{H^+} + PH^-$$
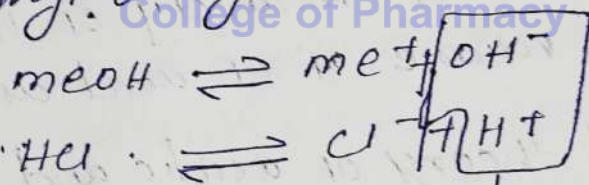
$$HCl \rightleftharpoons \boxed{H^+} + Cl^-$$

└ common ion effect

when phenopthalin is added to acid H^+ of a..
(HCl) supress H^+ of phenopthalin due to com..
ion effect.

Ⓑ methyl orange (meOH)

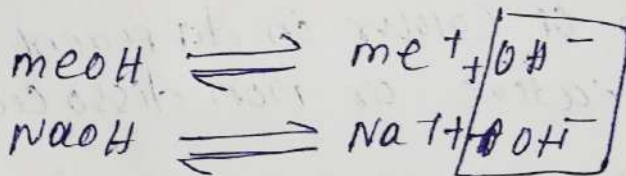$$meOH \rightleftharpoons H^+ + OH^-$$

(yellow)   (red)

when methyl orange is added to acidic medium

$$meOH \rightleftharpoons me + OH^-$$

$$HCl \rightleftharpoons Cl + H^+$$

↓
H_2O

OH^- of meoH is used by H^+ of HCl so dissoc..
state it will show red colour.

when base is added

$$meOH \rightleftharpoons me + OH^-$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

└ Common ion
Effect

due to common ion effect, OH^- conc of MeOH is supressed by OH^- of NaOH, to non dissociative state so yellow colour.

d) Discuss different types of solvent used in non aqueous titration?

A) There are basically 4 types of solvent used in the non aqueous titration.
- protophilic solvents
- protogenic solvents
- Amphoteric solvents
- Aprotic solvents

protophilic solvent

- The word protophilic stands for proton lover.
- protophilic solvents are basic in nature.
- They are used to dissolve acidic analytes
- They posses a high affinity of proton.

Example ÷ pyridine, amine etc

protogenic solvents

- The word protogenic stands for 'proton generator'
- protogenic solvents are acidic in nature ie they can donate proton.
- They are used to dissolve basic analytes.
- They have dielectric constant.

Example ÷ glacial acetic acid, formic acid

Amphiprotic solvents ÷

- They work as both protogenic and protophilic solvent.

- These solvent behave as acid as well as base.
- Amphiprotic solvent can either accept or donate proton.
  examples:- Alchols, methanol, Ethanol.

Aprotic Solvents
- These solvents are chemically inert.
- They are neither acidic or nor basic.
- They don't accept or donate proton
- They have low dielectric constant.
  examples ÷ Benzene, chloroform.

most commonly used non aquas solven
- glacial acetic acid
- Acetonitrile.
- Alchols
- Dioxane

e) write principle and application of diazotizatio titration?

A) Diazotisation titration is a method used t determine of primary aromatic amine compou

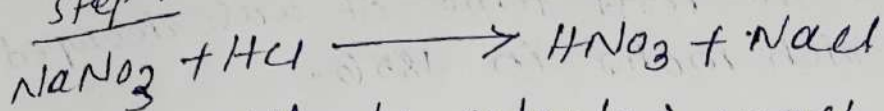- The diazotisation is nothing but simply the dete mination of primary aromatic amine to a diaz nium compound.

- The process was first discoverd by peter griessin in 1853.

- The method is mainly used for determination of dyes.
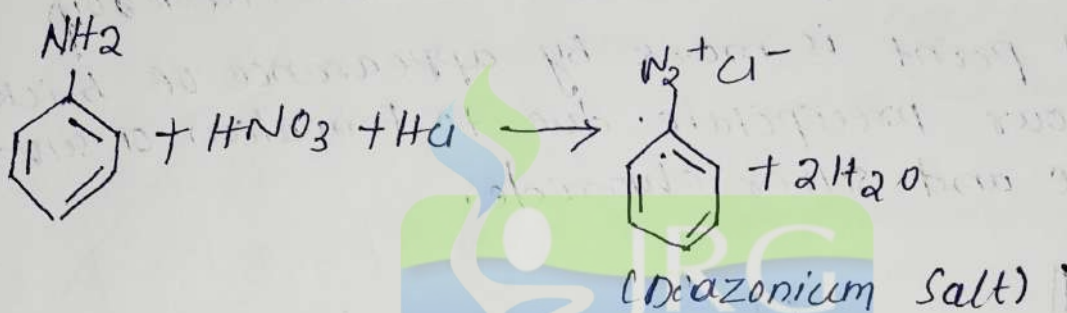
Principle of diazotisation titration

- Primary aromatic amine in the presence HCl react with sodium nitrate (NaNO₃) and from diazonium salt.

- The reaction completed in two steps.

Step-I

$$NaNO_3 + HCl \longrightarrow HNO_3 + NaCl$$

Sodium Nitrate (NaNO₃) react with HCl and from nitrous acid (HNO₂) and Sodium chloride (NaCl)

Step-ii

(Diazonium Salt)

The obtained nitrous acid react with diazonium salt.

End point determination of diazotisation reaction

- In diazotisation titration we use starch iodine paper as a indicator.

- At the end point of the titration. Starch iodine paper changes the colour into blue.

Application of Diazotisation Titration

- used in the determination of sulphonamides
- Used in the determination of chlorophenir-amine.
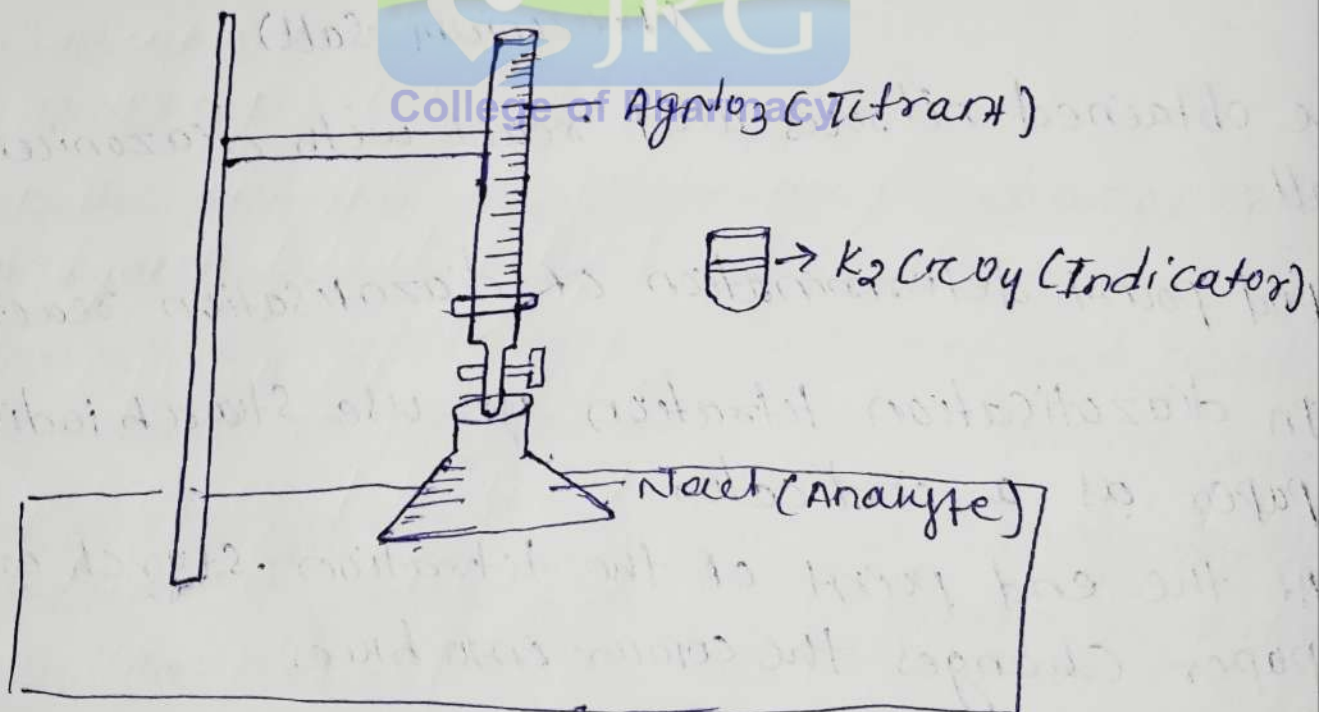- used in the determination of Procaine.

• used in the determination of dopamine.
• used in the determination of ephedrine.
etc.

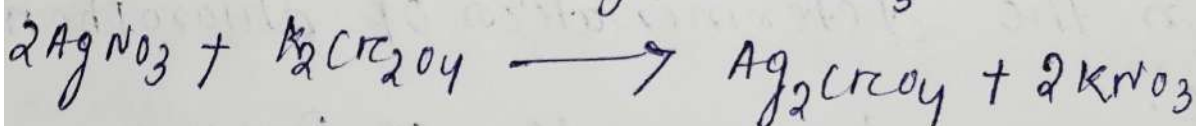P) Describe the principle behind mohr's method
Precipitation titration?

A) It is one of a compartant method of preci[?]
titration and for the first time it was dev[?]
by Karl friend rich mohr in 1856.

Principle

— This method involves the titration of silve[?]
nitrate against halide in neutral solution us[?]
2% solution of pottasium chromate (K_2CrO_4)
— The end point is mark by appearance of br[?]
red colour precipitate due to formation of sil[?]
chromate and silver chloride.

AgNO₃ (Titrant)

→ K_2CrO_4 (Indicator)

NaCl (Analyte)

Reaction

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$2AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4 + 2KNO_3$$

<u>Procedure</u>

- 1.2 gm of Nacl soln dissolve in water.
- 2ml of 0.1 m k2crqy indicator is added
- A burrete is filled with AgNo3 solution and inctial reading is noted.
- During tetration AgNo3 reacts with Nacl and form agcl ppt. (precipitation)
- Now, when all chloride ion is oo used AgNo3 reacts k2crqy indicator and form silver chromate (Agcrqy) in red colour appear in the end point.

<u>Limitation</u>

- It is not possible to use tetration in basic solution. other wise it will produce silver -hydroxide.
- It is not possible to use tetration in the presence of NH3 soln.

pharmaceutical application in mohr's method

. Some of important drug

1) Sodium chloride
ii) Chromate
iii) use determination of chloride, thiocynate Bromaite.

Explain the various types of EDTA titration?

EDTA (Ethylenediamine tetra acetic acid) titration are types of complexometric titration used to determine metal ions of the solution.

Direct titration
- It is the simplest method of complexometric titration.
- In this EDTA used as a titrant.
- In this end point is simply determined by colour change due to indicator.
- It is similar to acid-base titration.
- It is not suitable for slow complexometric titration.

Back titration
- It is also known as indirect titration.
- In this titration is performed by taking excess amount of EDTA.
- In this first we add excess amount of EDTA of the analyte. then remaining amount of EDTA is again titrated by soln of second metal ion.

Replacement titration
- This method is used when direct and back titration don't give sharp end point.
- In this titration, metal present in analyte displace another metal from metal-EDTA complex.
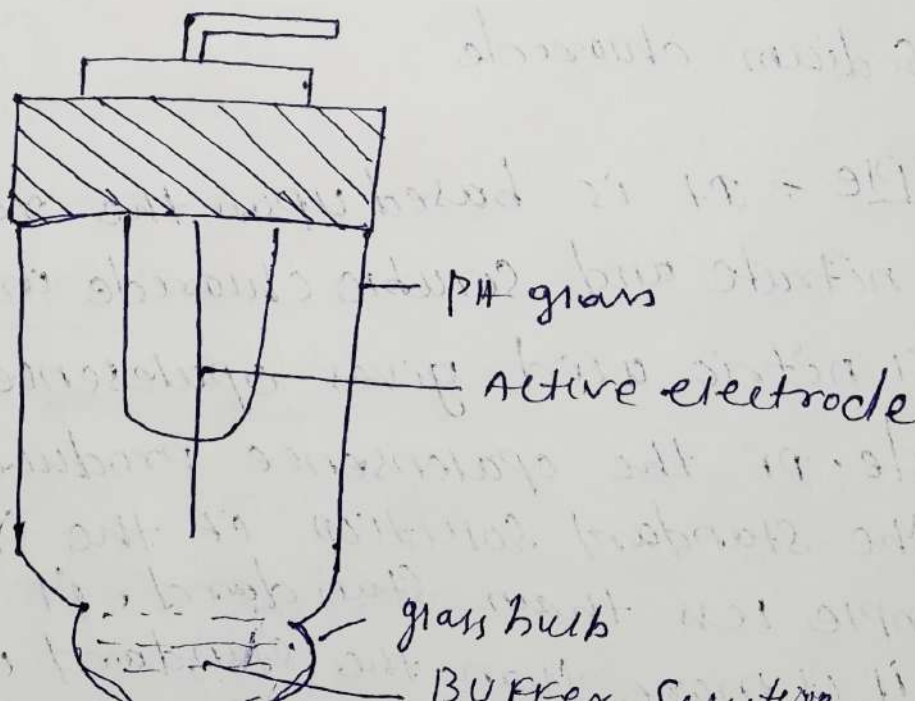
Alkalimetric titration

- It is used for the determination of anions which generally do not react with EDTA.
- In this method, the free H^+ ions get liberated during titration.
- The free H^+ ions is then titrated with standard solution of alkali using suitable indicator.

masking titration

- Some metal ions form complexes with EDTA at a slower rate.
- In such cases masking agents are added to the solution to mask interferring ions allowing to the titration proceed smoothly.

These are some common type of EDTA titration used in analytical chemistry for determining metal ion concentration.

h) Give the design and working of glass electrode?

Design of the electrode

- PH glass
- Active electrode
- glass bulb
- Buffer solution

- A glass electrode is made of a long glass tube with a thin walled glass membrane bulb at the bottom.

- A Pt wire of AgCl coated Ag wire is dipped in the 0.1 m HCl solution in the bulb.

Principle of glass electrode

When two solution of different $[H^+]$ are separated by a thin glass membrane, a potential difference is devloped by at the two surface of membrane. The potential difference devioped is propotional to the difference in $[H^+]$ of the two solution

(i) write briefly about limit test for chloride?

Apparatus chloride Required :-
 Nessler's cylinder
 glass rod
 Stand

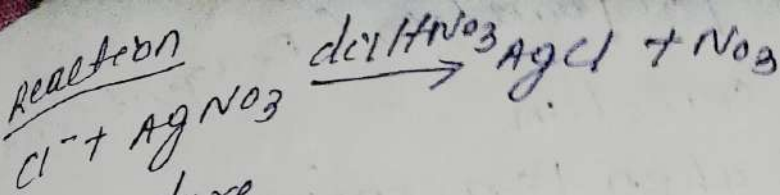Chemicals required
 Dilute nitric acid
 Silver nitrate
 Sodium chloride

Principle ÷ It is based upon the reaction between silver nitrate and soluble chloride in the presence of dil nitric acid gives opalesence or silver chloride. If the opalensence produced is compared with the standard solution if the opalesence in the sample less than standard. it passes the test. if it more than the standard it fails the test.

Reaction

$$Cl^- + AgNO_3 \xrightarrow{dil\ HNO_3} AgCl + NO_3$$

procedure

Take two 50 ml wesier's cylinder label as Test on and other is standard.

Test	Standard
- Dissolved the specified quantity of the substance in distilled water and transfer. Add 10ml dil HNO3. Dilute to 50 ml with water and 1ml of silver nitrate solution. Stirred immidietly with glass rod and allow to 5.mins.	- place 1ml of 0.05845% w/v solution of NaCl and transferd to Wesier cylinder. Add 10ml ok dil HNO3. Dilute to 50ml with water and add 1ml of silver nitrate solution. Stirr immidietly with a glass rod and allow to stand 5 mins.

Part-C 10 marks

Q) Define errors classify it ? Discuss the method of minimize Errors ?

A) Error the terms refers to it differentiate beetween true value and observed value or measured value.

Error - TV - mv

source of error

- Error by analyst (personal error)
- Error due to equipment (instrumental error)
- Experimetal error (Experiment)
  wrong

- Error during sample preparation (Reagent error)

- Error in method selection.

Error by analyst - when performing a test decision then the one wrong due to various types of that contaminate and destroy the final product.

Error by due to equipment - when equipment's are not able to work that if it is used for the test that contaminate the final product.

Experimental error - when a analyst is performing wrong Experiment like added to performing a limit test for chloride he is used silver chlorate but the actual use is silver nitrate. it indicates the experimental error.

Error during sample / preparation - If the sample taken is wrong and not to use and providing toxic effect then the Error due during sample preparation is occurs.

Error in method selection = If the method is error in the test then the Error in method selection is occurs.

Types of error

- errors divided into 2 types
- systemic error
- Random error

systemic error

- In this error a consistent or propotional difference beetween the observed values and true values. (It is determinable)

Random error

- Random error is likely to systemic error. (it is proper but not determinable)

methods of minimizing error

Random errors are unpredictable and therefore, it cannot control while but systemic error can be reduced by following methods.

a) **calibration of apparatus** :- By calibrating all the instruments, errors can be minimized and appropriate corrections are applied to the original measurement.

b) **Control determination** :- Standard substance is used in experiment in identical experimental condition to minimize errors.

c) **Blank determination** :- By ommiting sample, a determination is carried out identical condition to minimize the errors occurs due to impurities present in reagent.

d) **Parallel determination** :- Instead of singe determination duplicate or triplicate determination is carried out to minimize the possibilities of accidental error.
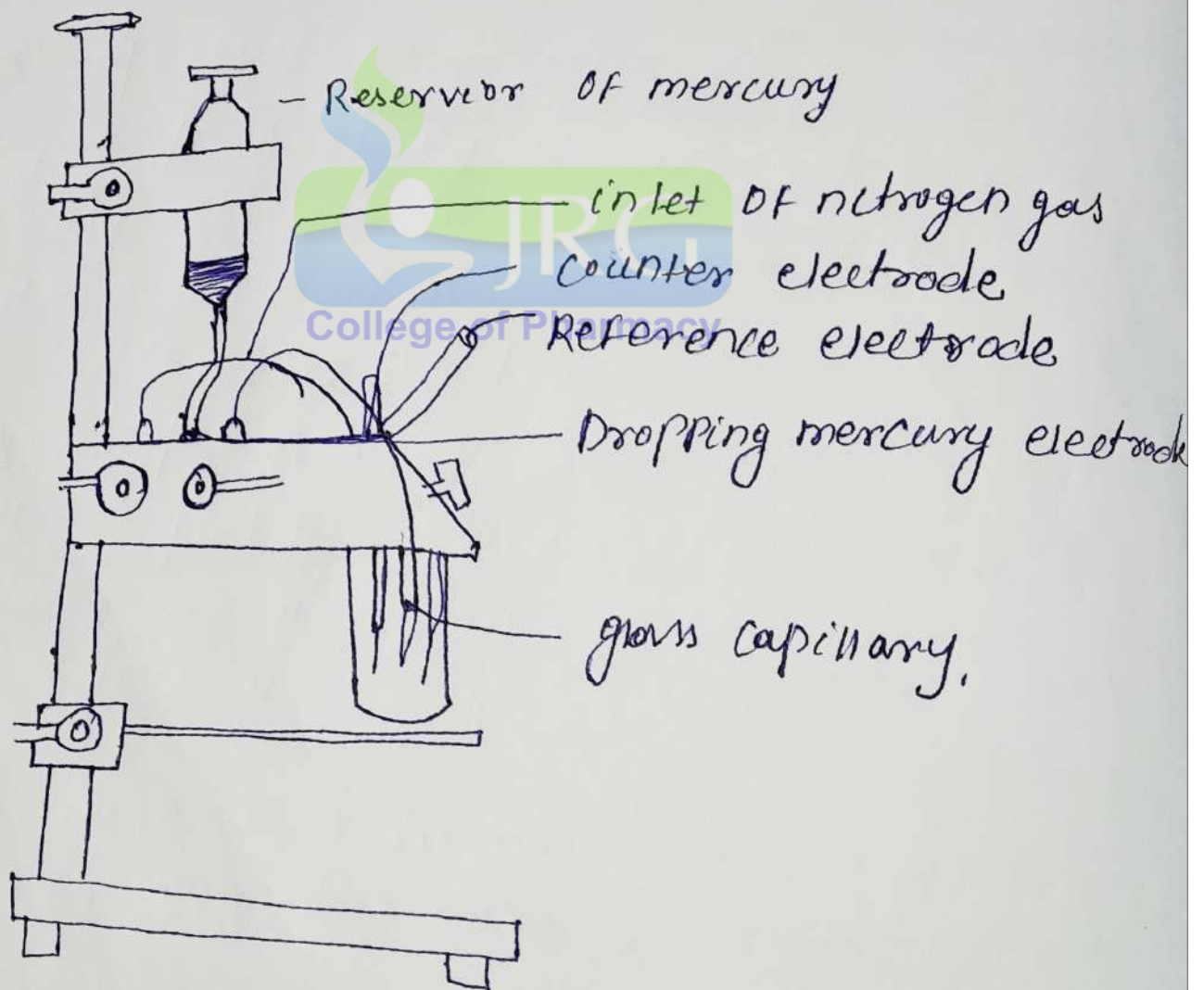
e) Amplification method: It is used when a very small amount of material is to be measured which is beyond the limit of the apparatus.

2) Discuss about different types of Conductometry and advantages and disadvantage?

3) Discuss about d. working and construction of dropping mercury method?

A) Dropping mercury electrode is a working electrode is a working arrangement for polarography in which mercury continously drops from a reservoir through a capillary tube into the solution. The optimum interval beetween drops for most analyses is beetween 1 and 5 s. The unique advantage to the use of DME is that the constant renwal of the electrode surface exposed to the test soultion, eliminates the effects of electrode poisoning

- Reservior of mercury
- inlet of nitrogen gas
- counter electrode
- Reference electrode
- Dropping mercury electrode
- glass capillary.

Construction

- Assembly consist of a mercury reservoir.
- consist of fine capillary having bore size ranged form 20-50 μ and 10-15 cm long.
- capillary connected to mercury reservoir by rubber tubing.
- small glass electrolysis cell in which the unknown solution is placed.
- Height of the mercury reservoir is adjusted each such that drop time 1-5 seconds.

working :

- Droping mercury electrode is a polarisable electrode and can act as a both anode and cathode.
- The counter electrode is non-polarisable electrode.
- To the analyte solution, electrolyte is KCl is added i.e 50-100 times of remove oxygen
- Then gradually increasing voltage is applied to the polarographic cell and current is recorded.
- graph is plotted beetween voltage applied and current.
- the graph is called polarography and the apparatus known as polarogram.
- The diffusion current is produced directly proportional to concentration of analyte

and this is used Quantitative analysis.

- The half wave potential is charecterstics of every compound and this is used Quantitative analysis.
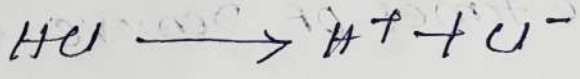
Q6) Describe the neutralization curve of strong acid when titrated against strong base mentions it. Significance?

A) Neutralization curve is also known as titration curves.

- A titration curve is a graph plot beetween PH of the analyte/Titrand

- As the equivalance point is reached in the titration there is a rapid change pH

Some important Terms in neutralization curve

Strong acid - A strong is an acid which is completly dissociates when dissolved in water or aqueous solution

$$HCl \longrightarrow H^+ + Cl^-$$

weak acid - A weak acid is an acid which don't completely dissociates when dissolved in water or aqueous solution

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Strong base - A strong base are those which completly dissociates when dissolved in water aquas solution

$$NaOH \longrightarrow Na^+ + OH^-$$

weak base ÷ weak bases are those which don't completly dissociates when dissolved in water or aqueous solution

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Strong acid vs strong base titration

suppose our analyte is hydrochloric acid (HCl) and tetrant is sodium hydroxide (NaOH), that are strong acid and strong base. Now if we plot a graph beetween pH of the analyte vs volume of tetrant added we will get a titration curve as shous below.

Volume of the tetrant added

point -1 — No NaOH is added in the HCl is o the pH of the analyte is very low due to strong acid HCl

Point-2 — This is point at which pH is recorded at a time Just before complete neutralization takes place.

point-3 — This is the equivalence point. At this time, moles of NaOH = moles of the HCl analyte The solution contain neutral salt

and hence ph is neutral i.e pH = 7

- Point4 — Addition of NaOH continoues, pH start become basir because HCl was neutralized at equivalance point and now excess of OH⁻ ions present in the solution