Unit – II

Acid – Base Titration

Acid – Base titration is also called as neutralization in which H^+ ion in solution is titrated with OH^- ion.

Ex:-

$$\underset{Acid}{HCl} + \underset{Base}{NaOH} \rightleftharpoons \underset{Salt}{NaCl} + H_2O \quad \{H^+ + OH^- \rightleftharpoons H_2O\}$$

$$\underset{weak\ acid}{CH_3COOH} + \underset{strong\ base}{NaOH} \rightleftharpoons CH_3COONa + H_2O$$

$$\underset{Strong\ acid}{HCl} + \underset{weak\ Base}{NH_4OH} \rightleftharpoons NH_4Cl + H_2O \quad \{\underset{Hydronium\ ion}{H_3O^+} + OH^- \rightleftharpoons H_2O\}$$

Acid-Base Theory:-

	Acid	Base
Arrhenius	H^+ Donor	OH^- Donor
Bronsted	Proton Donor	Proton Acceptor
Lewis	Electron pair Acceptor	Electron pair Donor.

Arrhenius Theory :- Acid is a substance that when dissolve in water gives H^+ ion while base is a substance that when dissolve in water gives OH^- ion.

Ex:-

$$\underset{Acid}{HA} \rightleftharpoons \textcircled{H^+} + A^-.$$

$$\underset{Base}{BOH} \rightleftharpoons B^+ + \textcircled{OH^-}.$$

Bronsted Theory:- Acid is a substance which donate proton (H^+) while Base is a substance which accept proton.

Ex:- Acid — Base

$$\underset{\text{Weak Acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Conjugate Strong Base}}{CH_3COO^-} + \underset{\text{Proton}}{\boxed{H^+}}$$

* **Note:-** Conjugate Base is obtained from an Acid after removal of a Proton.

$$\underset{\text{Strong Acid}}{H_2SO_4} \rightleftharpoons \underset{\text{Conjugate Weak Base}}{HSO_4^-} + \underset{\text{Proton}}{H^+}$$

Remark:- * The Conjugate base of weak Acid is strong base while the Conjugate base of strong acid is weak base.

Lewis Theory:- Any substance that can accept electron pair is called Acid while any substance that can donate e^- pair is called base.

Ex:- BF_3 — Lewis acid; $:NH_3$ — Lewis Base

Law of Mass Action:-

The rate of chemical reaction is directly proportional to the active masses (Conc.) of the reacting substances.

Rate of chemical reaction ∝ Active mass of Reactants.

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

$R_f \propto [A][B]$	$R_b \propto [C][D]$
$R_f = K_f[A][B]$	$R_b = K_b[C][D]$

At Equilibrium :-

$$R_f = R_b$$

$$K_f[A][B] = K_b[C][D]$$

$$\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]} , \quad \boxed{K = \frac{[C][D]}{[A][B]}}$$

→ Equilibrium Constant

Eg. $2A + 3B \rightleftharpoons 2C + 3D$

$$R_f = K_f[A]^2[B]^3$$

$$R_b = K_b[C]^2[D]^3$$

$$K = \frac{[C]^2[D]^3}{[A]^2[B]^3}$$

Acid - Base Equilibrium / Ionic Product of water :-

Consider a reversible chemical reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

Let us consider the dissociation of weak acid in water.

Acid:-

$$\underset{\text{Acid}}{HA} \rightleftharpoons A^- + \boxed{H^+}$$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

dissociation constant of Acid.

Base :- $A^- + H_2O \rightleftharpoons HA + \boxed{OH^-}$

$$K_b = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

dissociation Constant of Base

Water

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

$$K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_w = [H^+]\,[OH^-]$$

dissociation constant of water or Ionic product of water

Relation between Ka, Kb & Kw :-

$$K_a \times K_b = \frac{\cancel{[A^-]}[H^+]}{\cancel{[HA]}} \times \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}$$

$$K_a \times K_b = [H^+]\,[OH^-]$$

$$\boxed{K_a \times K_b = K_w}$$

pH :- pH is the negative logarithm of Hydrogen ion concentration.

$$\boxed{pH = -\log [H^+]}$$
$$= \log \frac{1}{[H^+]}$$

* $$\boxed{pOH = -\log [OH^-]}$$
$$= \log \frac{1}{[OH^-]}$$

* $$\boxed{pH + pOH = pK_w}$$

* $$\boxed{pH + pOH = 14}$$

Q. Find pH.

$[H^+] = 10^{-5}$

$pH = -\log[H^+]$

$= -\log[10^{-5}]$

$= -[-5]$

$= 5$ Ans

Q. If $[OH^-]$ of a solution is 10^{-11} the find the value of pH.

Solve:-

$pOH = -\log[OH^-]$

$= -\log[10^{-11}]$

$= -[-11]$

$= 11$

$pH + pOH = 14$

$pH + 11 = 14$

$pH = 14 - 11$

$pH = 3.$ Ans.

Q. Find the pH of 0.001 M HCl solution.

Solve:-

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

1 mol. 1 mol. 1 mol.

$pH = -\log[H^+]$

$= -\log[0.001]$

$= -\log[10^{-3}]$

$= -[-3]$

$= 3$ Ans

Q. Find the pH of 0.05 M H_2SO_4.

Solve:-

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

2 mol.

$pH = -\log[H^+]$

$= -\log[0.10]$

$= -\log[10^{-1}]$

$= -[-1]$

$= 1$ Ans.

Q. Determine the pH of 2×10^{-5} M HCl.

Solve:- $[H^+] = [2 \times 10^{-5}]$ $HCl \rightarrow H^+ + Cl^-$

1 mol. 1 mol.

$pH = -\log [H^+]$

$= -\log [2 \times 10^{-5}]$

$= -[\log 2 + \log 10^{-5}]$

$= -[0.03 + (-5)]$

$= -[0.3 - 5]$

$= -[-4.7]$

$= 4.7$ Ans

Q. Determine the pH of 3×10^{-7} N H_3PO_4.

Solve:- $M = \frac{N}{x\,factor} = \frac{\cancel{3} \times 10^{-7}}{\cancel{3}}$

$M = 10^{-7}$

$pH = -\log [H^+]$

$= -\log [3 \times 10^{-7}]$

$= -[\log 3 + \log 10^{-7}]$

$= -[0.47 + (-7)]$

$= -[0.47 - 7]$

$= 6.53$ Ans

Buffer Solution:-

Buffer solution is a solution which helps in maintaining a specific pH.

or

Buffer solution is a solution whose acidity and Basicity is reserive.

(i) Buffer solution of weak Acid & Strong Base:-

Eg.- CH_3COONa

(ii) Buffer solution of strong Acid and weak Base:-

Eg:- HCl , NH_4Cl NH_4OH

Acid Base

Hinderson Hasselbalch Equation :-

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + \underset{\text{Conjugate Base}}{A^-}$$

$$Ka = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = Ka \times \frac{[HA]}{[A^-]}$$

$$-\log[H^+] = -\log\left(Ka \times \frac{[HA]}{[A^-]}\right)$$

$$-\log[H^+] = -\left(\log Ka + \log\frac{[HA]}{[A^-]}\right)$$

$$pH = -\log ka - \log\frac{[HA]}{[A^-]}$$

$$\boxed{pH = pka + \log\frac{[A^-]}{[HA]}}$$

$$\boxed{pH = pka + \log\frac{[\text{Conjugate Base}]}{[\text{Acid}]}}$$

* This equation is used to Calculate the pH of Buffer solution.

Q.(i) A Buffer solution made by 0.2 M acetic acid (CH_3COOH) and 0.3 M Sodium acetate (CH_3COONa) is given. Calculate the pH of the solution. If the pka of the CH_3COOH is 4.76.

Solution:-

$$pH = pka + \log\frac{[A^-]}{[HA]}$$

$$= 4.76 + \log\frac{[0.3]}{[0.2]}$$

$$= 4.76 + \log\frac{[3]}{[2]}$$

$$= 4.76 + \log 3 - \log 2$$

$= 4.76 + 0.47 - 0.30$

$= 5.23 - 0.30$

$= 4.93$ Ans

Q(ii) The pH of given solution is lactic acid & lactate is 4.3 Calculate the pka value of lactic acid when the conc. of lactic acid & lactate of 0.02 M & 0.073 M respectively. {log 3.65 = 0.56}

Solve:-

$$pH = pka + \log \frac{[A^-]}{[HA]}$$

$$4.3 = pka + \log \frac{[0.073]}{[0.02]}$$

$4.3 = pka + \log 3.~~8~~65$ {log 3.65 = 0.56)

$pka = 4.3 - 0.$[illegible]56

$pka = 3.74$ Ans.

Q.(iii) what is the ratio of concentration of Acetic acid and acetate Ion required to prepare a Buffer ~~Sol~~ with pH 5.2. The pka of acetic acid is 4.76. (antilog of 0.44 = 2.75)

Solution:-

$$pH = pka + \log \frac{[A^-]}{[HA]}$$

$$5.2 = 4.76 + \log \frac{[acetate]}{[acetic\ acid]}$$

$$5.2 - 4.76 = \log \frac{[acetate]}{[acetic\ acid]}$$

$$0.44 = \log \frac{[acetate]}{[acetic\ acid]}$$

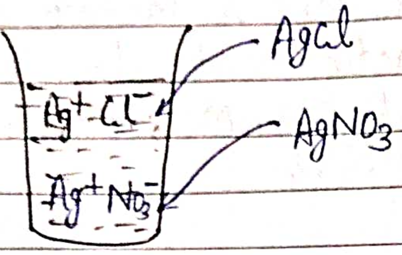
$$\log \frac{[A^-]}{[HA]} = 0.44$$

Antilog of 0.44 = 2.75

$$\frac{[A^-]}{[HA]} = 2.75$$ Ans

Common Ion Effect :-

Solubility of AgCl is decreased due to addition of $AgNO_3$ with one ion (Ag^+) in common.



$$AgCl \rightleftharpoons \boxed{Ag^+} + Cl^-$$
$$AgNO_3 \rightleftharpoons \boxed{Ag^+} + NO_3^-$$

#→ Solubility & Solubility Product :-

* Solubility of a substance is amount of that substance which can be dissolve in given amount of solvent at specific temperature & pressure.

* It is represented by 's'.

\# Solubility product (Ksp) is the product of dissolved ion concentration raised to the power of their coefficient.

$$Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$$
$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = \frac{[A^{y+}]^x\,[B^{x-}]^y}{[A_xB_y]}$$

$$\boxed{K_{sp} = [A^{y+}]^x\,[B^{x-}]^y}$$

Common Ion Effect :-

Common Ion effect refers to decrease in solubility of an electrolyte (salt) by addition of another electrolyte or salt with an ion common in both the electrolytes.

* Take a sparingly soluble salt AgCl and dissolve it in water:

$$AgCl \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{Cl^-}$$

$$K_{sp} = [Ag^+][Cl^-]$$
$$= \boxed{S \times S}$$

$$AgNO_3 \rightleftharpoons \underset{m}{Ag^+} + \underset{m}{NO_3^-}$$

$$AgCl^- \rightleftharpoons \underset{S'}{Ag^+} + \underset{S'}{Cl^-}$$

$$(m+S') \quad (S')$$

$$K_{sp} = [Ag^+][Cl^-]$$
$$= (m+S')(S')$$

$$S \times S = (m+S')(S')$$
$$\boxed{S' < S}$$

Acid - Base Indicator :-

* Acid - Base Titration is usually reaction in which H^+ ion in solution is titrated with OH^- ion which is also called as neutralization.

* The point at which complete neutralization is achieve called as End point are Equivalence point.

* An indicator is a substance which is used to determine the end point in a reaction / titration. It produce colour change at a particular stage of titration.

⇒ To theories have been proposed to explain the change of colours of Acid - Base Indicator with change in pH.

(i) Ostwald Ionic Theory
(ii) Quinonaid Theory (Resonance Theory)

(i) **Ostwald Theory:-**

This theory explains the colour change of Indicators when H^+ or OH^- ions are in corporated to the respective solution.

According to this theory -

(i) Acid - Base Indicator is either weak organic acid or weak organic Base. The Colour change is due to Ionization of Acid - Base Indicator. The Ionized form of Indicator has different Colour than unIonized form. If any acid indicator represented as -

$$\underset{\substack{\text{Colour (1)} \\ \text{(Colourless)}}}{HIn} \rightleftharpoons \underset{\substack{\text{Colour (2)} \\ \text{(Pink.)}}}{H^+ + In^-}$$

If a Basic indicator is represented by -

$$\underset{\substack{\text{Colour (1)} \\ \text{(Yellow)}}}{InOH} \rightleftharpoons \underset{\substack{\text{Colour (2)} \\ \text{(Red)}}}{In^+ + OH^-}$$

(ii) Since, A Indicator is either a weak Acid or weak Base Its ionization is affected in Acid or Base. In case the Indicator is weak Acid Its ionisation is very low in Acid due to common H^+ ions. while It is fairly Ionised in Basic solution. Similarly If the Indicator is a weak Base Its Ionisation is very low in Basic solution due to Common OH^- Ion. while It is fairly ionised in Acid.

Eg:- Phenophthaline is represented as HPh it ionises in solution as follows -

$$\underset{\text{(colourless)}}{HPh} \rightleftharpoons H^+ + \underset{\text{(Pink)}}{Ph^-}$$

Phenolphthalein In Acid

$$\begin{array}{c}COOH\\|\\COOH\end{array} \rightleftharpoons \begin{array}{c}COO^-\\|\\COO^-\end{array} + 2H^+$$

oxalic acid

Ionisation of HPh is decreased in Oxalic acid due to poresence of Common H^+ ions in both.

* In presence of an Acid Ionisation of HPh is negligible ~~at~~ as equilibrium shift to left hand side due to high Conc. of H^+ ion. The solution would remain Colourless.

* An addition of Base H^+ ions are absorbed by OH^- ions to form water. and the equilibrium ~~to~~ shift toward right hand side. And the Conc. of Ph^- ion increases giving pink colour to solution.

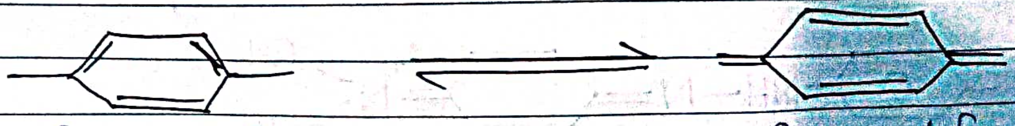
* Applying law of mass Action -

$$\boxed{K = \frac{[H^+][Ph^-]}{[HPh]}}$$

(2.) Quinonoid Theory (Resonance Theory) :-

According to this theory,

(i) The Acid-Base indicators exist in two tautomeric forms having different structures. Both forms are in equilibrium. One form is turned Benzenoid and other is Quinonoid forms.



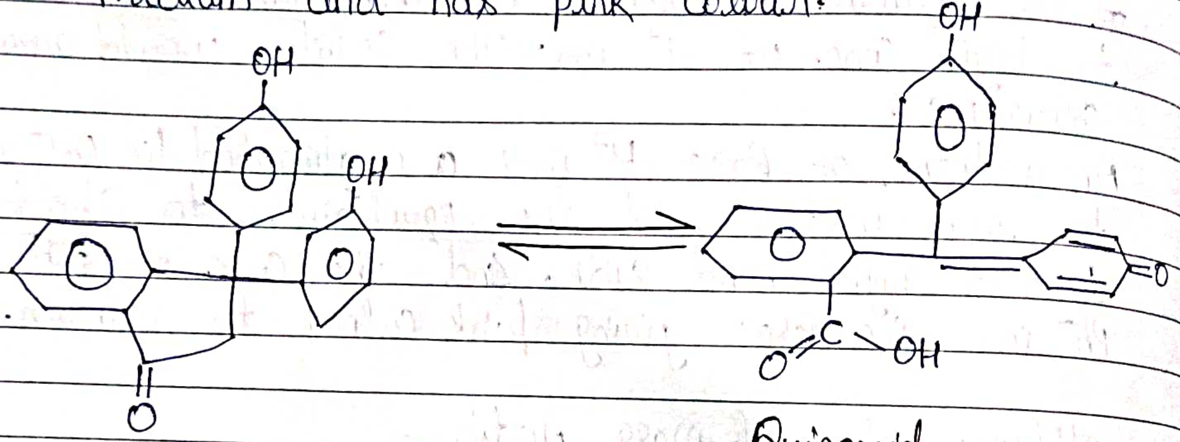
Benzenoid Form

Quinonoid form

(ii) Both forms has different Colour. The Colour Change due to interconversion of one tautomer to another.

(iii) One form mainly exist in Acidic medium and other in Alkaline medium.

Example:- 1. **Phenolphthaline :-** It has Benzenoid form in Acidic medium and Colourless while quinonoid form in Basic medium and has pink Colour.

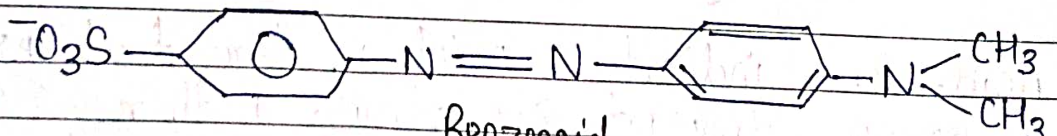


Benzenoid
(Colourless)

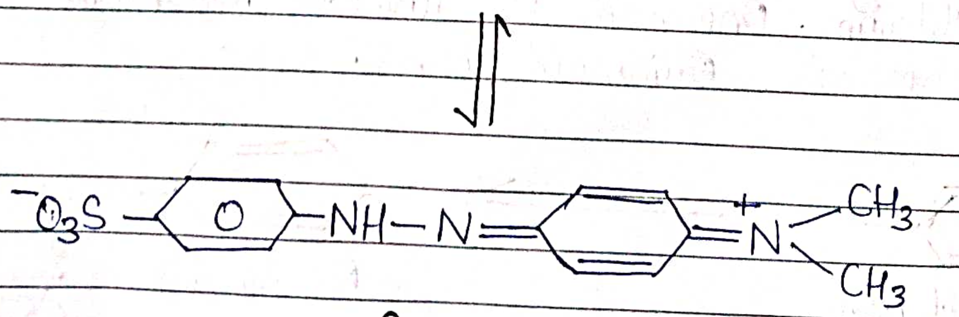
Quinonoid
(Pink)

Ex:- 2. **Methyl Orange:-**

It has Benzenoid form in Basic medium and Quinonoid form in Acidic medium.



Benzenoid



Quinonoid

Classification of Acid- Base Titration.

(i) Strong Acid Strong Base Titration.

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

(ii) Weak Acid Strong Base Titration.

Ex:- $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

(iii) Strong Acid Weak Base Titration.

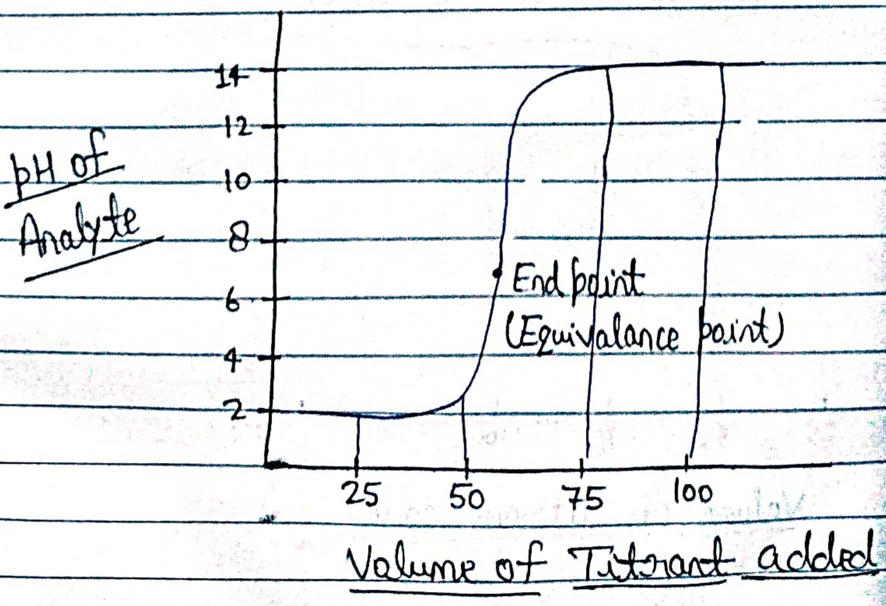
Ex:- $H_2SO_4 + NH_4OH \longrightarrow (NH_4)_2SO_4 + H_2O$

(iv) Weak Acid Weak Base Titration.

Ex:- $CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$

Neutralization Curve (Titration Curve):-

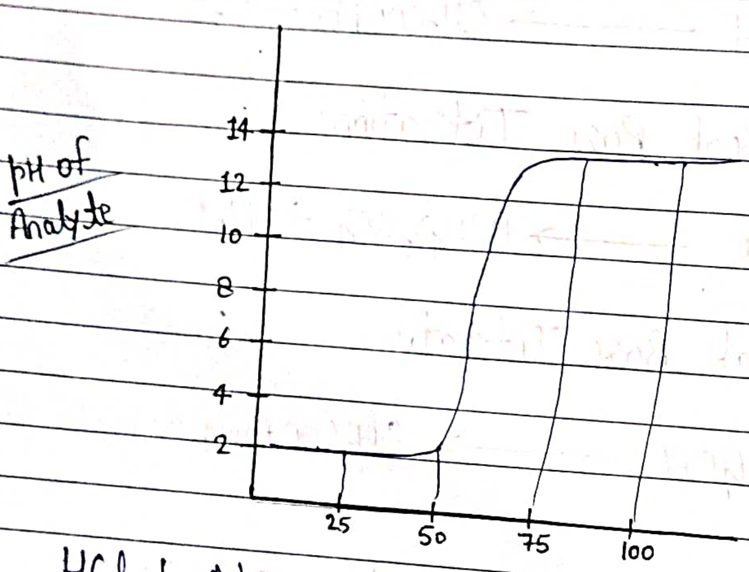
A titration curve is the plot of pH of the analyte solution v/s volume of titrant added as the titration progresses.



(i·) Titration Curve for Strong Acid Strong Base :-

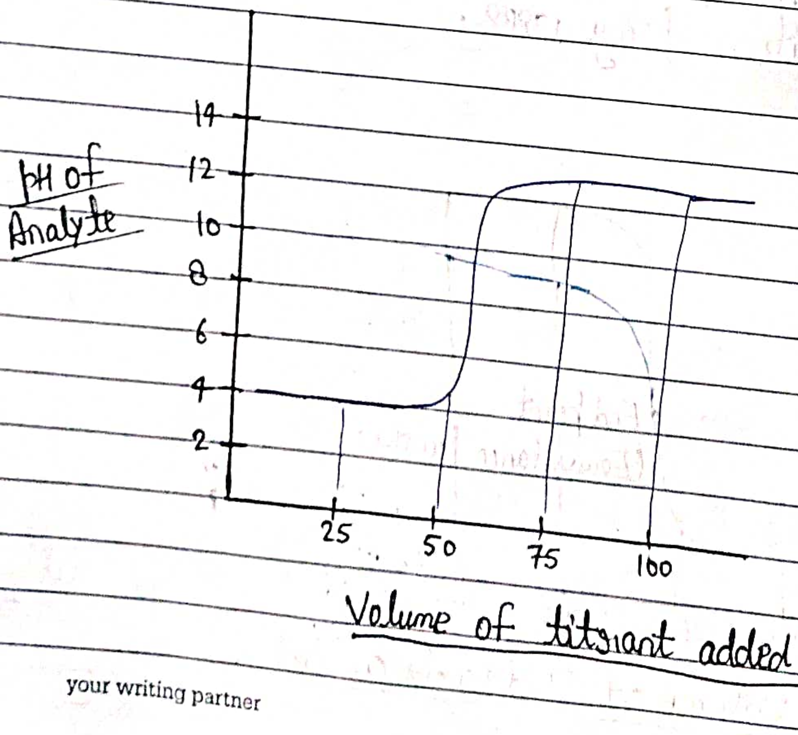
Here, lets assume analyte is HCl and titrant is NaOH. If we start plotting the pH of analyte against the volume of NaOH Consumed from the Burette we will get a titration Curve as follows:-

Titration Curve as shown below.

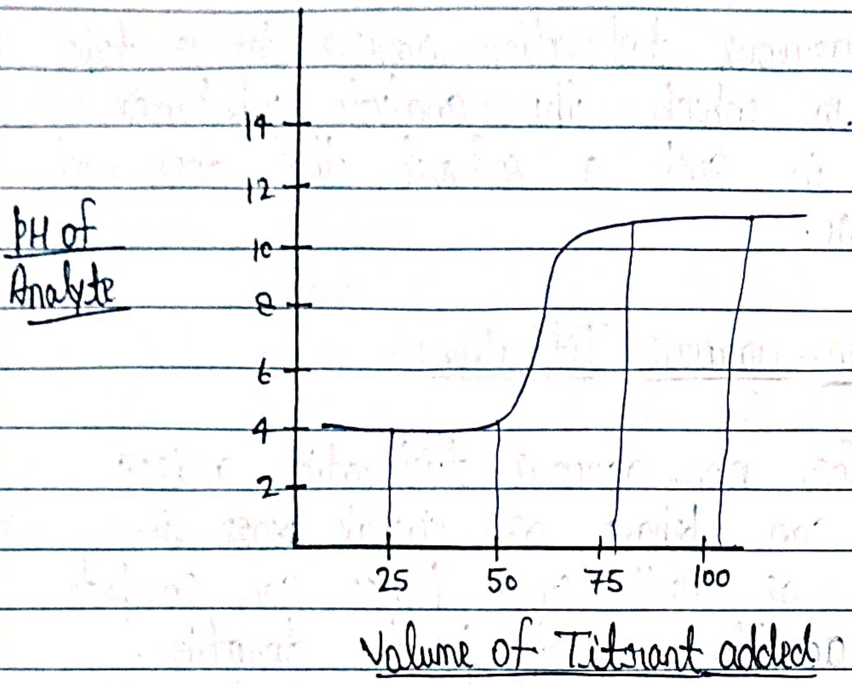


$HCl + NaOH \longrightarrow NaCl + H_2O$

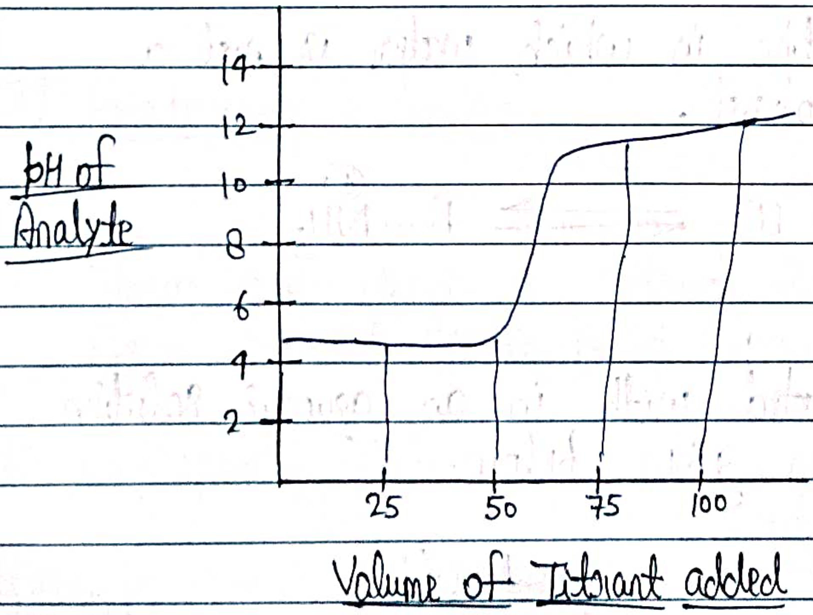
(ii) Titration Curve for weak Acid and Strong Base:-



(iii) Titration Curve for Strong Acid and Weak Base :-



(iv) Titration Curve for Weak Acid : Weak Base :-



Non- Aqueous Titration :-

Non- aqueous titration refers to a type of titration in which the analyte substance is dissolved in such a solvent that does not contain water.

Theory of Non-aqueous Titration:-

(i) The need for non-aqueous titration arises because water can behave as weak Base & a weak Acid as well and hence can compete in proton acceptance and proton donation with other weak base and weak Acid dissolved in it.

Example:- A reaction in which water is not a suitable solvent.

$$\underset{\text{(weak base)}}{R-NH_2} + H^+ \rightleftharpoons R-\overset{\oplus}{N}H_3$$

This is competed with in an aqueous solution by the reaction given below.

$$H_2O + H^{\oplus} \rightleftharpoons H_3O^{\oplus}$$

(ii) This type of competetion provided by water towards weak base or weak acid makes it difficult to detect the end point of the titration.

Types of Non-aqueous solvent :-

Typically there are 4 types of solvent used is non-aqueous titration of given analyte.

(1) Aprotic Solvent
(2) Protophilic Solvent
(3) Protogenic solvent
(4) Amphiprotic Solvent

(1) Aprotic Solvent :-

These solvent are neither Acidic nor Basic and are chemically Inert.

E.g.:- Chloroform and Benzene.

(2) Protophilic Solvent :-

* Protophilic solvent are slightly Basic in nature and they can accept proton.

* These are used to titrate acidic analyte.

E.g.:- Amines (NH_2 group), Pyridine, DMF (Dimethyl farmamide).

(3) Protogenic Solvent :-

* These are acidic in nature and they can donate the proton.

* These are used to titrate Basic analyte.

E.g.:- Glacial Acetic Acid, Formic Acid ($HCOOH$).

(4) Amphiprotic Solvent :-

These solvent work as both protogenic and protophilic. It means they are Acidic and Basic in nature

E.g.:- Alcohol.

Advantage of Non-Aqueous Titration :-

(i) Organic Acid and Base that are Insoluble in water are soluble in non-aqueous solvent.

(ii) It is useful for titration of Very weak Acid or Very weak Base that can not be titracted in water.

(iii) Non-aqueous titration is simple and accurate.
(iv) Non-aqueous solvent may help to titrate mixtu of Acids. The individual acid can give separat end point in different solvent.

Levelling Effect :-

* Levelling effect refers to the effect of solvent on the properties of Acids and Bases.

* The strength of strong Acid is limited (levelled) by basicity of the solvent. Similarly, the strength of a strong Base is levelled by the acidity of solvent.

Eg:- Water can act as an Acid or a Base hence it produce a levelling effect on strong Acid and strong Base

Non-Aqueous Indicator :-

The important indicators used for non-aqueous titration are as follows -

(i) Crystal Voilet :-

* It is the most common indicator for the ~~weak~~ titration of Weak Base.

* It gives Voilet Colour in Basic medium and Yellowish Green Colour in Acidic medium.

Eg:-
Titration of Pyridine with per-chloric Acid.

(ii) Thymol Blue :-

* Thymol Blue is used as an Indicator for the titration of weak Acid.

* The Colour Change is from Yellow to Blue.

Acidimetry and Alkalimetry Titration:-

(i) Non-Aqueous Titration of Weak Acid:-

* Many weak Acidic substance can be titrated in appropriate non-aqueous solvent. with a sharp end point.

E.g.:-

Phenal, Sulphonamide, Amino Acid etc.

* The solvent used in the titration of weak Acid are. Pyridine, Amines, DMF (Di Methyl Farmamide), Marpholine.

* The titrant used in the titration of weak Acid are Sodium methoxide, Potassium methoxide, Lithium methoxid Tetra Butyl Ammonium hydroxide etc.

* Indicator used in the titration of Weak Acid is Thymal Blue.

(ii) Non-Aqueous Titration of Weak Base:-

* Many weak Basic substances can be titrated in an appropriate non-aqueous solvent with a sharp End point.

E.g.:- Pyridine.

* Solvent used in the titration of Weak Base are Neutral Solvent (Chlorofarm, Benzene) and Acidic Solvent (Formic Acid, Glacial Acetic Acid).

* Titrant used in the titration of weak Base may be Per-Chloric Acid.

* Indicator used in the titration of weak Base is Crystal Voilet.

*