JRG COLLEGE OF PHARMACY

UNIVERSITY SOLVED QUESTION WITH ANSWER

Year : 2023-2024

Subject : Pharmaceutical Analysis

Subject Code : BP102T

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Registration No:

Total Number of Pages: (2)

Course: B.Pharm
SUB_CODE: 23PBP102

1st Semester (Regular) Examination: 2023-2024

SUBJECT NAME: Pharmaceutical Analysis - I
BRANCH:
Max Time: 3 Hours
Max Marks: 75

Sitting: 1st 10.00 AM to 1.00 PM
Q Code A005

Medium of Writing: English
The figures in the right-hand margin indicate marks.

Part- A

Q 1 Objective Type (Answer All) (10 x 2 Marks)

a) Which indicator is most suitable for titrating strong acid against weak base?
a) Methyl orange b) Phenolphthalein c) KMno4 d) Phenol red

b) The characteristic of a weak acid is:
a) Completely ionized in solution b) Incompletely ionized in solution
c) Give Low pH value d) Both a & c

c) Presence of appreciable quantity of water content may often Titrated by using _ reagent
a) Benedict reagent b) Molisch's reagent
c) Karl Fischer reagent d) None of the above

d) Precision refers to:
a) Standard deviation
b) Deference between the highest and lowest value of observed parameter
c) Agreement of measured parameter with the theoretical value
d) Agreement among the repetitive values of the measured parameters.

e) pH defined as:
a) $-\log [H^{+}]$ b) $+\log [OH^{-}]$ c) $+\text{Log} [H+]$ d) $-\log [OH^{-}]$

f) The molecular weight of KMnO4 is 158.03 and loss or gain of electron is 5, then what is the correct equivalent weight?
a) 31.60 b) 15.8 c) 63.2 d) 1.58

g) Ethylene Diamine Tetra Acetic acid (EDTA) is used in_
a) Precipitation titration b) Neutralization titration
c) Non-Aqueous titration d) Complexometry

h) Which of the following is Reference electrode?
a) Calomel electrode b) Saturated Hydrogen electrode
c) Silver–silver chloride electrode d) All of the above.

i) What is the correct technique for the minimization of systemic error?
a) Calibration of apparatus b) Analysis of standard samples
c) Running of blank determination d) all of the above

j) Starch-iodide paper is used to detect end point in_ assay.
a) Acid-base titration b) Complexometry
c) Non aqueous d). Diazotization titration

Q 2 Short Answer Questions (Answer any Seven out of Nine) (7 x 05 Marks)

a) Define Oxidizing and Reducing agents. Give any two examples for each category.

b) Write short note on: pM indicators and their applications.

PTO

c) What do you mean by complexometric titration? Mention some commonly employed complexing agents.

d) Describe the principle with example: Gravimetric Assay.

e) Differentiate between a) pH & pOH b) Accuracy & Precision.

f) Define the followings:
   a) Equalent weight b) Molarity C) Normality
   d) Primary standard e) Analyte

g) Write the Principle of Polarography with suitable diagram.

h) Describe the method of preparation and uses of one litre of 0.1 N Oxalic acid. [Mol weight=90g/Mol]

i) Write Short Note on: Masking and demasking agents.

Part- B (Answer Any Two)

Long Answer Question

Q 3 Discuss in detail 'Theories of acid-base indicators'. (1 X 10 Marks)

Q 4 Describe with diagram of the construction and working of any two Reference Electrodes. (1 X 10 Marks)

Q 5 Describe in detail the principle and applications of Diazotization titration. (1 X 10 Marks)

-: PART- A :-

Q.

a// Phenopthalein indicator is most suitable for titrating strong acid against weak base.

b// The characteristic of a weak acid is incompletely ionized in solution.

c// Presence of appreciable quantity of water content may often titrated by using Karl fischer reagent.

d// Precision refers to Agreement among the repetive values of the measured vaule/ parameter.

e// $pH = -\log H^+$

f// The molecular weight of $KMnO_4$ is 158.03 and loss or gain of electron is 5, then equivalant : weight is 31.5 gm.

g// EDTA is used in Complexometric titration.

h// Reference electrode includes saturated Hydrogen electrode, silver-silver chloride electrode and cali- electrode.

i// minimizing of systemic error include calibration of apparatus. Runing blank determination etc.

J// starch-iodide paper is used to detect end Poin in assay of Diazotization titration.

Q.2

a// oxidizing agent:-

↳ These are those substance which do oxidation of other and it self get reduced.

↳ We can simply say substance which gain e^- are called as oxidising agent.

* oxidation:-

oxidation can be defined as 3 ways

- Addition of oxygen : $SO_2 + O \rightarrow SO_3$
- Loss of Hydrogen: $H_2S + Cl_2 \rightarrow 2HCl + S$
- Loss of electron: $Na \rightarrow Na^+ + e^-$

It can be remembered by OIL (oxidation is loss of electron)

Reducing agent:-

↳ These are those substance which do Reduction of others and it self get oxidised

↳ we can simply say the substance which loss e^- are called as reducing agent.

* Reduction:-

Reduction simply defined in 3 ways

- Removal of oxygen :- $CuO + 2H \rightarrow Cu + 2H_2O$
- Gain of Hydrogen:- $C_2H_2 + 2H \rightarrow C_2H_4$
- Gain of electron:- $Cl + e^- \rightarrow Cl^-$

It can be remembered by RIG (Reduction is Gain of electron)

E.g:-

oxidizing Agent

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Reducing agent

b// **PM INDICATOR:-**

- Indicators that are used in complexometric titration are called as PM indicator.
- It is also known as metal ion indicator.

Mechanism action of PM Indicator:-

- Like all other indicators. PM indicators also shows colour change at the end point but it work some-how different.
- At first we add indicator in the analyte (metal ion) solution, now indicator formed a complex with analyte and colour of this complex is wine red. hensce we can say before end point colour of the analyte is wine red.
- At the end, the titrant (Ligands) breaks the bond between indicator and analyte & titrant self forms a complex with analyte which is called a metal ion complex or Ligand-metal ion complex.

- Now since indicator get free and the free form of indicator have blue colour. hence we can simple says at the end point shows blue colour.

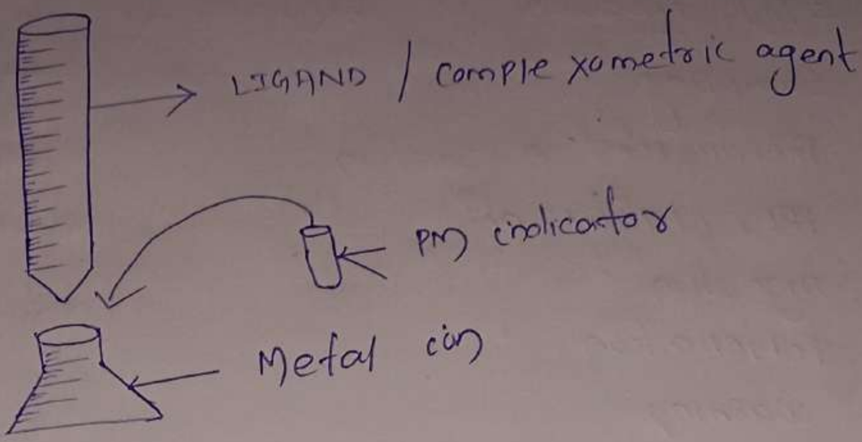
- Some commonly used indicators in Complexometric titration are: Eriochrome black T, calmagite, Murexide, mordant black, solochrome black-T

Q// COMPLEXOMETRIC TITRATION:-

- Complexometric titration are those type of titration which based on the complex formation betn titrant and analyte.
- It is also known as chelatometric titration.
- complexometric titration are mainly used for the determination of metal ion in a solution.
- End point of the titration is determined by change in colour of the solution due to complexometric reaction.
- EDTA is mainly used as a titrant in complexometric reaction. hensce it is called as EDTA Titration.

TYPES OF LIGANDS USED IN Complexometric titration on the basis of number of donor groups

↳ unidented ligands
↳ Bidented ligands
↳ Multi dented ligand



CLASSIFICATION :-

- Direct titration
- Indirect titration
- Replacement titration
- Alkalimetry titration

E.g :- EDTA, Citric acid, phosphates, phosphonates, Ammonia

d// GRAVIMETRIC ANALYSIS :-

- Gravimetric analysis is a methode of analysis in which we determine the quantity of analyte by measurment of mass.
- In gravimetric analysis analyte is convert into precipitate.

METHODES OF GRAVIMETRIC ANALYSIS :-

- Precipitation Gravimetry
- Volatization analysis
- Electro gravimetry.

STEP INVOLVED IN GRAVIMETRIC ANALYSIS:-

- Sampling
- Preparation of Solution
- PRECIPITATION
- Digestion
- Filteration
- washing
- Drying or Ignition
- weighing and Calculation

E.g:- Determining the amount of chloride in a Sample.

e//

pH	pOH
↳ pH is simply defined as the -ve logarithum of H^+ con.	↳ pOH is simply defined as the -ve logarithum of OH^- con.
↳ $pH = -\log[H^+]$	↳ $pOH = -\log[OH^-]$
↳ pH stands for "potential of Hydrogen".	↳ pOH stands for "potential of hydroxide".
↳ Range of the pH Scale is 0 to 14. here 7 is neutral.	↳ Range of pOH scale is inversly related to pH scale
below 7 values are acidic and above 7 value are basic.	↳ lower pOH values indicates higher hydroxide conc. while higher pOH value indicates lower OH^- concentration.
$pH + pOH = 14$	↳ $pH + pOH = 14$

Accuracy	PRECISSION
Accuracy refers to how close a measured vaule to words the true vaule or expected vaule.	Precission refers to the degree of closeness between Several measurment of Same quantity & of Sample.
measurment Can be accurate but not necessarily precise	Measurment Can be Precise but not necessarily accurate
Acccuracy may be affected with systemic error.	Precision may be affected with Random error.
Degree of Conformity	Degree of reproducability.

F// Equivalant weight:-

- It is defined as the molecular weight of the given substance upon it's basicity / acidity.
- It is denoted by 'E'.

$$Eq = \frac{\text{Molecular weight}}{X_f} \quad \because X_f = \text{Acidity}/\text{Basicity}$$

Molarity:-

- It is defined as no. of moles of solute that can be dissolved in 1000 ml of water.
- It is denoted by 'M'.

$$\boxed{M = \frac{w}{W} \times \frac{1000}{V}}$$

NORMALITY:-

- It is defined as gm equivalant of solute dissolve in 1000 ml of water.
- It is denoted by 'E'.

$$\boxed{N = \frac{w}{E} \times \frac{1000}{V}}$$

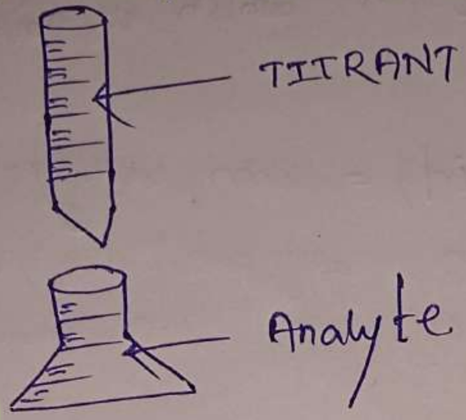
PRIMARY STANDARD:-

- Primary standard are reagents with accuratly known concentration and very high purity which after dissolving to known amount of Solvent gives Primary standard
- They have high Molecular weight

Eg:- Sodium tetraborate
KHP etc.

Analyte:-

- These are the substance which are mainly taken in conical flask.
- we have no idea about their concentration.
- It is also known as Titrand.



9) Polarography:-

- Polarography is an electrochemical analytical techniques that measures the current flowing through a solution as a function of an applied voltage, by using a dropping mercury electrode as the working electrode.
- It is invented by Jaroslav Heyrovsky.

PRINCIPLE:-

- In polarography, It is based on the Principle that when voltage (EMF) is applied between the electrodes, reduction / oxidation takes place and e^- moves and current flow.
- Now, this following current is measured which is depends on the concentration of ion.

Two electrodes :-

↳ Polarizable electrode - Dropping mercury Electrode

↳ Non-polarizable electrode - Calomel electrode

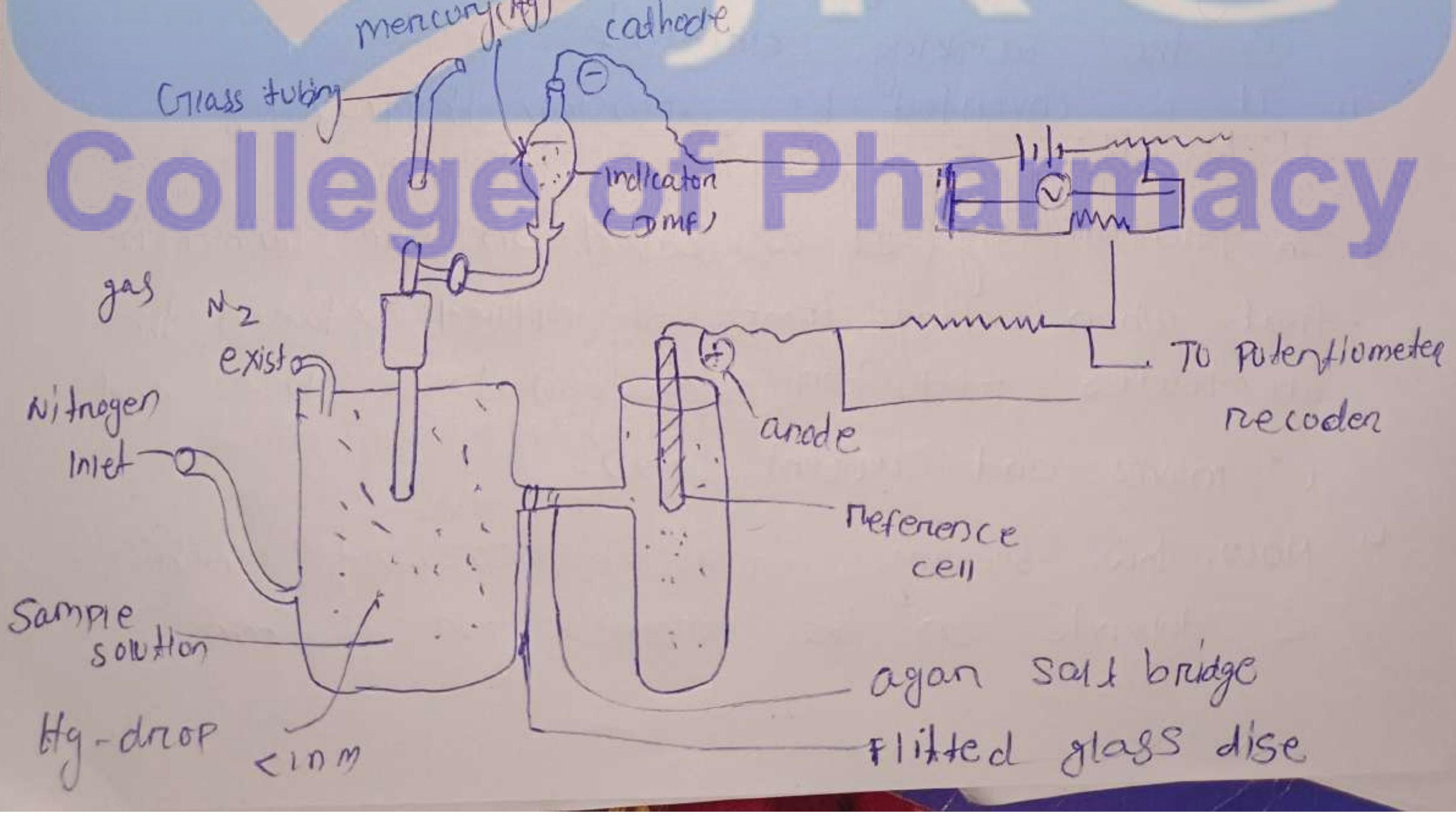
↳ The instrument is called polarograph and the curve is called polarogram which is formed as current-voltage curve.

* Diffusion current (id) = when voltage is applied in a solution diffusion of ion/analyte takes place which generate current i.e. known as diffusion current.

It is measured by ilkovic equation.

$$\boxed{i_d = 607 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot C}$$

$$\boxed{i_d \propto C}$$



h// PREPARATION OF 0.1 N oxalic acid :—

molecular weight of $C_2O_4H_2$ = 90 gm

Equivalant weight (E) = $\frac{9\cancel{0}}{\cancel{2}}$ = 45 gm

$$\boxed{N = \frac{W}{E} \times \frac{1000}{V}}$$

$$\Rightarrow 0.1 N = \frac{W}{45} \times \frac{\cancel{1000}}{\cancel{1000}}$$

$$\Rightarrow W = 0.1 \times 45 = 4.5 \text{ gm}$$

That means, Dissolve 4.5 gm of oxalic acid in 1000ml of distiled water for 0.1N oxalic acid Preparation

PREPARATION OF 0.1N NaOH :—

molecular weight of NaOH = 40 gm

Equivalant weight (E) = $\frac{40}{1}$ = 40 gm

$$\boxed{N = \frac{W}{E} \times \frac{1000}{V}}$$

$$\Rightarrow 0.1 N = \frac{W}{40} \times \frac{\cancel{1000}}{\cancel{1000}}$$

$$\Rightarrow W = 40 \times 0.1 = 4 \text{ gm}$$

That means, Dissolve 4 gm of NaOH in 1000 ml of distiled water for 0.1N NaOH preparation

TABULATION :—

Sl No.	Vol. of titrand	Burate reading		Means
		IBR	FBR	
1	10	50	40	10
2	10	40	30	10
3	10	30	20	10

CALCULATION :-

$N_1 V_1 = N_2 V_2$

Given.
$N_1 = ?$
$V_1 = 10$
$N_2 = 0.1 N$
$V_2 = 10$

According to the formula

$N_1 V_1 = N_2 V_2$

$N_1 \times 10 = 0.1 \times 10$

$N_1 = \frac{0.1 \times \cancel{10}}{\cancel{10}} = 0.1$

$\boxed{N_1 = 0.1 N}$

So Normality of oxalic acid is 0.1N.

(i) ↳ masking and demasking agent are generally used when analyte Solution contain 2 or more than 2 metal ion.

↳ Let consider we have a solution containing 3 different metal ions A, B, & C, now if we directly titrate the analyte, then we will get the concentration of all 3 metal A, B, C

↳ But in the Case, if we have to determine the concentration of A, B & C individually then we have to use masking and demasking agents.

masking agents :—

↳ masking agent are the reagents that form a complex with Some components of the analyte and Protect them from reaction with EDTA.

↳ masking agents are mainly used when the analyte sol^n contain 2 or More than 2 metal ions.

E.g:- KCN

Demasking agent :-

↳ Demasking agent are the reagents that releases metal ions from masking agent

↳ They break the complex formed between metal ion & masking agent

E.g:- formaldehyde.

Mechanism :-

Let's Consider we have an analyte sol^n contain 3 metal ion X, Y, Z. Then if we have to find their conc. individually.

STEP - I :-

$$\underbrace{X + Y + Z}_{\text{Sample (3 metals)}} + \text{masking agents} \longrightarrow \underset{\text{free}}{X} + \underbrace{\boxed{Y} + \boxed{Z}}_{\text{masked by masking agent}}$$

STEP. 2:-

$$X + \boxed{Y} + \boxed{Z} + \text{Titrated with EDTA} \rightarrow X\text{-EDTA} + \boxed{Y} + \boxed{Z}$$

Step - 3:-

$$\boxed{Y} + \boxed{Z} + \text{Demasking agent} \longrightarrow \underset{\text{Free}}{Y + Z}$$

PART-B

Q:3 Theory of Acid-base indicator:-

↳ An indicator is a substance which is used to identify the end point in a titration.

↳ The indicator which are used in the titration are generally organic indicator.

↳ They change their pH within a certain pH range.

E.g:- methy orange, Phenopthalien.

↳ There are two theory which are used to explain the colour changing nature of acid & base indicator.

a) ostwold's Theory:-

↳ According to this theory indicators are generally weak acid or weak base.

↳ The change in colour of the indicator is due to ionisation.

↳ The unionised form of indicator show different colour & ionised form of indicator show different colour.

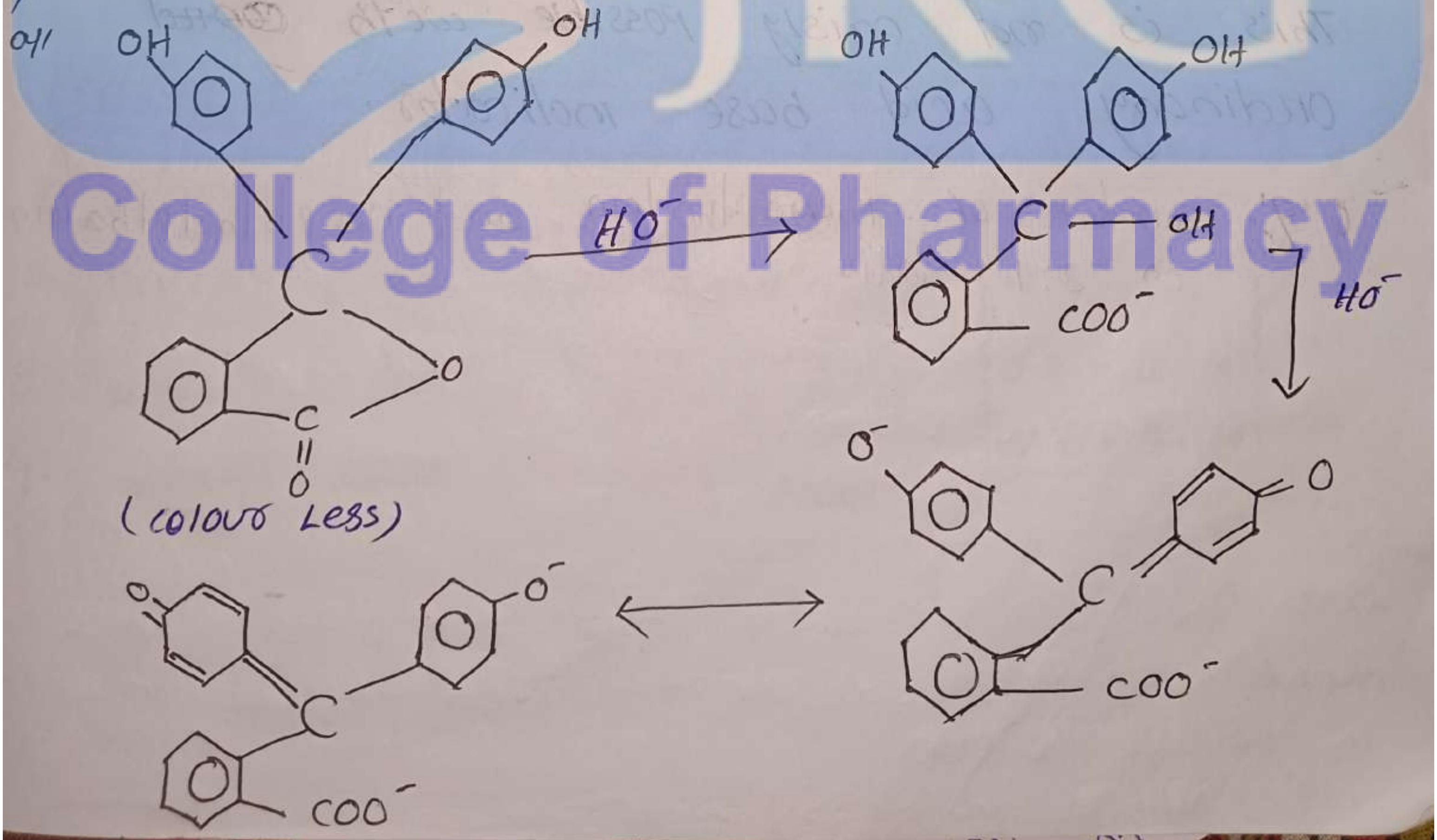
Now there can be cases;

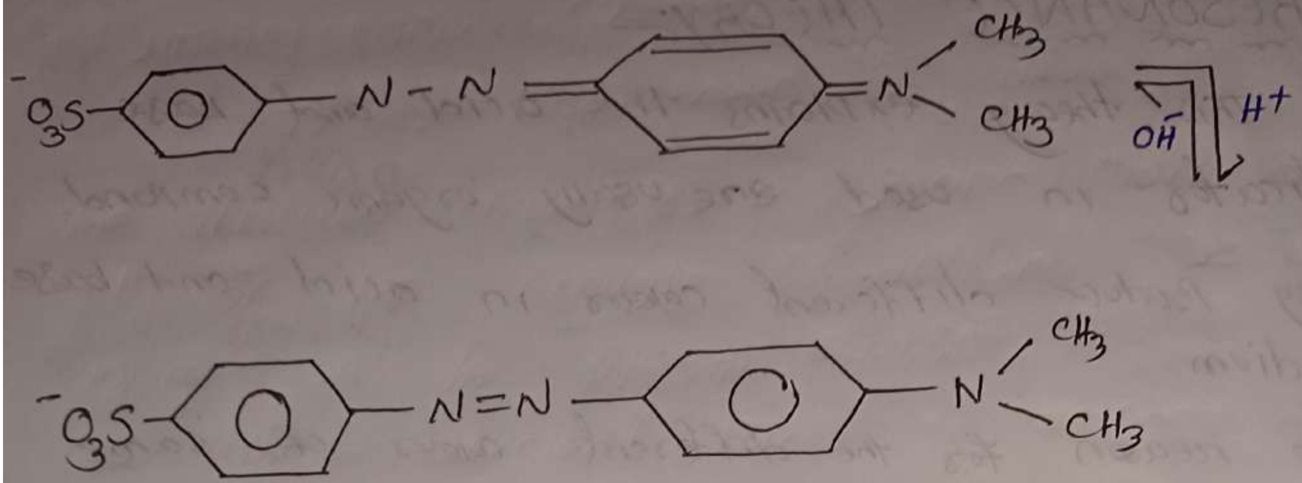
(i) Indicator is weak acid E.g:- Phenopthalien

(ii) Indicator is weak base E.g:- methyl orange

3. RESONANCE THEORY:—

- This theory explains the acid and base indicator in used are usally organic compound. They Produce different colour in acid and base medium.
- The reason for the different colour of same compound in different media is evidently due to diffenent in structure that the same compound in different media. well have to form
- Acid, Base indicator exist into two form
  1. Benzenoid form
  2. quenonoid form
- The two forms have different colour in different medium.
- Two form changes conc. with change in medium.





Quinonoid -Acedic solution (red).

MIXED INDICATOR:-

↳ The acid base indicator is widely used as the above maintioned theory.

The PH Range is very narrow and the colour changes over this range must be very sharp.

This is not eaisly possible with ordinary acid base indicator.

E.g:- mixture of phenopthalein and naphtholpthalein in 3:1 ratio

Q.4. potentiometry:-

↳ It is a technique where potential of an electrode is used to measure the conc^n of analyte Solution.

↳ Basically, It is the measurment of electrode potential i.e. Difference in voltage between the electrode by using electrochemical Shell.

ELECTRODE:-

↳ These are the Instrument which are mainly used to mesure the voltage

↳ They are mainly 2 types of electrode used in Potentiometry.

a. Reference electrode
  - ↳ standard hydrogen
  - ↳ Silver chloride electrode,
  - ↳ Calomel electrode.

b. Indicator electrode:-
  - ↳ Metal electrode
  - ↳ Glass electrode.

a) Reference electrode:-

↳ These are those electrode, which have known electrode potential.

↳ It is completely indipendent of the conc^n of the analyte Sol^n.

↳ But used for the determination of analyte by maintaining the fixed potential.

a// STANDARD HYDROGEN electrode (SHE) or NHE :-

↳ It contains a glass tube with a platinum wire sealed with in it.

↳ Platinum foil coated with pt black to increase surface area which immersed in 0.1 M HCl to maintain the concⁿ of H^+ ions.

↳ The Hydrogen (H_2) gas in pure form is continuously bubbled in the acidic solution at $T^\circ = 298K$ and Pressure = 1 atm.

↳ It is attached with another half cell with analyte solution.

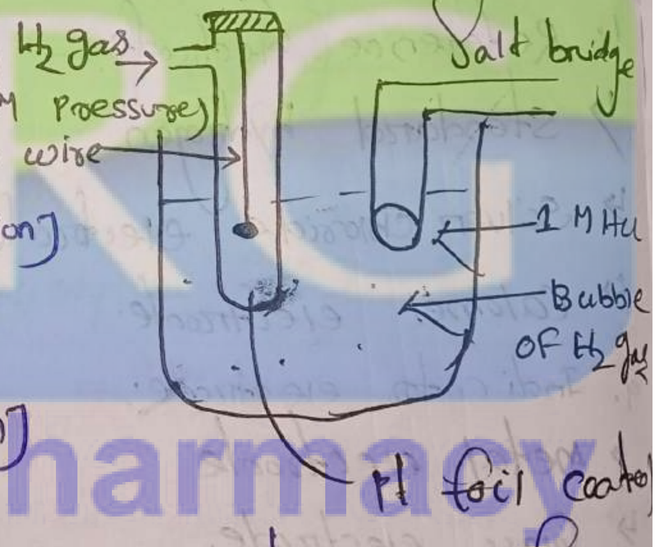
Working :-

When it act as anode :-

$H_2(g) \rightarrow 2H^+ + 2e^-$ [oxidation]

When it act as cathode :

$2H^+ + 2e^- \longrightarrow H_2(g)$ [reduction]



(b) Silver chloride electrode :-

↳ It is used in pH meters as the internal reference electrode.

Construction :-

↳ It contains a Silver wire coated with AgCl (Silver chloride).

↳ The electrode is immersed in Solution of KCl having 1M of Cl^- ion.

↳ It is represented as Ag. AgCl / Cl^- (1M)

Working :—

There is reaction betⁿ Ag and AgCl:

$$Ag^+ + Cl^- \rightleftharpoons AgCl + e^-$$

$$Ag^+ + e^- \rightleftharpoons Ag\ (s)$$

Q. 5// DIAZOTISATION TITRATION :—

↳ Diazotitration titration is a methode used for determination Primary aromatic amine Compounds

↳ The diazotization titration is nothing but Simply the convergcion of Primary aromatic amine to diazonium Compound

↳ The Process was first discovered by peter Griessin in 1853.

↳ The methode is mainly used for determination of dyes.

PRINCIPLE OF DIAZOTISATION TITRATION :—

↳ PRimary aromatic amines in the presence of HCl reacts with $NaNO_2$ and form Diazonium Salt

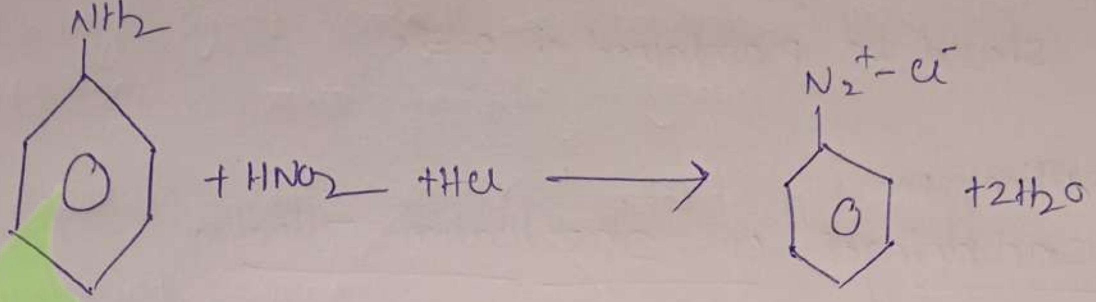
↳ The reaction completed in two Step.

Step. 1 :-

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

Sodium Nitrate react with Hcl and form Nitrous acid and Hcl.

step II :-



The obtained nitrous acid react with primary aromatic amine to forn diozonium salt.

End point Determination in diazotisation Titration

- In diazotisation titration we use starch Iodine paper as Indicator.
- At the end point of the titration, starch iodine paper changes the colour into blue.

Starch Iodine paper

→ Starch iodine paper is prepared by dipping the filter paper into potassium iodide KI and starch mucilage solution.

→ following reaction accure during end point determination

$KI + Hcl \longrightarrow HI + KCl$

$2HI + 2HNO_3 \longrightarrow I_2(\uparrow) + 2NO + 2H_2O$

$I_2 + \text{starch} \longrightarrow I_2^-$ starch complex

Condition For diazotisation Titration

maintaince of temperature is the main condition for diazotisation titration.

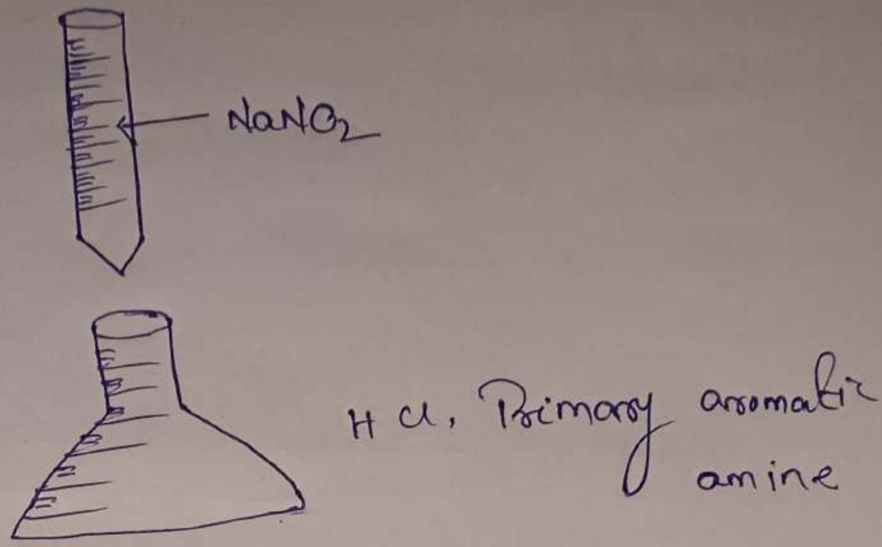
- The diazonium salt is not stable at high temp. so the temp should be maintained at 0-5°c

Disadvantages of Diazotisation Titration

- Applicable for very less variety of sampled.
- Relatively slow compared to other method.
- Required to maintained temp. conditions.
- End point detection is very difficult.

Methodology

- The general procedure is followed by weighing sampe and transferring it into standard flask.
- After that concentrated hydrochloric ~ acid and potassium bromide. are added and rest of the volume is filled with distilled water.
- The resulting solution is known as standard solution,
- The appropriate volume of the standard solution is pipette out and temp is maintaied 0-5°c.
- Now finally the solution is titrated withs sodium nitrite solution until starch iodide paper turns into blue colour.



Applications of Diazotisation Titration

- → Used in the determination of sulphonomides
- → used in the detemination of chlorophenomine. ~~procaine~~
- → used in the determination of Priocaine.
- → used in the determination of dopamine.
- → used in the determination
- → used in the determination of ephedrine etc,