PHARMACEUTICAL ANALYSIS – BP102T

UNIT : II ACID-BASE TITRATIONS AND NON-AQUEOUS TITRATIONS

CLASS:15

TOPIC: NEUTRALIZATION CURVES

Classification of Acid- Base Titrations:

Acid base titrations is based on neutralization titration where acid reacts with base and forms salt

Acids:

Strong acids- Those acids which dissociate completely and pH range is from 0-3.

Ex:- $HCl \rightarrow H^+ + Cl^-$

Weak acids:- Those acids which dissociates partially and pH range is from 3-7.

Ex:- $CH3COOH \rightarrow CH3COO^- + H^+$

Strong base:- Those bases which dissociates completely and pH range is from 11-15.

Ex:- $NaOH \rightarrow Na^+ + OH^-$

Weak bases:- Bases which dissociates partially and pH range is from 7-10.

Ex:- $NH_4OH \rightarrow NH4^+ + OH^-$

Process in these titrations understood by change in hydrogen ion concentration during titrations.

The pH near end point suggest the choice of indicator for that particular titration.

Based on strength and nature of an acid and base, acid-base titrations are classified into :

1) Titration of strong acid with strong base
2) Titration of weak acid with strong base
3) Titration of weak base with strong acid
4) Titration of weak base with weak acid
5) Titration of polybasic acid with strong base

1) **Titration of strong acid with strong base :**

HCl is a strong acid and it completely dissociates into $\mathbf{H^+}$ and Cl^-. While sodium hydroxide is a strong base and it completely dissociates into Na+ and OH- and chemical reaction between HCl and NaOH takes place

$$\mathbf{HCl \rightarrow H^+ + Cl^-}$$

$$\mathbf{NaOH \rightarrow Na^+ + OH^-}$$

$$\mathbf{HCl + NaOH \rightarrow NaCl + H2O}$$

If we consider 100ml of 0.1M HCl and 0.1N NaOH which is added gradually. When NaOH is added from burette, OH^- ions of NaOH reacts with $\mathbf{H^+}$ of HCl and convert into water

- where H+ ions continuously decreased.
- Once the total available $\mathbf{H^+}$ ions are converted into water, it indicates the completion of reaction or endpoint i.e when NaOH is added in the solution all the H+ ions are neutralized by OH- ions.
- At that point solution is nor acidic nor basic it is having neutral pH because NaCl salt which is formed during reaction doesn't hydrolyzed and cannot disturb pH.
- From above discussion it is concluded that the equivalence point in the titration is at pH 7.
- But for the proper selection of indicator, pH at the endpoint is needed for that we have to study change in pH during titration.

Volume of	pH changes in

NaOH added	0.1M solution
0	1.0
50	1.5
75	1.8
98	3.0
99	3.3
99.8	4.0
99.9	4.3
100	7.0
100.1	9.7
100.2	10.0

- In the above table we observe that equivalent point the pH change is very sharp i.e 4.3 at 99.9 to 9.7 at 100.1. Therefore for 0.1M solutions the range from pH 4.3 to 9.7. Any indicator have pH range between this inflection range can be used for this titration.
- Phenolphthalein indicator has pH range 8.2 to 10.0 therefore phenolphthalein is the indicator of choice for this titration.
- Neutralization curve obtained for this titration is as follows:

Similarly 0.01M solution has inflection range from pH 5.5 to 8.5 and phenol red will be the suitable indicator while 1M solution has inflection range of pH 3 to 10.5 for that

- phenolphthalein will be suitable.

2) **Titration of Weak acid with Strong base:**

Acetic acid is a weak and sodium hydroxide is a strong base. Titration is performed similarly as performed for strong acid and strong base. The chemical reaction between acetic acid and sodium hydroxide can be described as follows:

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

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

But in case of acetic acid there are some differences:

- Due to being a weak acid it dissociates poorly therefore give smaller concentration of ions but initial pH is higher.
- When strong base is added to the weak acid it form salt which gives common ion effect which suppress the dissociation of weak acid and decrease hydrogen ion concentration which results increase in pH.

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$ (Poorly dissociated)

$CH_3COONa \leftrightarrow CH_3COO^- + Na^+$ (strongly dissociated)

- Due to hydrolysis of salt formed on the completion of reaction pH of the solution is more than 7.

$CH_3COONa + H_2O \rightarrow CH_3COOH + Na^+ + OH^-$

- Titration of 0.1M acetic acid with 0.1 M NaOH is performed similarly as performed in strong acid with strong base. Only difference is the initial pH is higher, rate of increase of pH is higher and pH at equivalent point is also higher due to salt formation.
- At equivalence point, pH change is very sharp i.e at 7.7 at 99.9 to 10.0 at 100.2
- For 0.1M solution, the pH range is from 7.7 to 10.0

  Ex:- phenolphthalein indicator (8.2 to 10)

3) **Titration of weak base with strong acid:**

Aqueous solution of ammonia is a weak base and hydrochloric acid is a strong acid. The chemical reaction between ammonium hydroxide and hydrochloric acid takes place and the reaction as follows:

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

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

When strong acid is added in the solution of weak base and the salt is formed which further undergoes hydrolysis,

$NH_4Cl + H_2O \rightarrow NH_4OH + H^+ + Cl^-$

In these titration, due to hydrolysis of salt there is formation of H^+ ions and the pH of solution at equivalence point is less than 7.

If 100ml of 0.1M NH_4OH is titrated against 0.1M HCl the inflection range is from pH 3 to 6.5.

Methyl red has pH range from 4.8 to 6.0 therefore, it is a indicator of choice for this titration.

1) **Titration of weak base with weak acid:**

Acetic acid is weak acid and ammonium hydroxide is weak base. The chemical reaction between

acetic acid and ammonium hydroxide takes place. The reaction as follows:

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

The salt which is formed during titration is further hydrolyzed.

$CH_3COONH_4 + H_2O \rightarrow CH_3COOH + NH_4 + OH^-$

If 100ml of 0.1 M ammonium hydroxide solution is titrated with 0.1M acetic acid solution. The inflection range is between pH 6 to 8. Therefore it is difficult to detect end point by indicators and accurate results are difficult to determine.

So mixed indicators is used which have sharp colour change at pH range.

2) **Titration of polybasic acid with strong base:**

Polybasic acid is an acid which has basicity more than one or which contain more than one ionizable hydrogen. They are also called polyprotic solvents.

Ex: sulphurous acid, carbonic acid is dibasic and orthophosphoric acid is tribasic acid.

Polyprotic solvent dissociates in stepwise manner and has more than one dissociation constant and behave like mixture of acid.