Theory of Acid-Base / Theory of acid base titrations :-

There are three theory of acid base. They are listed as following—

1. Arrhenius Theory
2. Bronsted and Lowry Theory
3. Lewis Theory

1. Arrhenius Theory :-

According to arrhenius theory an acid is a substance which produces / gives H^+ ions in solution.

Example :

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

According to arrhenius theory a base is a substance which produces / gives OH^- ions in solution.

Example :

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

2. Bronsted and Lowry Theory :-

According to Bronsted and Lowry theory an acid is a substance from which a proton can be removed.

Example:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

According to this Bronsted and Lowry theory a base is a substance which can accept a proton.

Example:

$$NH_2 + H_3O^+ \longrightarrow NH_3 + H_2O$$

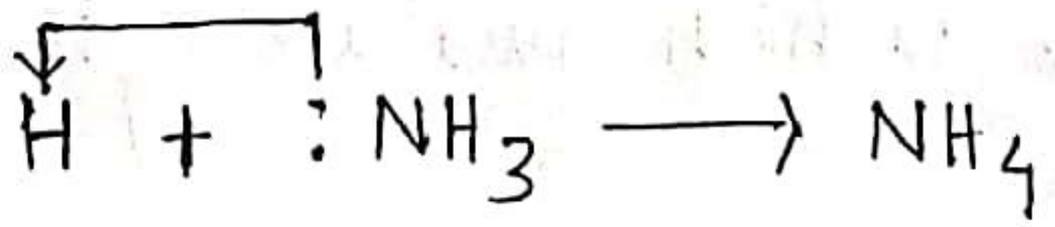
Acid is "Proton donor".

Base is "Proton accepter".

3. Lewis Theory:-

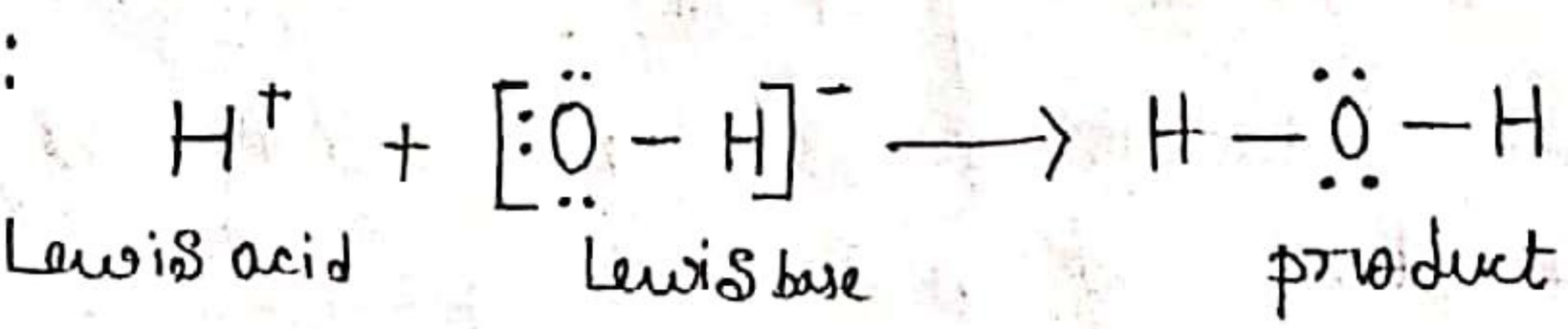
According to Lewis theory an acid may be defined as which can accept an electorn pair to form coordinate bond.

Example:



According to this lewis theory a base may be defined as which can donate an electorn pair to form coordinate bond.

Example:



Acid is "Electorn pair accepter"

Base is "Electorn pair donor".

Acid Base Indicator:-

An acid base indicator is the substance which is used to determine the end-point of acid base titration by changing the colour of reaction mixture.

Theory of Indicator:-

There are two theory of indicator. They are listed as following.—

1. Ostwald's Theory
2. Quinonoid Theory

1. Ostwald's Theory:

According to Ostwald theory an acid base indicator is a weak acid or base in nature. These substances give different colour in different medium. The formation of colour in different medium depends upon dissociative or non dissociative state of indicator.

Example: a. Phenolphthalein
b. Methyl orange

@ Phenolphthalein (HPh)

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

(colourless) (pink)

when phenolphthalein is added to acidic med.

$$HPh \rightleftharpoons \boxed{H^+} + Ph^-$$

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

→ common ion effect

When phenolphthalein is added to acid H^+ of acid (HCl) suppress H^+ of phenolphthalein due to common ion effect. So it will remain in non dissociative form and then show no colour.

⑥ Methyl orange (MeOH)

$$\underset{\text{(Yellow)}}{MeOH} \rightleftharpoons \underset{\text{(red)}}{Me^+} + OH^-$$

When methyl orange is added to acidic medium

$$MeOH \rightleftharpoons Me^+ + \boxed{OH^-}$$

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

$$\boxed{OH^-} + \boxed{H^+} \rightarrow H_2O$$

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

When base is added

- $MeOH \rightleftharpoons Me^{+} + \boxed{OH^{-}}$

$NaOH \rightleftharpoons Na^{+} + \boxed{OH^{-}}$

↳ common ion effect

due to common ion effect OH^{-} ions of MeOH is suppressed by OH^{-} of NaOH, to non dissociative state so yellow colour.

2. Quinonoid Theory:

According to quinonoid theory indicator exist in two forms

ⓐ benzenoid form (benzene nucleus)

ⓑ quinonoid form (quinone nucleus)

The different form of indicator give different colour in different medium.

Example: A. Phenolphthalein

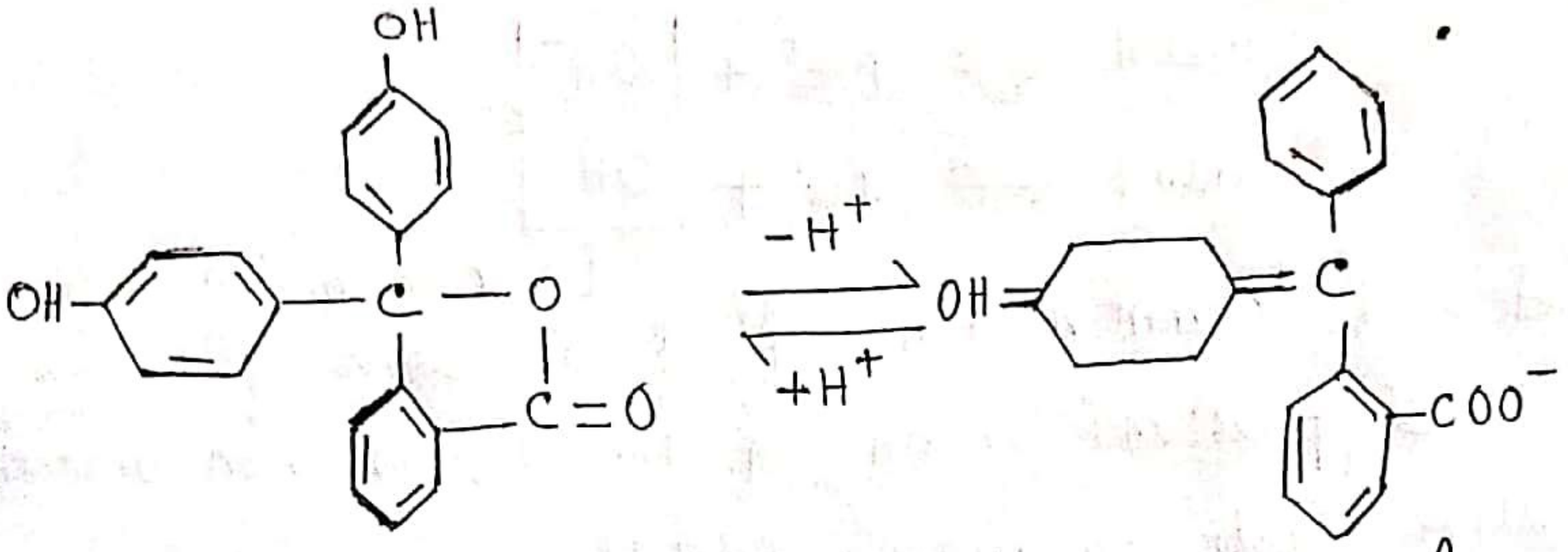
B. Methyl orange

A. Phenolphthalein:-

Phenolphthalein shows bezenoid form in acidic medium which gives no colour.

On the other hand phenolphthalein shows quinonoid form in basic medium which gives pink

colour.

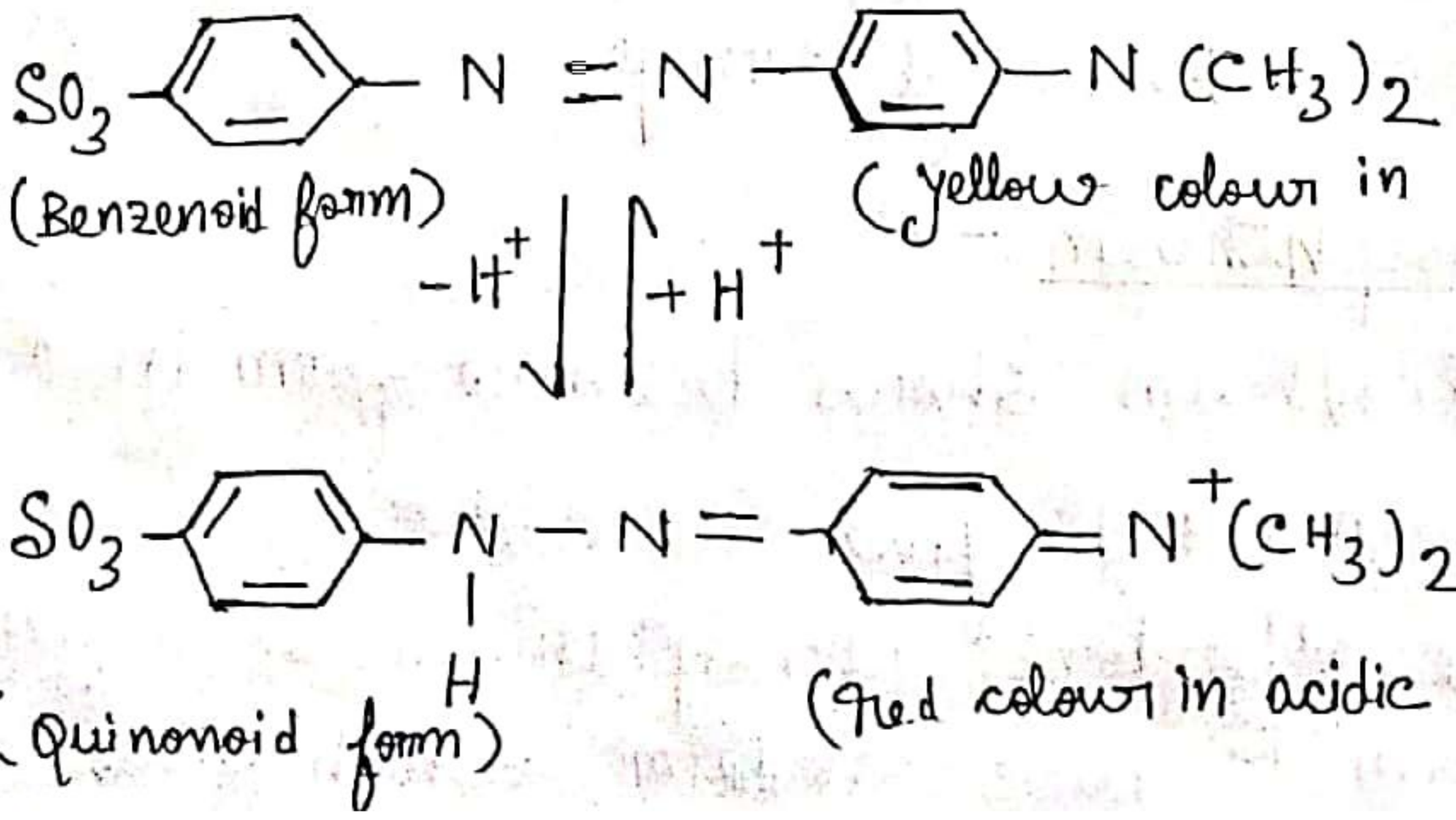


Benzenoid form
(colourless in acidic medium)

Quinonoid form
(Pink colour in basic medium)

B. Methyl Orange :-

Methyl organge shows benzenoid form in basic medium which gives yellow colour.
On the other hand methyl orange shows quinonoid form in acidic medium which gives red colour.



(Benzenoid form) (yellow colour in basic medium)

(Quinonoid form) (red colour in acidic medium)

Neutralization Curve :-

It is a graphical representation between the amount of acid or base and the change of pH during the acid base reaction.

Different neutralization curve for different acid base titration ——

Neutralization Curve of

1. Strong acid and Strong base
2. Weak acid and Strong base
3. Strong acid and weak base
4. Weak acid and Weak base

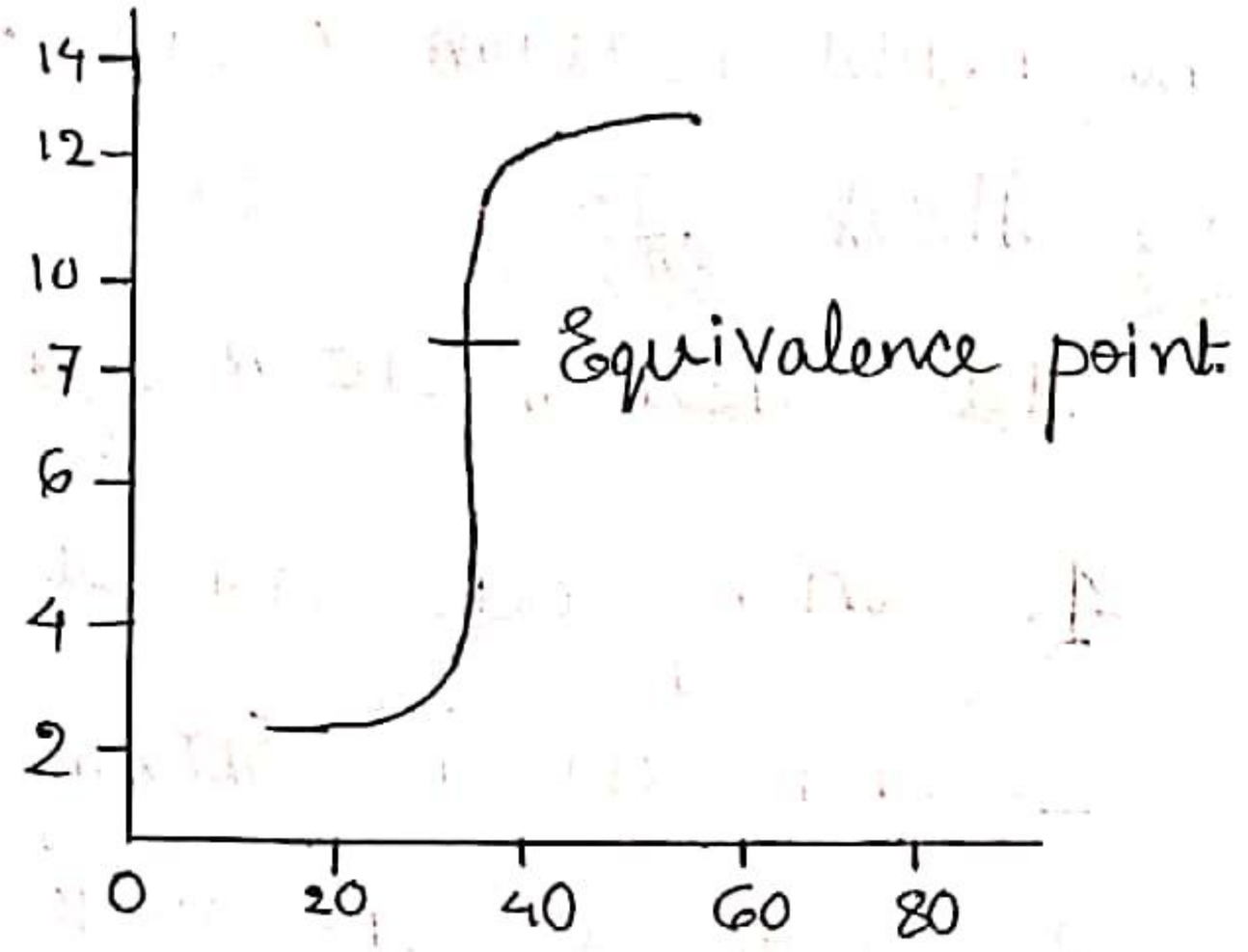
1. Neutralization Curve of Strong acid Strong base :-

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

HCl = Hydrochloric acid
NaOH = Sodium Hydroxide
NaCl = Sodium Chloride
H_2O = Water

The initial graph will show low pH because Hydrochloric acid (HCl) is Strong acid, when Sodium Hydroxide (NaOH) is added to Hydrochloric acid

(HCl) more and more H^+ ion combine with ion to form H_2O which decreases the concentration of H^+. In the beginning curve will be flat, but when all H^+ ion neutralized by OH^- ion there will be sudden rise in pH.



2. Neutrialization curve of weak acid and Strong base :-

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

CH_3COOH = Acetic acid

$NaOH$ = Sodium Hydroxide

CH_3COONa = Sodium acetate

H_2O = Water

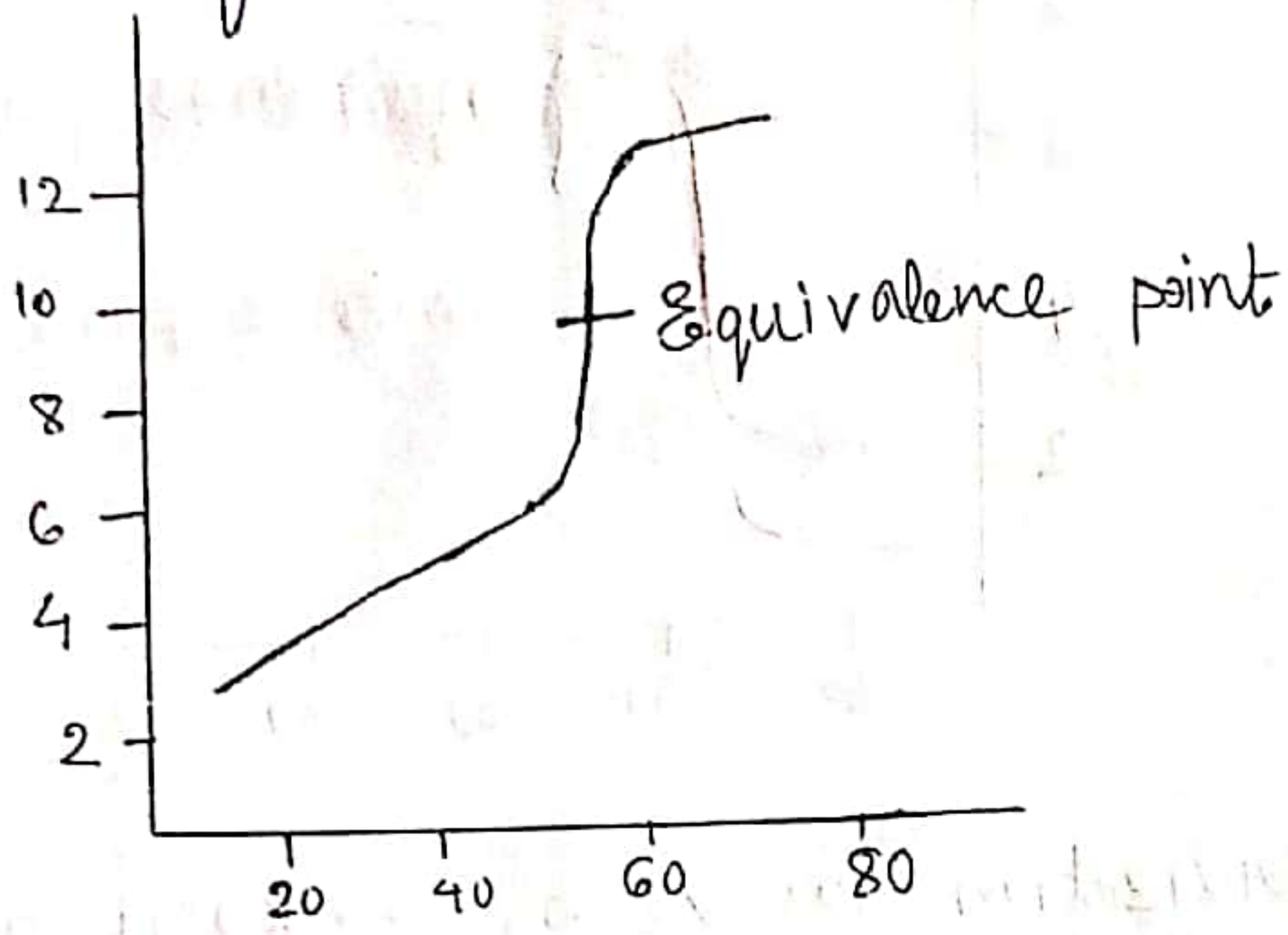
The graph at initial will start at pH 2-4 because Acetic acid is weak acid, when Sodium hydroxide is added to acetic acid (CH_3COOH) H^+ ion is neutralized by OH^- ion, but at the same time

acetate

of weak acid due to

and H^+ ion concentration decreases the

in rise of pH of solution.



3. Neutralization curve of Strong acid and weak base

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

NH_4OH = Ammonium hydroxide

HCl = Hydrochloric acid

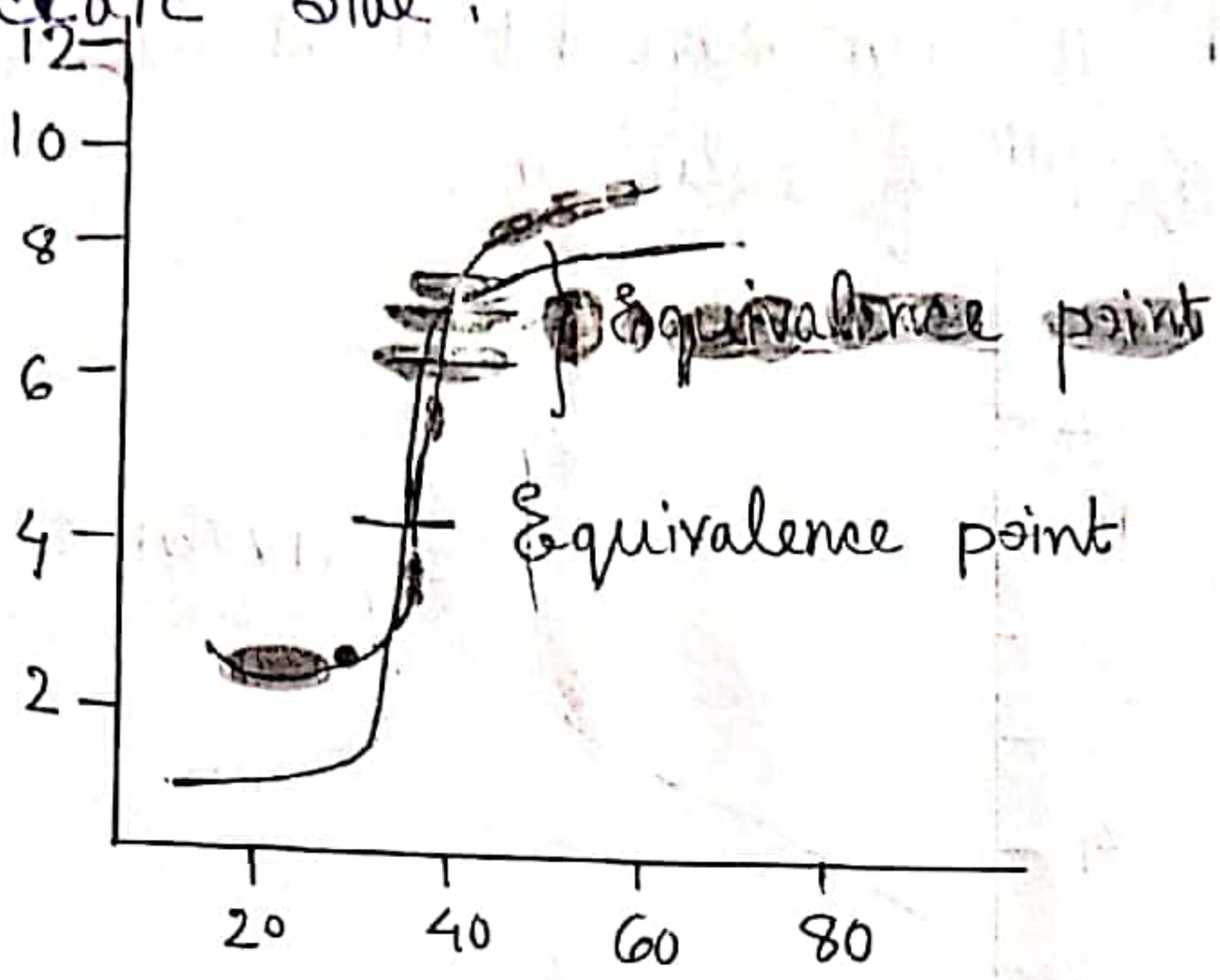
NH_4Cl = Ammonium Chloride

H_2O = Water

The graph will start at above low pH because Hydrochloric acid (HCl) is Strong acid, when Ammonium hydroxide (NH_4OH) is added to Hydrochloric acid (HCl) H^+ ion is neutralized by OH^- ion but at a slow rate. The rise in pH is seen by sudden change in pH. But due to hydrolysis

Ammonium Chloride (NH_4Cl)

on acidic Side.



4. Neutralization curve of Weak acid and Weak base :—

$$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$$

CH_3COOH = Acetic acid

NH_4OH = Sodium Ammonium hydroxide

CH_3COONH_4 = Ammonium acetate

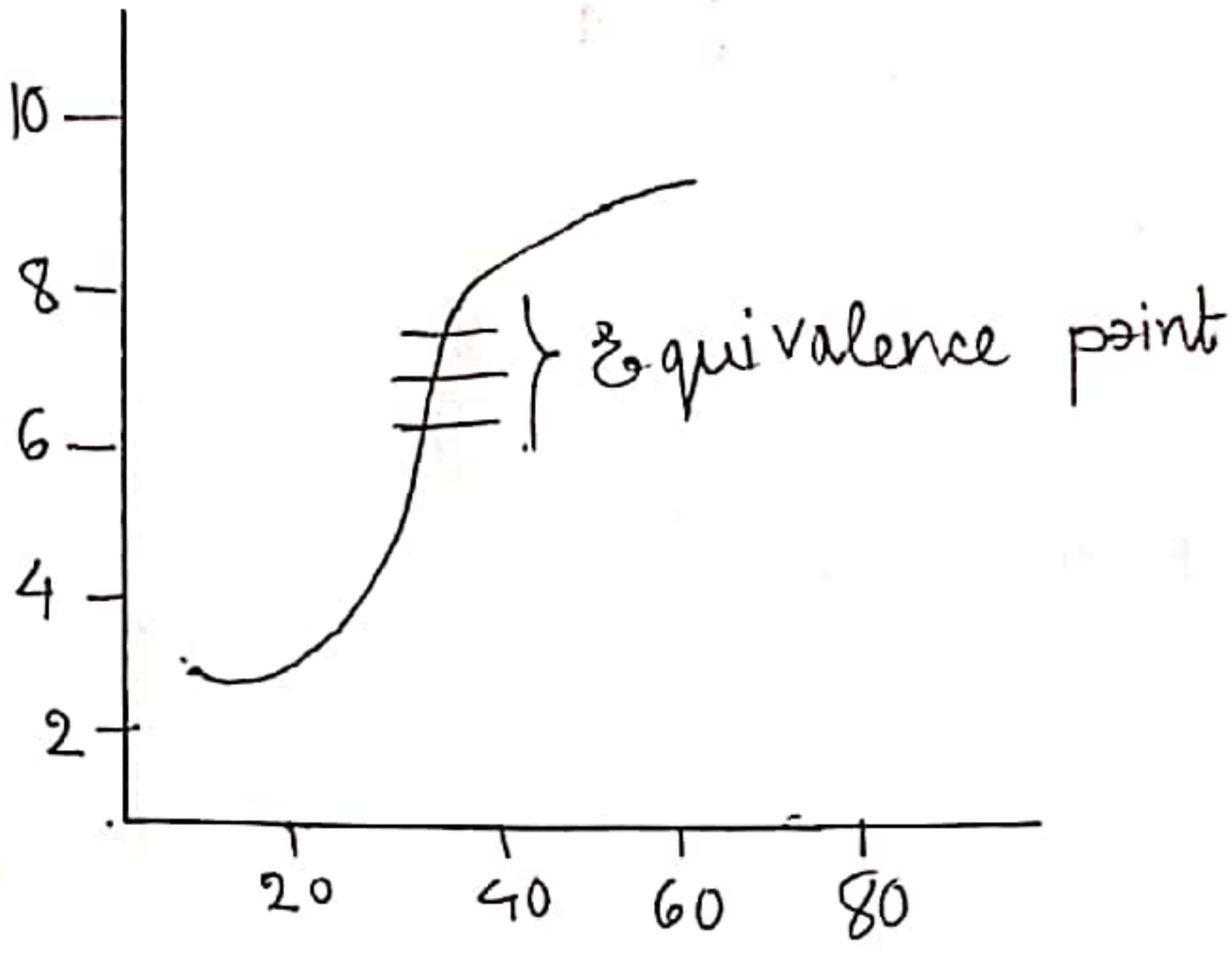
H_2O = Water

The graph will start show low pH because Acetic acid (CH_3COOH) is weak acid. After the addition of base there will slight increase in pH as ammonium hydroxide (NH_4OH) is a weak base. There will be three pH range depend on the dissociation of titrant.—

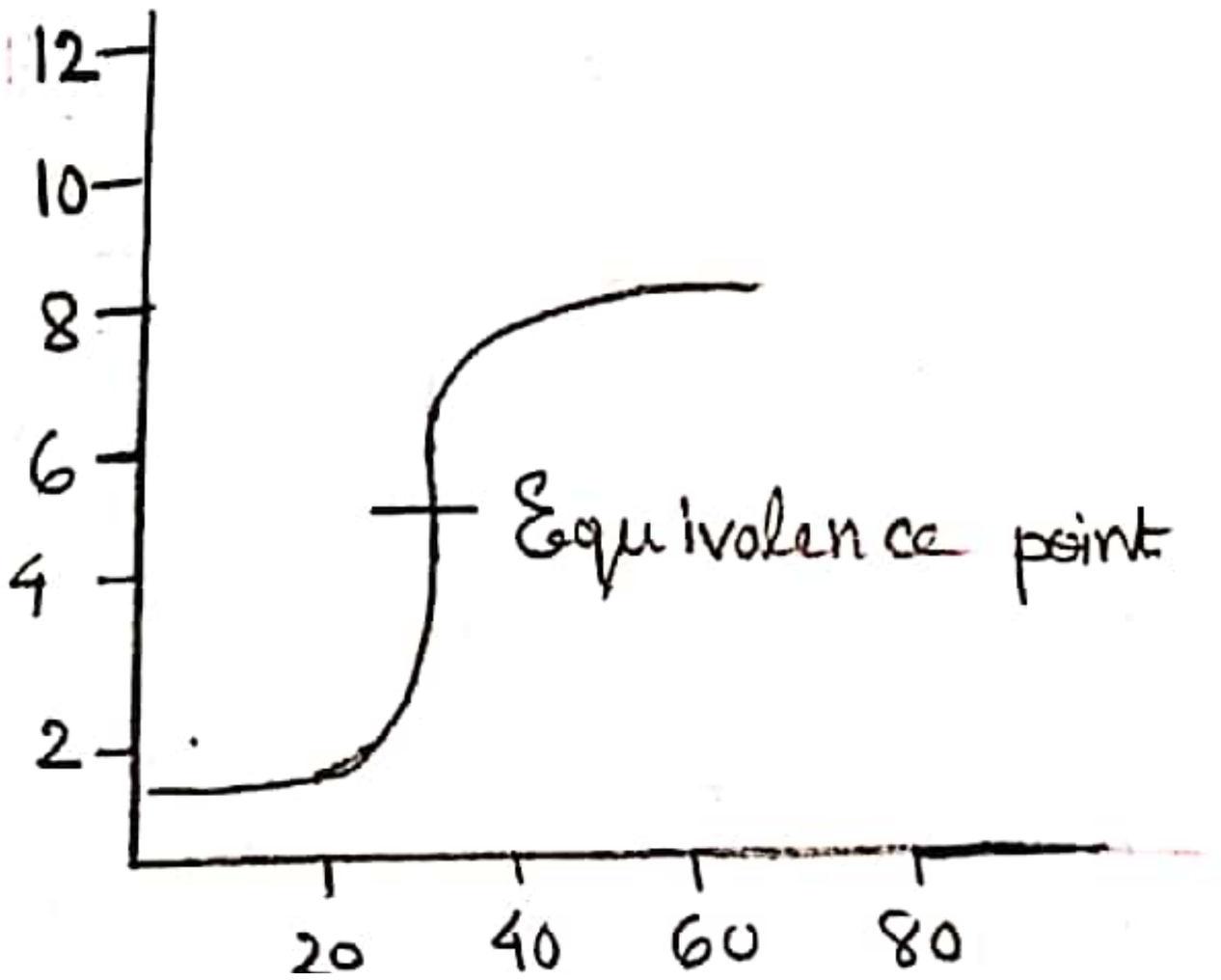
(i) $K_a = K_b$ p^H will be 7

(ii) $K_a > K_b$ it will be less than 7

(iii) $K_a < K_b$ it will be more than 7



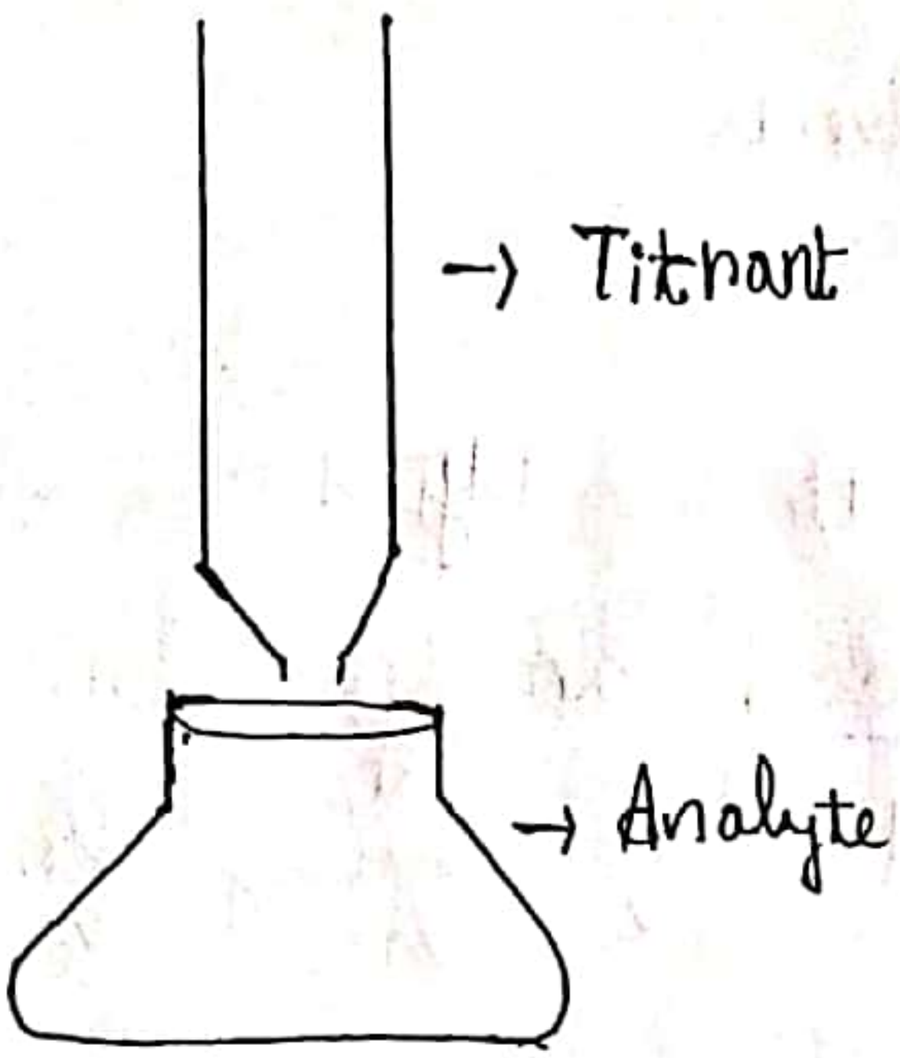
No 3 graph (Strong acid and weak base)



Non Aqueous Titration

Definition:

The Non-aqueous titration is this type of titration in which we use the solvent other than water.



Aqueous – If Solvent H_2O

Non-aqueous – If Solvent other than H_2O (organic Solvent)

When Titrant and Analyte mixed in other than water (organic Solvent) then the titration called Non-aqueous Titration

Why we use Non-aqueous Titration

Drug Nature
- Acidic
  - Strong acidic: $HCl \rightarrow H^+ + Cl^- - 100\%$
  - Weak acidic: $CH_3COOH \rightarrow CH_3COO^- + H^+ - < 100\%$
- Basic
  - Strong basic: $NaOH \rightarrow Na^+ + OH^- - 100\%$
  - Weak basic: $NH_4OH \rightarrow NH_4^+ + OH^- - < 100\%$

If drug nature is weak acidic and weak basic, then we use Non-aqueous titration.

Solvents :

Following Solvents are used in Non- aqueous titration —

(i) Protophilic Solvents

(ii) Protogenic Solvents

(iii) Amphiprotic Solvents

(iv) Aprotic Solvents

(i) Protophilic Solvents :

Protophilic Solvents are those types of Solvents that are used for weak acid analysis. And this type of Solvent take proton forcefully from weak acid.

Example – liquid ammonia, amines.

(ii) Protogenic Solvents :

protogenic Solvents are those types of Solvents that are used for weak base analysis. And this type of Solvent give proton forcefully to weak base.

Example – Sulfunic acid
hydrogen fluoride

(iii) Amphiprotic Solvents:

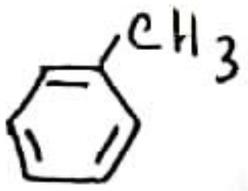
Amphiprotic Solvents are those types of Solvents that can show acid and base both character. This type of Solvent can give proton and can take proton.

Example [redacted], Alcohol, Weak organic acid.

(iv) Aprotic Solvent:

Aprotic Solvent are these types of Solvents that control the rate of reaction. This type of Solvent can not take participate in the reaction and can not give proton and can not take proton.

Example: Benzene 

toluene 

Character of

Acid → Proton দেয়

Base → Proton নেয় অথবা ইলেকট্রন গ্রহণ করে

- protophilic → weak acid থেকে proton নেয়
- protogenic → weak base কে Proton ফেরত দেয়
- Amphiprotic → both নেয় আবার দেয় প্রোটন
- Aprotic → reaction rate control, not participate in the reaction.

Acidimetry and Alkalimetry Titration:

Types of Non-Aqueous Titration

- Acidimetry Titration
- Alkalimetry Titration

1. Acidimetry Titration:

→ If any drug have weak acid and weak base nature then we use Non-aqueous ~~bidradepose~~ Solvent instead of water (H_2O).

→ It is a type of Non-aqueous titration.

→ In this type of titration we use Strong acid as a Solvent for weak basic nature drug.

Example: Estimation of Sodium benzoate
& Estimation of Ephedrine HCl

2. Alkalimetry Titration:

→ It is a type of Non-aqueous Titration.

→ In this type of titration we use Strong base as a Solvent for weak acidic nature

drug.

Example: Estimation of Sodium methoxide

Acidimetry – Solvent (strong acid) – For weak basic nature of drug

Alkalimetry – Solvent (strong base) – For weak acidic nature of drug

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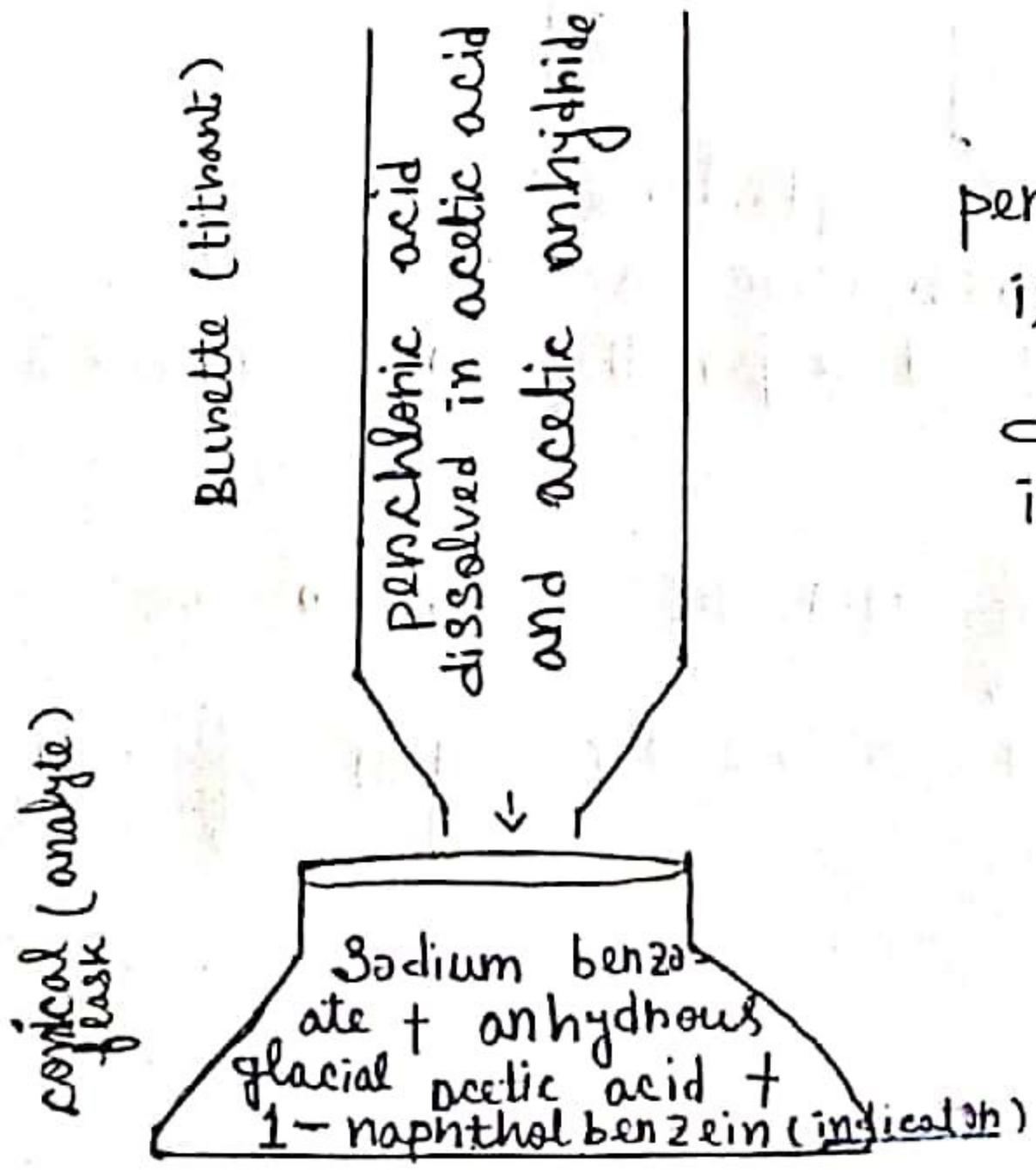
◼ Estimation of Sodium Benzoate:

Principle: It is Acidimetry titration in which measure amount of acid (perchloric acid) used in titration for analysis of base (Sodium benzoate) using napthol-benzen solution as an indicator.



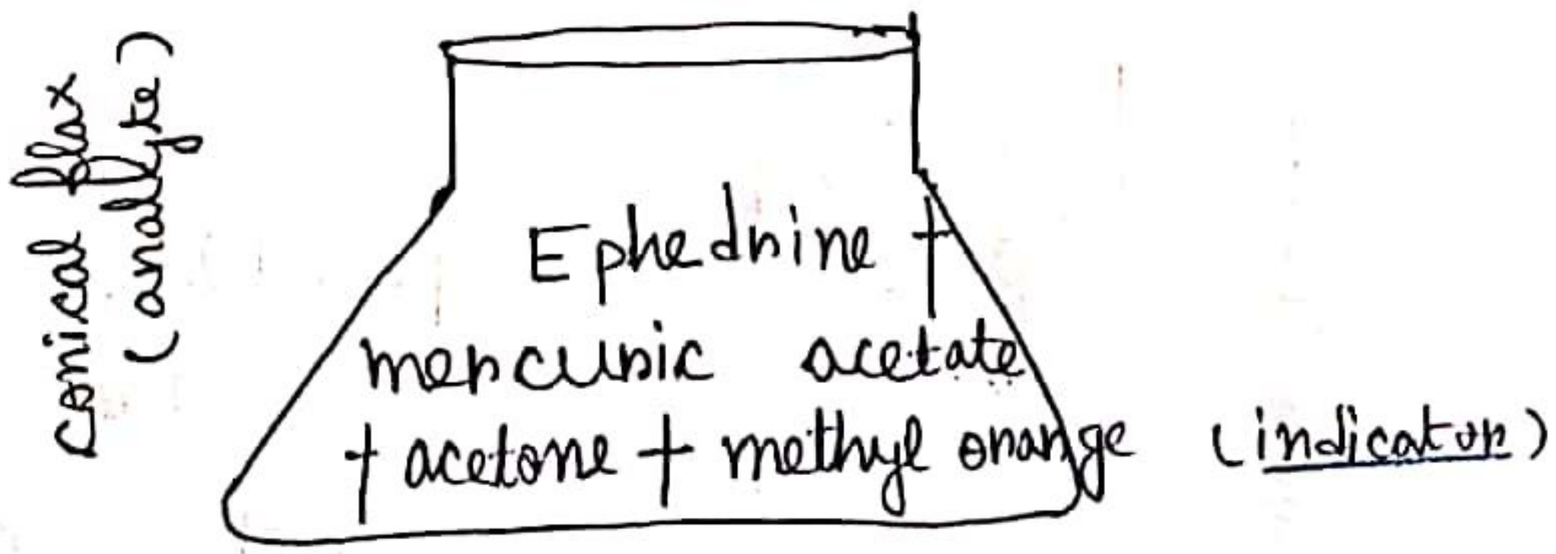
Factor: 1ml of 0.1 M perchloric acid is equivalent to 0.014441 gm of Sodium benzoate.

◪ Estimation of Ephedrine HCl:

Burette (titrant)

Perchloric acid dissolved in acetic acid and acetic anhydride

perchloric acid is added untill red colour is obtained.



Factor 1ml of 0.1 M perchloric acid is equivalent to 0.02017 gm of Ephedrine HCl.