

**SHREE H. N. SHUKLA INSTITUTE OF
PHARMACEUTICAL EDUCATION AND
RESEARCH**



B.PHARM

(SEMESTER -I)

SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I

SUBJECT CODE: BP102TP

UNIT 2 (a): ACID-BASE TITRATION

Content

(a) **Acid-base Titration-** Theories of acid-base indicators, classification of acid base titrations and theory involved in titrations of strong, weak and very weak acids and bases, neutralization curves

INTRODUCTION

With the help of acid-base titrations many inorganic and organic acids and bases can be determined with a high degree of precision and accuracy.

What is Acid-Base Titration?

Acid-base titration is a method of quantitative analysis for determining the concentration of an acid and base. The principle is based on the neutralization reaction occurring between acids and bases. This is called as **acid-base neutralization titration**.

In this titration reaction unknown amount of acid or base is titrated with the standard solution of acid or base having known concentration.

Upon dissociation, acid gives hydrogen ion. Hydrogen ion do not occur in free-state, it is always combined with one molecule of water to give H_3O^+ .



The acids which are completely ionized in water are called strong acid e.g. HCl, H_2SO_4 .

The acids which are partially ionized are called weak acids e.g. acidic acid.

Upon dissociation, base gives hydroxyl ion. E.g. NaOH, KOH.

The bases which are completely ionized in water are called strong base. E.g. NaOH.

The bases which are partially ionized are called as weak base. e.g. NH_4OH

Acid-base neutralization titration are usually reactions in which is H_3O^+ in solution is titrated by OH^- . When moles of H^+ ions are equal to moles of OH^- ion, it indicate the completion of reaction means neutralization occurs between the acid and base.

The point at which moles of H^+ ions become equal to moles of OH^- ion is generally called as equivalence point. Indicator is used to mark the **equivalence point**.

Acid-Base Theories

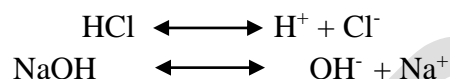
There are following different acid-base theories that proposed to explain acidic and basic properties of a substance.

1. Arrhenius theory:

The most commonly used concept of acids and bases was developed by **Savante Arrhenius** in 1884, termed as Arrhenius Theory.

According to this theory-

- “Acid is a compound that is capable of producing hydrogen ion when dissolved in water” or “it ionizes in water to give proton” and “base is a compound that is capable of producing hydroxyl ion when dissolved in water” or “it ionizes in water to give hydroxyl ion.”



- Arrhenius theory is applicable in aqueous solution only.

It is first scientific theory giving definitions for acid and base.

Limitations:

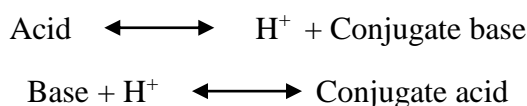
- Acids and bases have been defined only in terms of solution and not as a solid substance.
- This theory failed in elaborating the acidic and basic properties of a substance in non-aqueous solvents. It is only helpful in aqueous media.
- There are many basic substances which do not have OH^- ions but are basic in nature. This fact cannot be explained by **Arrhenius** theory. For e.g. NH_3 .
- Acidic properties of many salts (AlCl_3 in aqueous solution) could not be explained by this theory.

2. Bronsted and Lowry theory

J.N. Bronsted and **J.M. Lowry** in **1923** gave a broader concept of acids and bases.

According to this theory

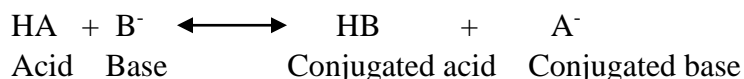
- “Acid is compound which has a tendency to lose a proton” and “base is a compound having tendency to accept a proton.
- According to this theory a proton donor and acceptor must be present in the system. The acid will transfer proton to base.
- Acid by loss of proton produces conjugate base and base by accepting proton produces conjugate acid.



Conjugate Acid-Base Pairs

The acid (HA) involved in an acid-base reaction produces a new base (A^-) by donating its proton (H^+). This new base is known as conjugate base which is related to the original acid.

Similarly, after accepting a proton (H^+) the original base (B^-) produces a new acid (HB), known as the conjugate acid.

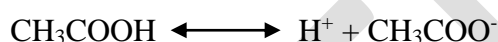


Classification of Bronsted Acids and Bases

Bronsted acids and bases can be classified as follows:

1) **Bronsted Acids:** These are further classified into:

i. **Monoprotic Acids:** They can donate only one proton, e.g., acetic acid.



ii. **Polyprotic acid:** They can donate more than one proton, e.g., carbonic acid (H_2CO_3), hydrosulphuric acid, H_2SO_4 , H_3PO_4



2) **Bronsted Bases:** These are further classified into:

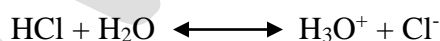
i. **Monoprotic Bases:** They can accept only one proton, e.g., sulphide, etc. water.



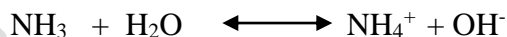
ii. **Polyprotic Bases:** They can accept more than one proton, e.g., anions of diprotic and triprotic acids.



3) **Amphiprotic Substances:** These are molecules or ions which can behave both as Bronsted acid and base, for example water acts as a base and accepts a proton when react with HCl.

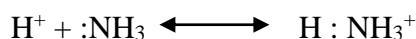


On the other hand, water acts as an acid and donates a proton when react with ammonia.



3. Lewis theory:

- According to this theory “acid is a substance that can accept an electron pair and base is a substance that donate an electron pair”
- By this theory, lewis acids are positive molecules containing unfilled octet of electrons and lewis bases are negative molecules containing unshared pair of electron.
- Basic compound usually contains oxygen or nitrogen as an electron pair donor.

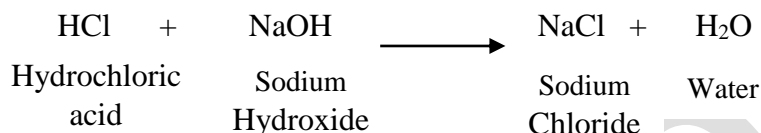


Classification of Acid-Base Titration

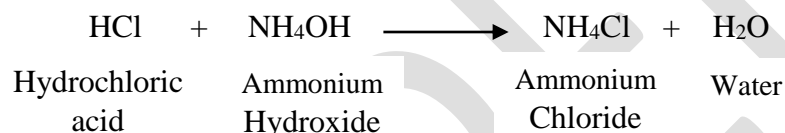
When neutralization reaction occurs between acid and base, salts and water are formed as products.

Based on the nature of an acid and base, these reactions can be classified into:

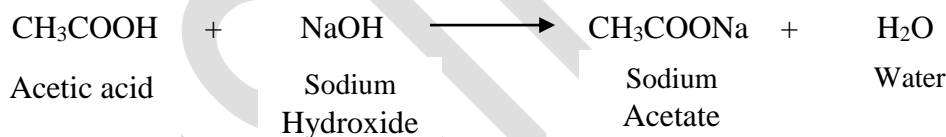
- 1) **Strong Acid and Strong Base:** A neutral salt results from the reaction between a strong acid and a strong base.



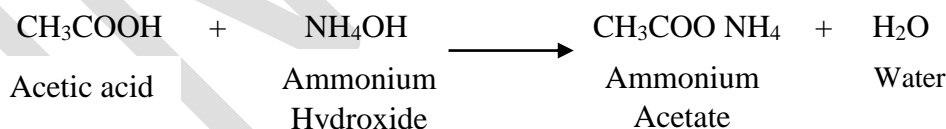
- 2) **Strong Acid and Weak Base:** An acidic salt results from the reaction between a strong acid and a weak base.



- 3) **Weak Acid and Strong Base:** An alkali salt results from the reaction between a weak acid and a strong base.



- 4) **Weak Acid and Weak Base:** A neutral salt results from the reaction between a weak acid and a weak base.



Assay by Acid-Base Titrations

In Acid-Base titrations, alkali solutions are titrated with standard acid solutions and acid solutions are titrated with standard alkali solutions.

Estimating an acid solution with a standard solution of alkali is known as alkalimetry, while estimating an alkali solution with a standard solution of acid is known as acidimetry.

Acidimetry Titrations:

Acidimetry titration estimates strength of base using a standard solution of acid, or in other words this method is used to measure the volume of a standard acid.

Acidimetry titrations are classified into:

1. **Direct Titrations:** In these titrations, an acid (present in the burette) is titrated with a base (present in the conical flask). For example in the direct titration of sodium carbonate with hydrochloric acid, strength of sodium carbonate is estimated.



2. **Residual Titrations:** In these titrations, the base reacts with a large concentration of standard acid; further the unreacted amount of acid is titrated with a standard base.

For example, in the assay of zinc oxide, excess amount of standard solution of sulphuric acid reacts with zinc oxide to yield zinc sulphate. Further the excess of standard acid (sulphuric acid) is titrated with a standard base (sodium hydroxide).

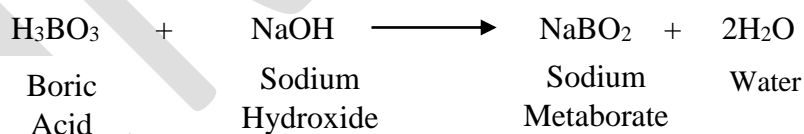


Alkalimetry Titrations:

Alkalimetry titration estimates strength of an acid using a standard base, or in other words this method is used to measure the volume of a standard base.

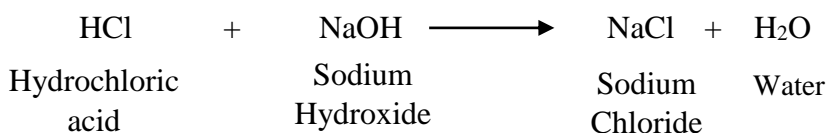
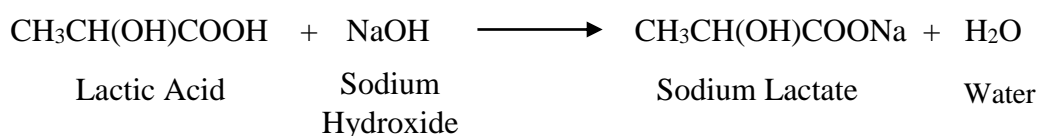
Alkalimetry titrations are classified into:

3. **Direct Titrations:** In these titrations, a base (present in the burette) is titrated with an acid (present in the conical flask). For example assay of boric acid.



4. **Residual Titrations:** In these titrations, the acid reacts with a large concentration of standard base; further the unreacted amount of base is titrated with a standard acid.

For example, assay of lactic acid.



End point detection in acid-base titrations:

The purpose of acid base titration is to find out the equivalent quantity of the titrant required for neutralization.

The point at which complete neutralization is achieved is called end point or equivalent point.

The end point detection in acid base titration can be achieved by two methods:

1. Neutralization indicator or Acid-Base indicator or pH indicator.
2. Instrumental methods

Acid-Base Indicators:

The purpose of titrating a standard alkaline solution with a solution of an acid is the determination of the amount of acid. This amount of acid should exactly equivalent chemically to the base present.

The point at which this is reached is the equivalence point, stoichiometric point or theoretical end point. At that point, the resulting aqueous solution contains the salt. This salt may either neutral or slightly acidic or slightly basic.

Depending the nature of these salts resulting solution have different pH. For e.g. if both the acids and base are strong electrolytes, the solution at the end point will be neutral due to formation of neutral salt and pH of the solution becomes 7.

If one of the acid or base is a weak electrolyte, the salt will be hydrolyzed to a certain degree, and the solution at the equivalence point will be either slightly alkaline or slightly acidic.

For any actual titration the correct end point will be characterized by a definite value of the hydrogen ion concentration of the solution.

Acid-Base indicators (weak organic acids and bases) having different colours depending upon the concentration of H⁺ ions in the solution are available.

These indicators exhibit a colour change from an acidic colour to and alkaline colour. This colour change does not occur suddenly or rapidly, but takes place with in a small pH range or interval, which is known as the **colour change interval** or **pH range**.

The commonly used Acid-Base indicators are as follows:

Indicator	pH range	Colour in acid	Colour in base
Thymol Blue	1.2-2.8	Red	Yellow
Bromophenol Blue	3.0-4.6	Yellow	Purple
Methyl orange	3.0-4.6	Red	Orange
Bromocresol green	3.8-5.2	Yellow	Blue
Methyl red	4.2-6.4	Red	Yellow
Phenol red	6.6-8.2	Yellow	Red

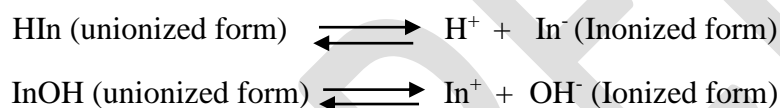
Phenolphthalein	8.2-10	Colourless	Pink
Thymolphthalein	9.3-10.5	Colourless	Blue

Thus, Indicators are the substances which exhibit different colours at various value of pH. Indicators are weak acids or weak bases. For an acid-base titration, we select an indicator which will show a distinct colour change at pH close to the equivalent point.

There are two different theories of indicators:

A. Ostwald theory: First theory to explain the behavior of indicators was explained by W. Ostwald.

According to this theory colour change of the acid-base indicator is the result of its ionization because the ionized and unionized forms differ in colour. For e.g. unionized indicator acid [HIn] or a base [InOH] has a colour different than its ion.



If indicator is a weak acid, its ionization in acid is very low. (Due to **common ion (H⁺)** effect).

In similar manner, if indicator is a weak base, its ionization in acid is high and low in base. (Due to **common ion (OH⁻)** ion effect)

Common ion effect:

The process by which ionization of compound is suppressed by addition of one of its ion is called common ion effect.

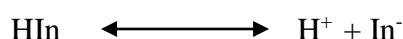
Example:



If base is added to above solution H⁺ ion is used in reaction with OH⁻ ions and therefore removal of H⁺ ions results in more ionization of acetic acid to maintain equilibrium.

If HCl is added to above solution then H⁺ ion concentration will increase and to maintain equilibrium, ionization of acetic acid will be suppressed.

For an acid indicator equivalent can be written as:



In acid solution, there is depression of ionization of indicator due to common ion effect. Hence, initially concentration of HIn is greater than that of In⁻ and the colour exhibited will be that of the unionized form.

As the titration proceeds the alkali medium will promote removal of H⁺ and therefore gradually increase in concentration of ionized form In⁻ and the solution acquires colour of ionized form.

By applying law of mass action.

$$K_{Ina} = \frac{[H^+][In^-]}{[HIn]}$$

$$[H^+] = \frac{[K_{In}][HIn]}{[In^-]}$$

By taking negative log on both side of equation,

$$-\log [H^+] = -\log K_{Ina} - \log \frac{[HIn]}{[In^-]}$$

$$pH = -\log K_{Ina} + \log \frac{[In^-]}{[HIn]}$$

For colour change ratio $\frac{[In^-]}{[HIn]}$ should be 1/10.

$$pH = pK_{Ina} + \log \frac{1}{10}$$

$$pH = pK_{Ina} - \log 10$$

$$pH = pK_{Ina} - 1 \text{ (For Acid)}$$

For weak base indicator,



Applying law of mass of action,

$$K_{Inb} = \frac{[In^+][OH^-]}{[InOH]}$$

$$[OH^-] = \frac{K_{Inb} [InOH]}{[In^+]}$$

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

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

Substituting this value in above equation,

$$[H^+] = \frac{K_w [In^+]}{K_{Inb} [InOH]}$$

Taking $-\log$ on both side,

$$-\log [H^+] = -\log K_w - (-\log K_{Inb}) + \left(-\log \frac{[In^+]}{[InOH]} \right)$$

$$\text{pH} = \text{pK}_w - \text{pK}_{I_b} - \log \frac{[In^+]}{[InOH]}$$

$$\text{pH} = \text{pK}_{I_a} + \log \frac{[InOH]}{[In^+]}$$

For colour change ratio $\frac{[InOH]}{[In^+]}$ should be 10/1.

$$\text{pH} = \text{pK}_{I_a} + 1$$

In general, the pH range in colour change is observed is

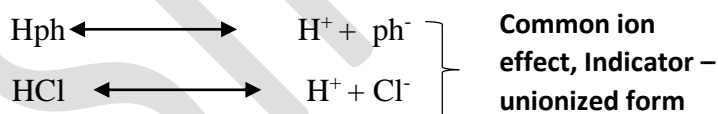
$$\text{pH} = \text{pK}_{I_a} \pm 1$$

This is called as transition interval of the indicator.

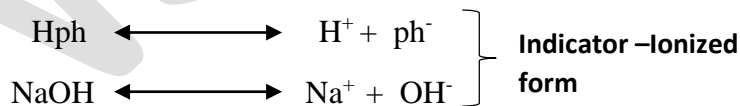
Weak acidic indicator remains unionized in the acidic solution due to common ion effect of H^+ ions. While in the weak base it ionized.

Example: Phenolphthalein is a weak acid indicator. Unionized form of the phenolphthalein is colourless and ionized form of phenolphthalein is pink in colour.

Phenolphthalein (weak acid) in the hydrochloric acid (acidic) remains as unionized form thus gives colourless solution.

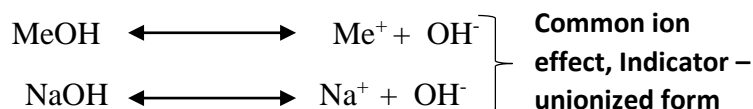


In sodium hydroxide solution (basic), phenolphthalein is ionized and thus gives pink colour.

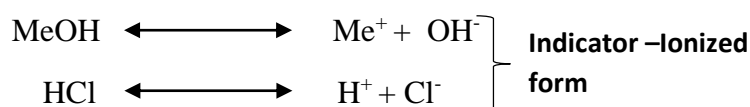


Example: Methyl Orange is a weak base indicator. Unionized form of the methyl orange is yellow in colour and ionized form of methyl orange is pink in colour.

Methyl orange (weak base) in the sodium hydroxide solution (basic) remains as unionized form thus gives yellow colour solution.



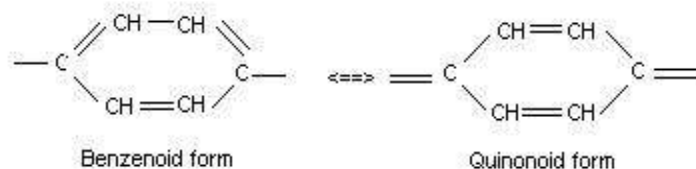
In Hydrochloric acid solution (acidic), methyl orange is ionized and thus gives pink colour.



B. Quinonoid theory (Resonance theory):

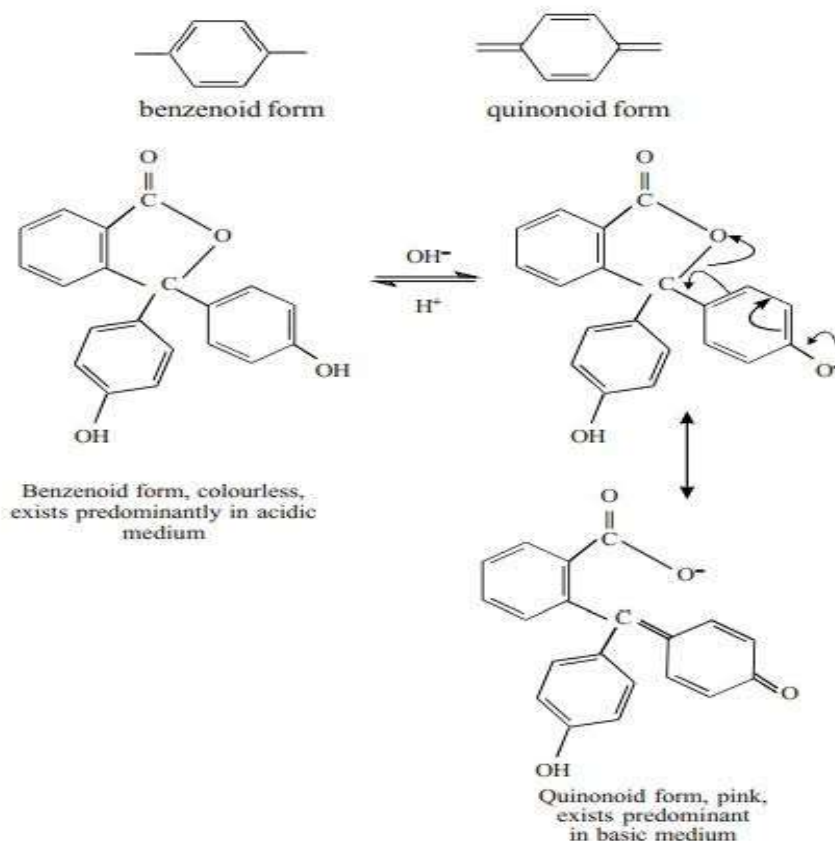
The acid base indicators have two tautomeric forms (with different structures) existing in equilibrium.

Both the forms are of different colours due to inter conversion of one one tautomeric form into another.

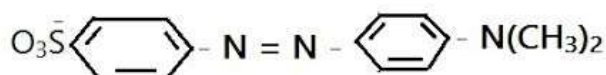


One form of acid-base indicator exists in acidic medium while other form in alkaline media and both forms have different colour.

For e.g. **Phenolphthalein** is a weak acid. It is colourless in acidic media because in acidic media phenolphthalein remains as a benzenoid form. While in alkaline (basic) media phenolphthalein is converted in to Quinonoid form and thus colour of phenolphthalein is pink in alkaline media.

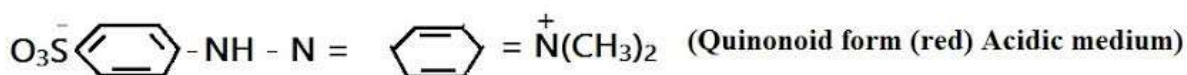
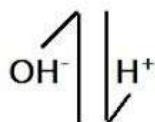


Methyl orange is a weak base. It is yellow in alkaline media because in alkaline media methyl orange remains as a benzenoid form. While in acidic media methyl orange is converted in to Quinonoid form and thus colour of methyl orange is pink or red in acidic media.



Benzenoid form (yellow)

Basic medium



Mixed Indicators:

In some cases, the pH range is very narrow and the colour change over this range must be very sharp. This is not easily possible with ordinary acid-base indicators. The result may be achieved by use of the suitable mixture of indicators.

Mixed indicators are selected in such a way that their ionization constant values are close and overlapping and colours are complementary at an intermediate pH values.

For example, A mixture of equal parts of neutral red (0.1% solution in alcohol) and methylene blue (0.1% solution in alcohol) gives a sharp colour change from violet blue to green in passing from acid to alkaline solution at pH 7.

A mixture of phenolphthalein (3 parts of 0.1 %) and α -naphtholphthalein (1 part 0.1 %) passes from pale rose to violet at pH 8.9.

INDICATOR	pH	COLOUR CHANGE
Neutral Red + Methylene Blue	7	Violet blue to green
Bromocresol green + Methyl Orange	4.3	Orange to blue to green
Thymol Blue + Cresol Red	8.3	Yellow to Violet

The colour change of a single indicator may also be improved by the addition of a pH sensitive dye to produce the complement of one of the indicator colour.

For example: additions of xylene cyanol FF to methyl orange. Here, colour changes from alkaline to acid side is green –grey – magenta.

By mixing suitable indicators colour change may be obtained over a considerable portion of the pH range. They are known as universal indicators.

BUFFER SOLUTIONS & BUFFER CAPACITY

Buffers are those solutions which resist the change in the pH, when adding small amount of acid or base.

A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base (its salt) or a weak base and its conjugate acid (its salt).

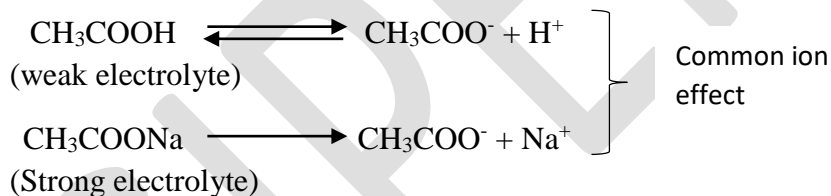
Buffer solutions are used as a means of keeping pH at a nearly constant value.

There are three types of buffers:

1. Acidic Buffers
2. Basic Buffers
3. Neutral Buffers

1) Acidic buffers:

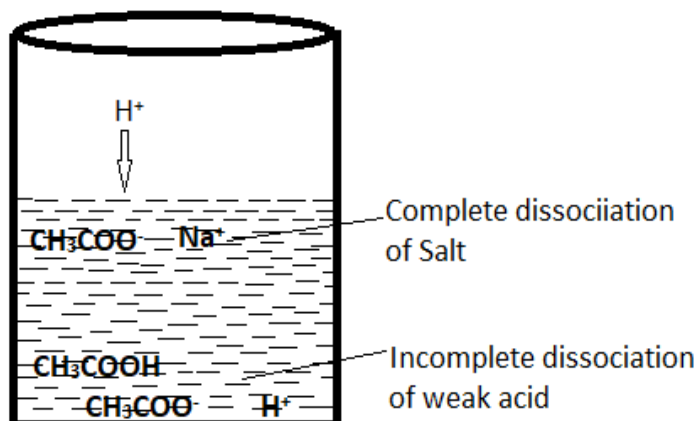
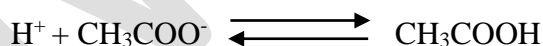
This buffer is made by mixing weak acid and the salt (Na^+ & K^+) of its conjugate base.



Here, CH_3COOH is a weak acid and thus its ionization is incomplete and reversible, while its salt (conjugate base) is a strong electrolyte and it will be ionized completely.

Thus, maximum CH_3COO^- ions are coming from CH_3COONa , while CH_3COO^- ions from CH_3COOH are very less or negligible.

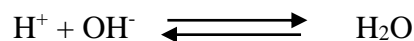
When small amount of acid is added,



Generally, H^+ is increased when small amount of acid is added, therefore pH of solution should be decreased but this is not to be happened because upon addition of acid, H^+ ions react with CH_3COO^- and convert it into CH_3COOH .

Undissociated form of CH_3COOH will not help to decrease pH of the solution. It will resist the change in pH of the solution.

When small amount of base is added,



Here H^+ ions are consumed and more CH_3COOH will be converted into CH_3COO^- & H^+ ions to form equilibrium and therefore H^+ ions replace the H^+ consumed by addition of OH^- (base). Thus, pH will remain same.

Calculation of pH for varying concentration of Acid/Salt

Example: 30 g (CH_3COOH) and 41 gm (CH_3COONa) in 1 L solution. ($\text{pK}_a = 4.7447$)

$$[\text{Salt}] = 41/82 = 0.5 \text{ M}$$

$$[\text{Acid}] = 30/60 = 0.5 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = 4.7447 + \log \frac{0.5}{0.5}$$

$$\text{pH} = 4.7447 + 0$$

$$\text{pH} = 4.7447$$

By increasing concentration of acid for example 60g CH_3COOH .

$$[\text{Salt}] = 41/82 = 0.5 \text{ M}$$

$$[\text{Acid}] = 60/60 = 1 \text{ M}$$

$$\text{pH} = 4.7447 + \log \frac{0.5}{1}$$

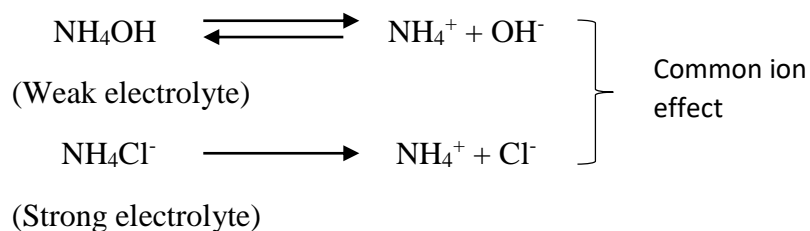
$$\text{pH} = 4.7447 + \log 0.5$$

$$\text{pH} = 4.7447 + (-0.301)$$

$$\text{pH} = 4.4437$$

2) Basic buffers:

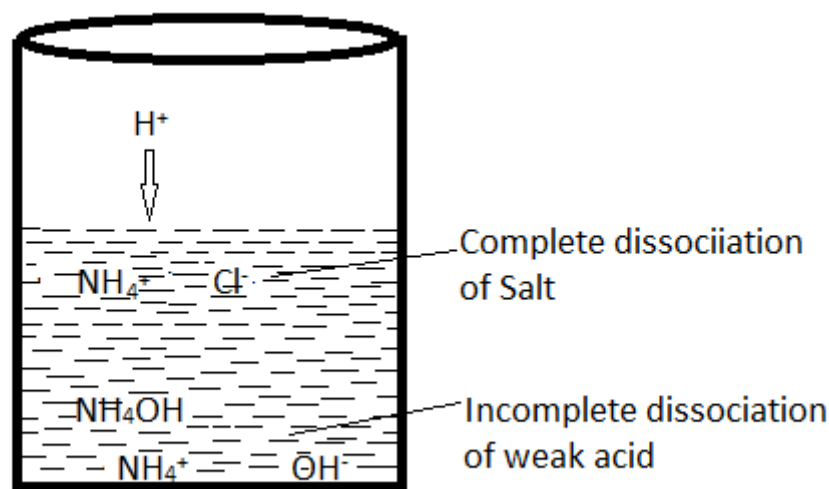
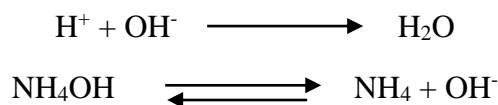
This are made by mixing of weak base and the salt of its conjugate acid.



Here, NH_4OH is a weak base and thus its ionization is incomplete and reversible, while its salt (conjugate acid) is a strong electrolyte and it will be ionized completely.

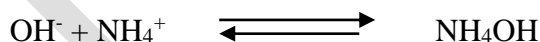
Thus, maximum NH_4^+ ions are coming from NH_4Cl , while NH_4^+ ions from NH_4OH are very less or negligible.

When small amount of acid is added,



When small amount of acid (H^+) is added, H^+ combines with OH^- and forms H_2O . Here, to maintain equilibrium more NH_4OH will be converted into NH_4^+ and OH^- . These, OH^- will replace the consumed OH^- . Thus, there is no change in OH^- concentration and pH will remain unchanged.

When small amount of base is added,



Here, very small amount of NH_4OH will be reversibly converted into NH_4^+ and OH^- . Mostly NH_4OH remains as undissociated form. Undissociated form of NH_4OH will not help to increase the pH.

Calculation of pH for varying concentration of Base/Salt

Example: 17.5 g (NH_4OH) and 26.75 gm (NH_4Cl) in 1 L solution. ($\text{pK}_b = 4.7447$)

$$[\text{Salt}] = 26.75/53.5 = 0.5 \text{ M}$$

$$[\text{Base}] = 17.5/35 = 0.5 \text{ M}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pOH} = 4.7447 + \log \frac{0.5}{0.5}$$

$$\text{pOH} = 4.7447 + 0$$

$$\text{pOH} = 4.7447$$

$$\text{pH} = 9.2553$$

By increasing concentration of base for example 35 g NH₄OH.

$$[\text{Salt}] = 26.75/53.5 = 0.5 \text{ M}$$

$$[\text{Base}] = 35/35 = 1 \text{ M}$$

$$\text{pOH} = 4.7447 + \log \frac{0.5}{1}$$

$$\text{pOH} = 4.7447 + \log 0.5$$

$$\text{pOH} = 4.7447 + (-0.301)$$

$$\text{pOH} = 4.4437$$

$$\text{pH} = 9.5563$$

Buffer Capacity & Buffer Index

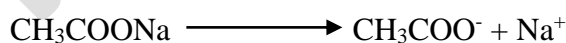
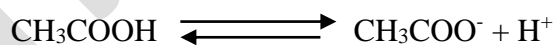
It tells us that how much acid or base that we can add before pH of buffer does changes.

The capacity of the buffer solution is a measure to its effectiveness in resisting changes in pH upon the addition of Acid or Base.

If higher concentration of acid or base in the buffer solution, the buffer capacity will be higher.

If lower concentration of acid or base in the buffer solution, the buffer capacity will be lower.

Example:



$$[\text{CH}_3\text{COOH}] = 0.4 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = 0.8 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}, \quad \text{K}_a = 1.8 \times 10^{-5}$$

$$\text{pK}_a = -\log \text{K}_a = -\log (1.8 \times 10^{-5}) = 4.7447$$

$$\text{pH} = 4.7447 + \log \frac{0.8}{0.4}$$

$$\text{pH} = 5.0457$$

<p>Buffer 1: Adding 0.03 M of NaOH to 1 L Solution (in which concentration of acid= 0.4 M)</p> <p>$[\text{CH}_3\text{COOH}] = 0.4 \text{ M} - 0.03 \text{ M} = 0.37 \text{ M}$ $[\text{CH}_3\text{COONa}] = 0.8 \text{ M} + 0.03 \text{ M} = 0.83 \text{ M}$</p> <p>$\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$ $\text{OH}^- + \text{CH}_3\text{COOH} \longrightarrow \text{H}_2\text{O} + \text{CH}_3\text{COO}^-$</p> <p>$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$</p> <p>$\text{pH} = 4.7447 + \log \frac{0.83}{0.37}$</p> <p>$\text{pH} = 4.7447 + 0.3509$</p> <p>$\text{pH} = 5.0956 \longrightarrow 5.0457 \text{ (actual),}$ Difference = 0.0499</p>	<p>Buffer 2: Adding 0.03 M of NaOH to 1 L Solution (in which concentration of acid= 0.04 M)</p> <p>$[\text{CH}_3\text{COOH}] = 0.04 \text{ M} - 0.03 \text{ M} = 0.01 \text{ M}$ $[\text{CH}_3\text{COONa}] = 0.08 \text{ M} + 0.03 \text{ M} = 0.11 \text{ M}$</p> <p>Add 0.03 M of NaOH to 1 L solution.</p> <p>$\text{pH} = 4.7447 + \log \frac{[0.011]}{[0.01]}$</p> <p>$\text{pH} = 4.7447 + \log 11$</p> <p>$\text{pH} = 4.7447 + 1.0414$</p> <p>$\text{pH} = 5.7861 \longrightarrow 5.0457 \text{ (actual),}$ Difference = 0.7404</p>
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HENDERSON HESSELBALCH EQUATION

It is applicable on buffer solutions.

Weak Acid:



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

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

By taking negative log,

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

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \dots\dots\dots (1)$$

It is a Henderson Hasselbalch equation and it is used for calculations required in preparation of buffer solutions.

Specific conditions:

- 1) If $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$, Concentration of salt = concentration of acid

If $\text{pH} = \text{pK}_a$, means acid is half dissociated.

- 2) When pH increases or decreases by 1 unit with respect to pK_a , then proportion of the salt & acid will be 10 folds.

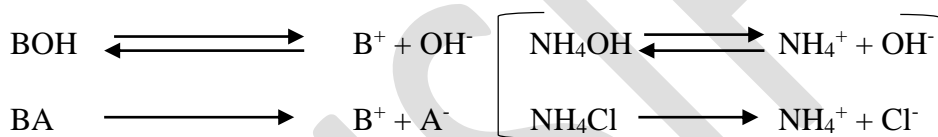
$$\text{pH} = 7, \text{pK}_a = 6, [\text{Salt}]/[\text{Acid}] = 10$$

$$\text{pH} = 6, \text{pK}_a = 7, [\text{Salt}]/[\text{Acid}] = 1/10 = 0.1 = 10^{-1}$$

- 3) $\text{pH} < \text{pK}_a$, $[\text{Salt}]/[\text{Acid}]$ ratio will be < 1

$\text{pH} > \text{pK}_a$, $[\text{Salt}]/[\text{Acid}]$ ratio will be > 1

Weak Base:



$$K_a = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

$$[\text{OH}^-] = \frac{K_b [\text{BOH}]}{[\text{B}^+]}$$

By taking negative log,

$$-\log [\text{OH}^-] = -\log \left(K_b \frac{[\text{BOH}]}{[\text{B}^+]} \right)$$

$$\text{pOH} = -\log K_b - \log \frac{[\text{BOH}]}{[\text{B}^+]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{B}^+]}{[\text{BOH}]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \dots \dots \dots (2)$$

$$\text{pH} = \text{pK}_w - \text{pOH} \dots \dots \dots (3)$$

Equation (2) is a Henderson Hasselbalch equation for base buffer solution.

Thus, equation (1) and (2) are equation of Henderson Hasselbalch equation.

HYDRLYSIS OF SALTS

Salts may be divided into four main classes:

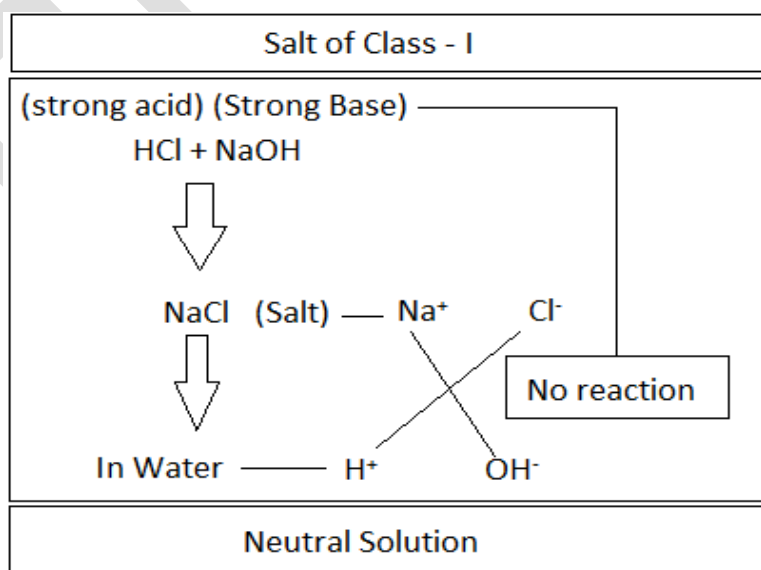
- (1) Those derived from strong acids (HCl) and strong bases (NaOH), e.g. Sodium chloride (NaCl);
- (2) Those derived from weak acids (CH₃COOH) and strong bases (NaOH), e.g. sodium acetate (CH₃COONa);
- (3) Those derived from strong acids (HCl) and weak bases (NH₄OH), e.g. ammonium chloride (NH₄Cl); and
- (4) Those derived from weak acids (CH₃COOH) and weak bases (NH₄OH), e.g. ammonium acetate (CH₃COONH₄).

With an aqueous solution of a Salt of class (1), neither do the anions (Cl⁻) have any tendency to combine with the hydrogen ions (H⁺) nor do the cations (Na⁺) with the hydroxide ions (OH⁻) of water, since the related acids and bases are strong electrolytes.

Thus hydrogen and hydroxide ions in water remain as such after addition of salt. It will leads to the equilibrium between the hydrogen and hydroxide ions in water:

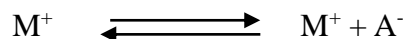


This equilibrium is therefore not disturbed and the solution remains neutral.

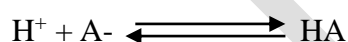


With an aqueous solution of a Salt (CH_3COONa) of class (II), anions (CH_3COO^-) have a tendency to combine with H^+ ions of water as it is a ion of weak acid but cations (Na^+) obtained from strong base (NaOH) and therefore they have no tendency to combine with OH^- ions of water.

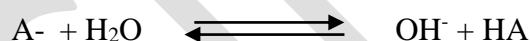
If **MA** is a salt derived from a weak acid (**HA**) and strong Base (**BOH**), Salt is completely dissociated in aqueous solution.



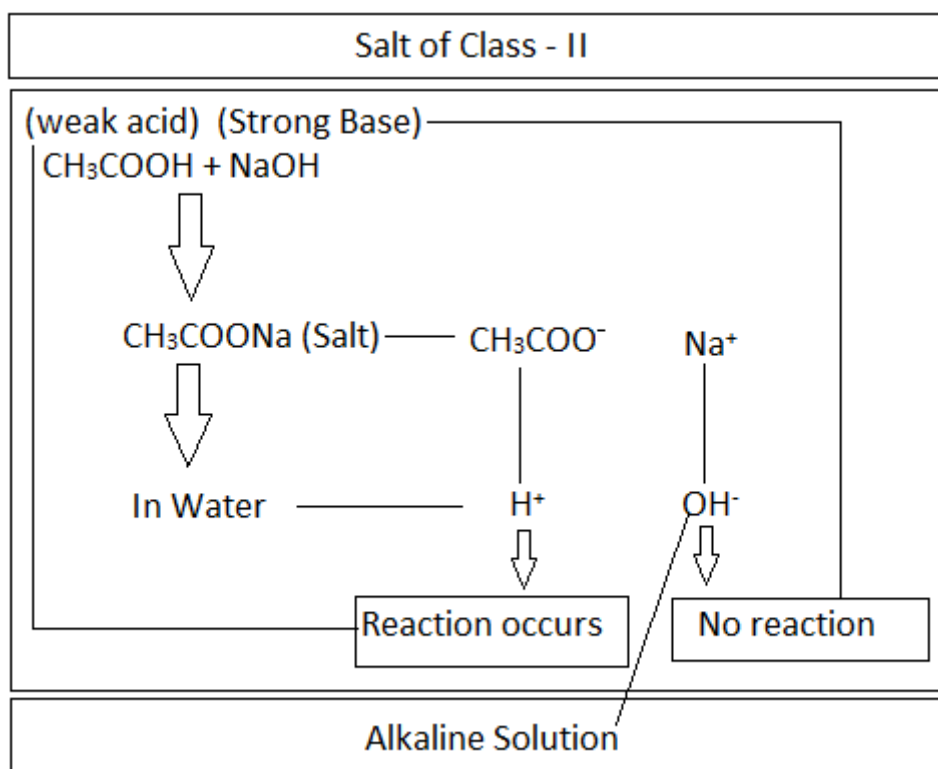
A very small concentration of hydrogen and hydroxide ions, originating from the small ionisation of water, will be initially present. HA is a weak acid, i.e. it is dissociated only to a small degree; the concentration of A^- ions which can exist in equilibrium with H^+ ions is accordingly small. In order to maintain the equilibrium, the large initial concentration of A^- ions must be reduced by combination with H^+ ions to form undissociated HA:



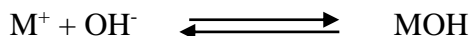
The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA; consequently the hydroxide ion concentration of the solution will increase and the solution will be alkaline.



The interaction between the ion of a salt and water is called 'Hydrolysis'.

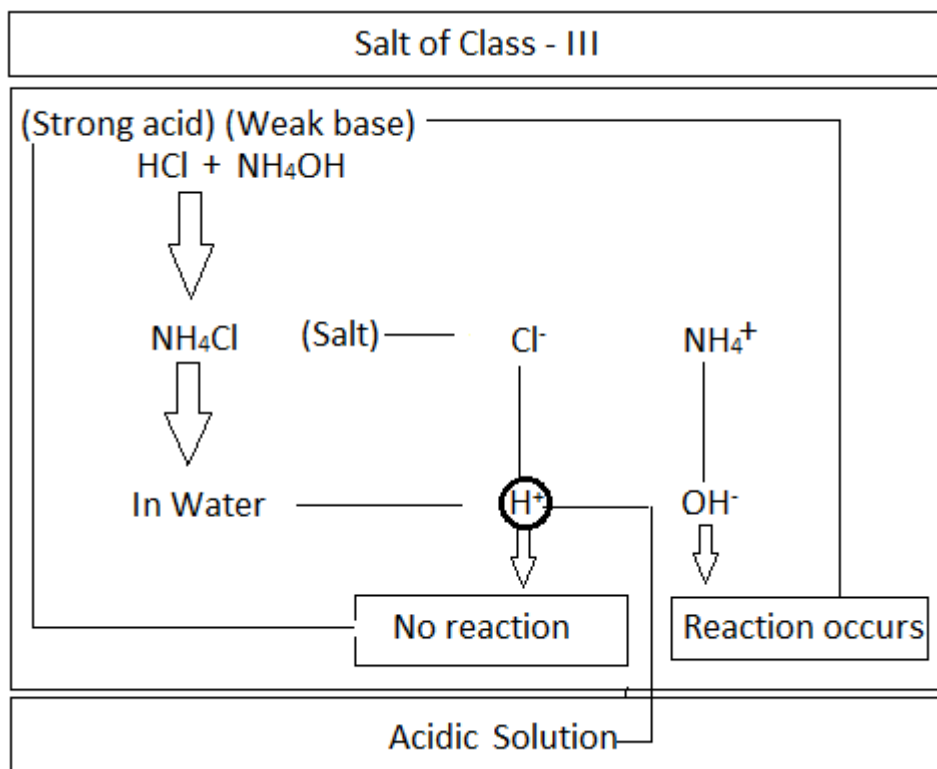
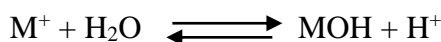


Consider now the Salt of a strong acid and a weak base {class (3)} (NH_4Cl) Here the initial high concentration of cations M^+ will be reduced by combination with the hydroxide ions of water to form the little-dissociated base MOH until the equilibrium:



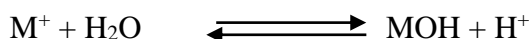
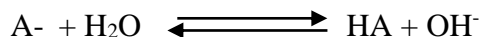
is attained.

The hydrogen ion concentration of the solution will thus be increased, and the solution will become acid. The hydrolysis is here represented by:



For salts of class (4) ($\text{CH}_3\text{COONH}_4$), in which both the acid and the base are weak, two reactions will occur simultaneously.

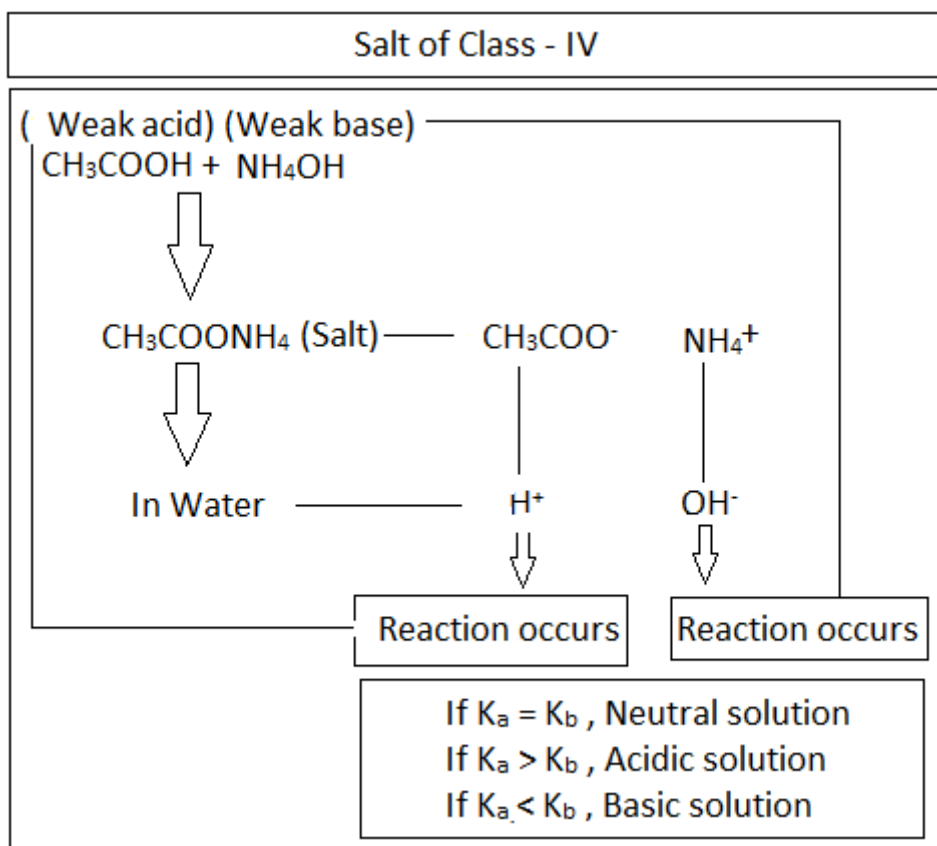
Anion (M^+) will react with OH^- ions of the water and cation (A^-) will react with H^+ ions of the water.



The reaction of the solution will clearly depend upon the relative dissociation constants of the acid and the base. If they are equal in strength, the solution will be neutral; if $K_a > K_b$ it will be acid, and if $K_b > K_a$, it will be alkaline.

Having considered all the possible cases, we are now in a position to give a more general definition of hydrolysis.

“Hydrolysis is the interaction between an ion (or ions) of a Salt and water with the production of (a) a weak acid or a weak base, or (b) of both a weak acid and a weak base.”



HYDROLYSIS CONSTANT AND DEGREE OF HYDROLYSIS

Case 1. Salt of a weak acid and a strong base.

The equilibrium in a solution of salt MA may be represented by:



Applying the Law of Mass Action, we obtain

$$\frac{a_{\text{OH}^-} \times a_{\text{HA}}}{a_{\text{A}^-}} = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \times \frac{\gamma_{\text{OH}^-} \times \gamma_{\text{HA}}}{\gamma_{\text{A}^-}} = K_h \dots\dots\dots (1)$$

Where K_h is the hydrolysis constant. The solution is assumed to be dilute so that the activity of the un-ionised water may be taken as constant, and the approximation that the activity coefficient of the un-ionised acid is unity and that both ions have the same activity coefficient may be introduced. Equation (1) then reduces to:

$$K_h = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \dots\dots\dots (2)$$

This is often written in the form:

$$K_h = \frac{[\text{Base}][\text{Acid}]}{[\text{Unhydrolysed salt}]}$$

The free strong base and the unhydrolysed salt are completely dissociated and the acid is very little dissociated.

The degree of hydrolysis is the fraction of each mole of anion A^- hydrolysed at equilibrium. Let 1 mole of Salt be dissolved in V L of solution, and let x be the degree of hydrolysis. The concentrations in mol L^{-1} are:

$$[HA] = [OH^-] = x/V; [A^-] = (1 - x)/V$$

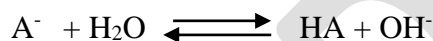
Substituting these values in equation (2):

$$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{(1-x)}{v}} = \frac{x^2}{(1-x)v}$$

This expression enables us to calculate the degree of hydrolysis at the dilution V ; it is evident that as V increases, the degree of hydrolysis x must increase. The two equilibria:



Must co-exist with the hydrolytic equilibrium:



Hence the two relationships:

$$[H^+][OH^-] = K_w \quad \text{and} \quad \frac{[H^+][A^-]}{[HA]} = K_a$$

must hold in the same solution as:

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

$$\text{But, } \frac{K_w}{K_a} = \frac{[H^+][OH^-][HA]}{[H^+][A^-]} = \frac{[OH^-][HA]}{[A^-]} = K_h$$

$$\text{Therefore, } K_w/K_a = K_h \text{ or } pK_h = pK_w - pK_a.$$

The hydrolysis constant is thus related to the ionic product of water and the ionisation constant of the acid. Since K_a varies slightly and K_w varies considerably with temperature, K_h and consequently the degree of hydrolysis will be largely influenced by changes of temperature.

The hydrogen ion concentration of a solution of a hydrolysed Salt can be readily calculated. The amounts of HA and of OH^- ions formed as a result of hydrolysis are equal; therefore, in a solution of the pure salt in water, $[HA] = [OH^-]$. If the concentration of the Salt is $C \text{ mol L}^{-1}$, then:

$$\frac{[OH^-][HA]}{[A^-]} = \frac{[OH^-]^2}{C} = K_h = \frac{K_w}{K_a}$$

$$\text{And, } [OH^-] = \sqrt{C \cdot K_w/K_a}$$

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

$$[H^+] = \frac{K_w}{\sqrt{C \cdot K_w / K_a}} \text{ (By putting value of } [OH^-])$$

$$[H^+] = \sqrt{K_w \cdot K_a / C}$$

By taking log on both sides,

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

To be consistent we should use **pc = -log c** so that the equation becomes:

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} p C \dots\dots\dots (3)$$

Equation (3) can be employed for the calculation of the pH of a solution of a Salt of a weak acid and a strong base.

Case 2. Salt of a strong acid and a weak base.

The hydrolytic equilibrium is represented by:



By applying the Law of Mass Action along the lines of Case 1, the following equations are obtained:

$$K_h = \frac{[H^+][MOH]}{[M^+]} = \frac{[Acid][Base]}{[Unhydrolysed\ salt]} = \frac{K_w}{K_b}$$

$$K_h = \frac{x^2}{(1-x)v}$$

K_b , is the dissociation constant of the base. Furthermore, since $[MOH]$ and $[H^+]$ are equal:

$$K_h = \frac{[H^+][MOH]}{[M^+]} = \frac{[H^+]^2}{c} = \frac{K_w}{K_b}$$

$$\text{And, } [H^+] = \sqrt{C \cdot K_w / K_b}$$

Taking log on both side,

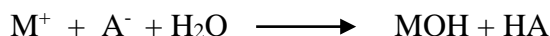
$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b + \frac{1}{2} p C \dots\dots\dots (4)$$

Equation (4) may be applied to the calculation of the pH of solutions of salts of strong acids and weak bases.

Case 3. Salt of a weak acid and a weak base.

The hydrolytic equilibrium is expressed by the equation:

Applying the Law of Mass Action and taking the activity of un-ionised water as unity, we have:



$$\frac{a_{MOH} \times a_{HA}}{a_{M^+} \cdot a_{A^-}} = \frac{[MOH][HA]}{[M^+][A^-]} \times \frac{y_{MOH} \times y_{HA}}{y_{M^+} \cdot y_{A^-}} = K_h$$

By the usual approximations, i.e. by assuming that the activity coefficients of the un-ionised molecules and, less justifiably, of the ions are unity, the following approximate equation is obtained:

$$K_h = \frac{[MOH][HA]}{[M^+][A^-]} = \frac{[Base] \times [Acid]}{[Unhydrolysed Salt]^2}$$

If x is the degree of hydrolysis of 1 mole of the Salt dissolved in V litres of solution, then the individual concentrations are:

$$[MOH] = [HA] = x/V; \quad [M^+] = [A^-] = (1 - x)/V$$

leading to the result

$$K_h = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\left(\frac{1-x}{V}\right) \cdot \left(\frac{1-x}{V}\right)} = \frac{x^2}{(1-x)^2}$$

The degree of hydrolysis and consequently the pH is independent of the concentration of the solution.

It may be readily shown that:

$$K_h = \frac{K_w}{K_a \times K_b}$$

$$\text{Or } pK_h = pK_w - pK_a - pK_b$$

This expression enables us to calculate the value of the degree of hydrolysis from the dissociation constants of the acid and the base.

The hydrogen ion concentration of the hydrolysed solution is calculated in the following manner:

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} = K_a \times \frac{\frac{x}{V}}{\frac{1-x}{V}} = K_a \times \frac{x}{1-x}$$

$$\text{But } \frac{x}{1-x} = \sqrt{K_h}$$

$$\text{Hence } [H^+] = K_a \sqrt{K_h} = K_a \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{K_w \times \frac{K_a}{K_b}}$$

By taking log on both side,

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b \dots\dots\dots (5)$$

If the ionisation constants of the acid and the base are equal, that is $K_a = K_b$, $pH = \frac{1}{2} pK_w = 7.0$ and the solution is **neutral**, although hydrolysis may be considerable. If $K_a > K_b$, $pH < 7$ and the solution is **acid**, but when $K_b > K_a$, $pH > 7$ and the solution reacts **alkaline**.

NEUTRALIZATION CURVES

In neutralization titration acid reacts with base and gives salt and water. At equivalent point, colour change is observed by indicator.

Mechanism of neutralization procedure is understood by studying the change in H^+ ion concentration during the titration, because change in pH near the equivalent point is very important for selection of proper indicator to detect the colour change at equivalent point.

The curve obtained by plotting pH against % of acid neutralized (or number of millimeters of alkali added) is known as neutralization curve.

1. Strong acid - strong base titration

- Consider the titration of 100 ml of 1 M HCl. As the titration progresses H^+ ion concentration decreases and pH increases.
- At equivalent point this change is very rapid.

When 0 ml of 1 M NaOH is added, the pH of 1 M HCl is 0.

$$\begin{aligned} [H^+] &= 100/100 = 1 \\ \text{pH} &= -\log [H^+] \\ &= -\log 1 \\ \text{pH} &= 0 \end{aligned}$$

When 50 ml of 1 M NaOH is added,

$$\begin{aligned} [H^+] &= 50/150 = 0.33 \\ \text{pH} &= -\log [H^+] \\ &= -\log 0.33 \\ \text{pH} &= 0.48 \end{aligned}$$

When 90 ml of 1 M NaOH is added,

$$\begin{aligned} [H^+] &= 10/190 = 0.053 \\ \text{pH} &= -\log [H^+] \\ &= -\log 0.053 \\ \text{pH} &= 1.3 \end{aligned}$$

When 99 ml of 1 M NaOH is added,

$$\begin{aligned} [H^+] &= 1/199 = 0.0050 \\ \text{pH} &= -\log [H^+] \\ &= -\log 0.0050 \\ \text{pH} &= 2.3 \end{aligned}$$

When 99.9 ml of 1 M NaOH is added,

$$\begin{aligned} [H^+] &= 0.1/199.9 = 0.0005 \\ \text{pH} &= -\log [H^+] \end{aligned}$$

$$= -\log 0.0005$$

$$\text{pH} = 3.3$$

When 100 ml of 1 M NaOH is added, now solution is of NaCl and pH is of water

$$\text{pH} = 7$$

When 100.1 ml of 1 M NaOH is added,

After equivalent point, OH⁻ ion will be in excess. Thus pH will be calculated from [OH⁻].

$$[\text{OH}^-] = 0.1/200.1 = 5 \times 10^{-4}$$

$$\text{pOH} = 0.1/200.1 = 5 \times 10^{-4}$$

$$\text{pH} + \text{pOH} = 14 = \text{pK}_w$$

$$\text{pH} = 14 - 3.3$$

$$\text{pH} = 10.7$$

When 101 ml 1 M NaOH is added,

$$[\text{OH}^-] = 1/201 = 0.00497$$

$$\text{pOH} = -\log [\text{OH}^-]$$

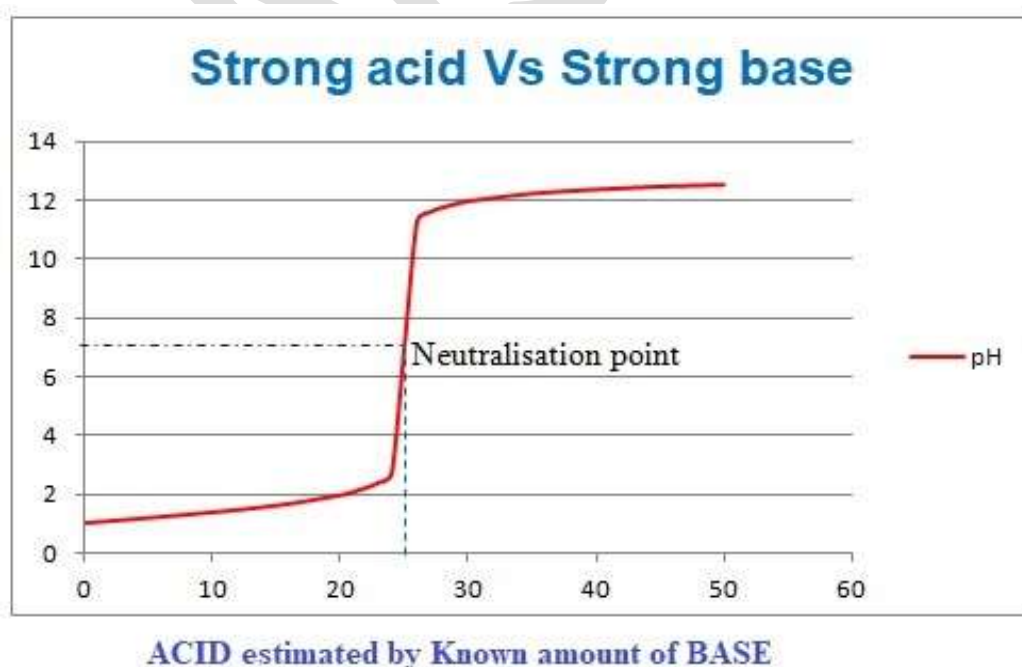
$$= -\log [0.00497]$$

$$\text{pOH} = 2.30$$

$$\text{pH} = 14 - 2.3$$

$$\text{pH} = 11.7$$

- At equivalent point pH changes rapidly from 3.3 (99.9 ml) to 10.7 (100.1 ml).
- For 1 M solution, pH range (for indicator) = 3 to 10.5
 - For 0.1 M Solution, pH range (for indicator) = 4.5 to 9.5
 - For 0.01 M solution, pH range (for indicator) = 5.5 to 8.5



- When 1 M HCl is titrated with 1 M NaOH

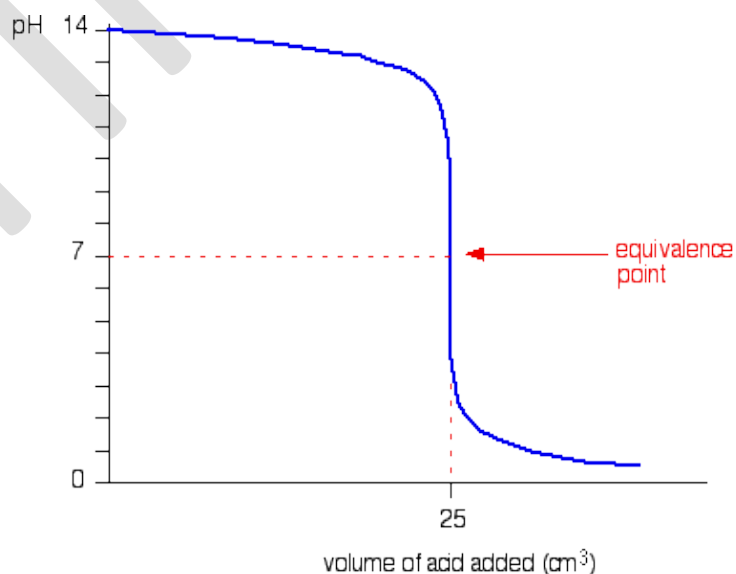
NaOH added (ml)	1 M HCl solution (pH)
0	0.0
50	0.5
75	0.8
90	1.3
98	2.0
99	2.3
99.5	2.6
99.8	3.0
99.9	3.3
100	7.0
100.1	10.7
100.2	11.0
100.5	11.4
101	11.7
102	12.7

For the titration of 1 M HCl by 1 M NaOH, indicators which gives colour changes between the pH ranges of 3.3 – 10.7 will be effective and gives minimum error.

i.e following indicators are used to detect end point in case of strong acid and strong base titration.

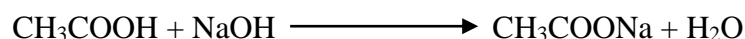
- Phenolphthalein –pH range: 8.3 – 10
- Bromothymol Blue- pH range: 6.0 – 7.6
- Methyl red- pH range: 4.2 – 6.3

Similarly, Neutralization curve for Strong Base and Strong Acid. pH initially high due to high concentration of OH^- . As titration progresses, pH decreases.



2. Weak Acid- Strong Base Titration

Consider the neutralization of 100 ml of 0.1 M Acetic acid with 0.1 M NaOH solution.



$$K_a = 1.82 \times 10^{-5}$$

(a) H^+ ion concentration is small as the start of the titration, so pH will be higher.

e.g. $0.1 \text{ M HCl} = [\text{H}^+] = 0.1$, $\text{pH} = -\log(0.1) = 1.0$

$0.1 \text{ M CH}_3\text{COOH}$, $[\text{H}^+] = 1.34 \times 10^{-3}$

$$\text{pH} = -\log(1.34 \times 10^{-3})$$

$$\text{pH} = -\log 10^{-3} - \log 1.34$$

$$\text{pH} = 3 - 0.1271$$

$$\text{pH} = 2.87$$

law of mass of action,

$$\frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = K_a$$

Here, $[\text{H}^+]$ & $[\text{CH}_3\text{COO}^-]$ are same,

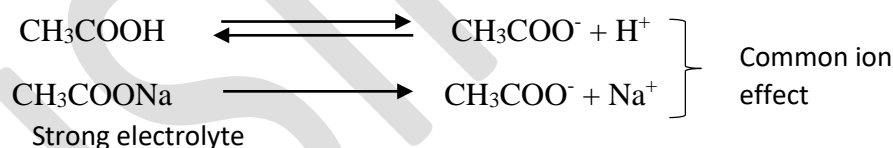
$$\frac{[\text{H}^+]^2}{0.1} = 1.82 \times 10^{-5}$$

$$[\text{H}^+]^2 = 1.82 \times 10^{-6}$$

$$[\text{H}^+] = 1.34 \times 10^{-3}$$

(b) When 0.1 M NaOH (alkali solution) is added, it will produce the salt which will give common ion effect.

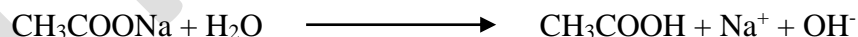
Due to common ion effect dissociation of weak acid will be further decreased.



Here, strong electrolyte suppress the ionization of acetic acid (Backward reaction).

Since, acetic acid is a weak acid, it remains unionized in solution and the OH^- ions makes the solution basic or alkaline.

(c) In titration between strong acid and strong base pH at the equivalence point is 7, but in this titration pH at the equivalence point will always be more than 7 because hydrolysis of salt.



Due to OH^- ions after hydrolysis of salt pH will always be higher than 7 in these types of titration.

The pH of the solution at the equivalence point is given by,

$$\text{pH} = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$K_w = 10^{-14}$$

$$pK_w = -\log 10^{-14} = 14$$

$$K_a = 1.8 \times 10^{-5}$$

$$100 \text{ ml of } 0.1 \text{ M CH}_3\text{COOH}$$

$$100 \text{ ml of } 0.1 \text{ M NaOH}$$

$$200 \text{ ml total}$$

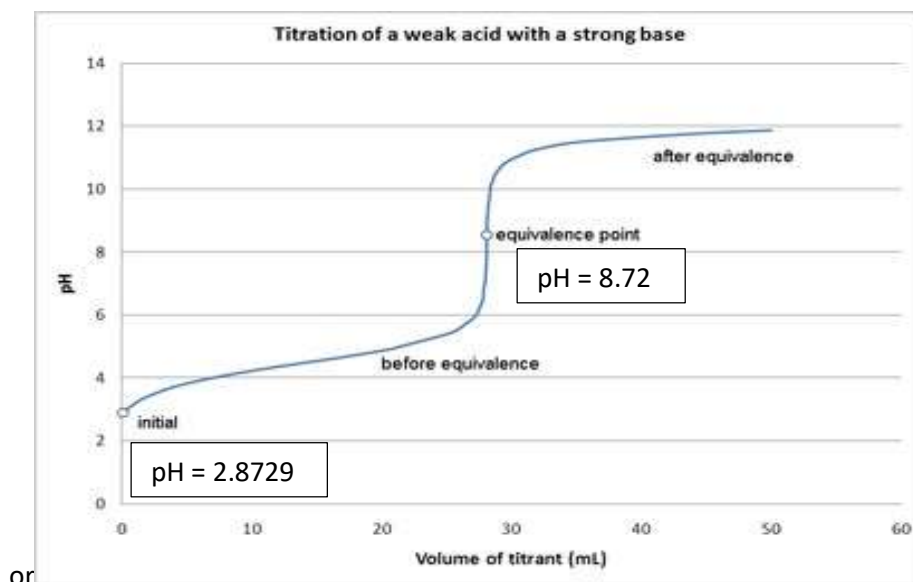
$$pK_a = 4.7447$$

$$pH = \frac{1}{2} 14 + \frac{1}{2} 4.7447 + \frac{1}{2} \log 0.05$$

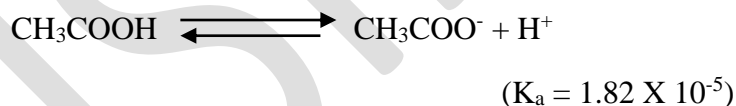
$$pH = 7 + 2.3724 + \frac{1}{2} (-1.30)$$

$$pH = 9.3724 - 0.65$$

$$pH = 8.7224$$



By applying law of mass of action,



$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = K_a$$

$$\text{Or } [H^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]}$$

By taking log on both sides

$$\text{Or } pH = \log \frac{[Salt]}{[Acid]} + pK_a$$

$$\text{Or } \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.82 \times 10^{-5}$$

$$\text{Or } \frac{[H^+]^2}{0.1} = 1.82 \times 10^{-5}$$

$$\text{Or } [H^+] = \sqrt{1.82 \times 10^{-6}}$$

$$[H^+] = 1.35 \times 10^{-3}$$

$$\text{Or } pH = 2.87$$

When 50 ml of 0.1 M alkali have been added,

$$[\text{Salt}] = \frac{50 \times 0.1}{150} = 3.33 \times 10^{-2}$$

$$[\text{Acid}] = \frac{50 \times 0.1}{150} = 3.33 \times 10^{-2}$$

$$\text{pH} = \log \left(\frac{3.33 \times 10^{-2}}{3.33 \times 10^{-2}} \right) + 4.74$$

$$\text{pH} = 4.74$$

pH of the 0.1 M acetic acid at other points on the titration curve can be calculated.

When 90 ml of 0.1 M NaOH is added,

$$[\text{CH}_3\text{COO}^-] = \frac{90 \times 0.1}{190} = 0.047$$

$$[\text{CH}_3\text{COOH}] = \frac{10 \times 0.1}{190} = 0.0053$$

$$\text{pH} = \log \left(\frac{0.047}{0.0053} \right) + 4.74$$

$$\text{pH} = 5.69$$

When 99 ml of 0.1 M NaOH added,

$$[\text{CH}_3\text{COO}^-] = \frac{99 \times 0.1}{199} = 0.050$$

$$[\text{CH}_3\text{COOH}] = \frac{1 \times 0.1}{199} = 0.00050$$

$$\text{pH} = \log \left(\frac{0.050}{0.00050} \right) + 4.74$$

$$\text{pH} = 6.7$$

When 99.9 ml of 0.1 M NaOH added,

$$[\text{CH}_3\text{COO}^-] = \frac{99.9 \times 0.1}{199.9} = 0.050$$

$$[\text{CH}_3\text{COOH}] = \frac{0.1 \times 0.1}{199.9} = 0.000050$$

$$\text{pH} = \log \left(\frac{0.050}{0.000050} \right) + 4.74$$

$$\text{pH} = 7.7$$

When 100 ml of 0.1 M NaOH added,

$$\text{pH} = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$\text{pH} = 8.7224$$

When 100.1 ml of 0.1 M NaOH added,

$$[\text{OH}^-] = \frac{0.1 \times 0.1}{200.1} = 5 \times 10^{-5}$$

$$\text{pOH} = 4.3$$

$$\text{pH} = 14 - 4.3$$

$$\text{pH} = 9.7$$

Volume of NaOH added (ml)	0.1 M CH ₃ COOH
0	2.9
10	3.8
25	4.3
50	4.7
90	5.7
99	6.7
99.5	7.0
99.8	7.4
99.9	7.7
100	8.7
100.1	9.7
100.2	10.0
100.5	10.4
101	10.7
110	11.7
125	12.0
150	12.3
200	12.5

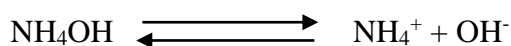
For the titration of 0.1 M CH₃COOH by 1 M NaOH, indicators which gives colour changes between the pH ranges of 7.7 – 10.0 will be effective and gives minimum error.

i.e following indicators are used to detect end point in case of weak acid and strong base titration.

- Thymol Blue –pH range: 8.0 – 9.6
- Thymolphthalein- pH range: 9.3 – 10.5
- Phenolphthalein- pH range: 8.3 – 10.0

3. Weak Base- Strong Acid Titration

Titration of 100 ml of 0.1 M aqueous ammonia ($K_a = 1.85 \times 10^{-5}$) with 0.1 M HCl



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.8 \times 10^{-5}$$

When 0 ml of 0.1 M HCl is added,

Initially, $[\text{NH}_4^+] = [\text{OH}^-]$

$$\frac{[\text{OH}^-]^2}{0.1} = 1.8 \times 10^{-5}$$

$$[\text{OH}^-]^2 = 1.8 \times 10^{-6}$$

$$[\text{OH}^-] = \sqrt{1.8 \times 10^{-6}}$$

$$[\text{OH}^-] = 1.34 \times 10^{-3}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log (1.34 \times 10^{-3})$$

$$\text{pOH} = 2.87$$

$$\text{pH} = 11.13$$

When 50 ml of 0.1 M HCl is added,

As HCl is added, it will neutralize ammonium hydroxide and forms equivalent quantity of ammonium ion.

$$[\text{NH}_4^+] = \frac{50 \times 0.1}{150} = 0.033$$

$$[\text{NH}_4\text{OH}] = \frac{50 \times 0.1}{150} = 0.033$$

$$\text{pOH} = \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} + \text{pK}_b$$

$$\text{pOH} = \log (0.033/0.033) + [-\log (1.8 \times 10^{-5})]$$

$$\text{pOH} = 4.74$$

$$\text{pH} = 14 - 4.74$$

$$\text{pH} = 9.26$$

When 90 ml of 0.1 M HCl is added,

$$[\text{NH}_4^+] = \frac{90 \times 0.1}{190} = 0.047$$

$$[\text{NH}_4\text{OH}] = \frac{10 \times 0.1}{190} = 0.0053$$

$$\text{pOH} = 5.69$$

$$\text{pH} = 8.31$$

When 99 ml of 0.1 M HCl is added,

$$[\text{NH}_4^+] = \frac{99 \times 0.1}{199} = 0.050$$

$$[\text{NH}_4\text{OH}] = \frac{1 \times 0.1}{199} = 0.00050$$

$$\text{pOH} = 6.7$$

$$\text{pH} = 7.3$$

When 99.9 ml of 0.1 M HCl is added,

$$[\text{NH}_4^+] = \frac{99.9 \times 0.1}{999.9} = 0.050$$

$$[\text{NH}_4\text{OH}] = \frac{1 \times 0.1}{199.9} = 0.000050$$

$$\text{pOH} = 7.7$$

$$\text{pH} = 6.3$$

When 100 ml of 0.1 M HCl is added, that is equivalent point and pH is calculated from,

$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b + \frac{1}{2} \text{p}C$$

Here 100 ml of 0.1 M NH_4OH is neutralized,

$$\text{Therefore, } [\text{NH}_4^+] = \frac{100 \times 0.1}{200} = 0.05$$

$$\text{p}K_b = 4.74, \text{p}K_w = 14$$

$$\text{pH} = \frac{1}{2} (14 - 4.74 + 1.30)$$

$$\text{pH} = 5.28$$

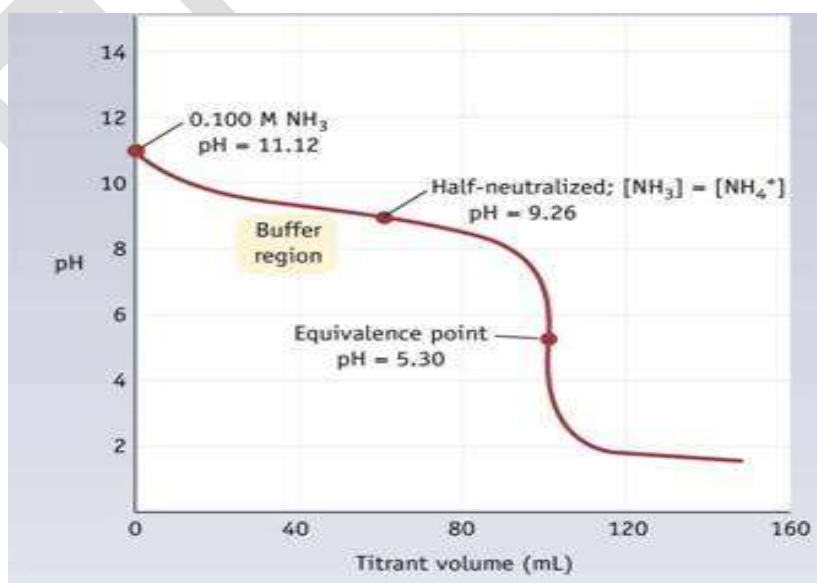
After equivalent point, HCl are added in excess and pH is calculated from concentration of $[\text{H}^+]$ ion.

When 100.1 ml of 0.1 M HCl is added,

After equivalence point. H^+ ion will be excess and pH will be calculated from $[\text{H}^+]$ ion concentration.

$$[\text{H}^+] = \frac{0.1 \times 0.1}{200.1} = 5 \times 10^{-5}$$

$$\text{pH} = 4.3$$



At equivalent point, pH is 5.28 so indicator selected should be such that the pH is slightly acidic side.

E.g. Methyl orange- pH range: 2.9 - 4.6

Bromocresol green- pH range: 3.6 – 5.2

Methyl red-pH range: 4.2 – 6.3

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