"बेटी बचाओ, बेटी पढ़ाओ"

JAYOTI VIDYAPEETH WOMEN'S UNIVERSITY, JAIPUR

Faculty of Pharmaceutical Science

Faculty Name - JV'n Dr. Parveen Parihar

Course - B. Pharm (1st sem)

Session - Pharmaceutical Analysis – (Classification of acid base titration)

Academic Day starts with –

- Greeting with saying **'Namaste'** by joining Hands together following by 2-3 Minutes Happy session, Celebrating birthday of any student of respective class and **NationalAnthem**

Acid Base Titration

Acid Base Titration:

Titrations in which the acid is titrated with base and vice-versa is called acid base titration

Classification:

Acid base titration is classified into four categories:

1. Titration of strong acid with strong base
2. Titration of weak acid with strong base
3. Titration of strong acid with weak base

4. Titration of weak acid with weak base

1. Titration of strong acid with strong base:

Let us consider titration of 100ml 0.1N HCl with the 100ml 0.1N NaOH

The p^H of the solution before titration is the p^H of 0.1N HCl.

After adding 1ml solution of titrant (NaOH), the volume in conical flask become 101ml and the acid equivalent is 99ml.

$$[H+] = \frac{99}{101}$$

$$P^H = -\log \left[\frac{99}{101}\right]$$

$$P^H = 0.0086$$

After addition of 50ml titrant

$$P^H = -\log \left[\frac{50}{150}\right]$$

$$P^H = 0.47$$

Adding 75ml of titrant

$$P^H = -\log \left[\frac{25}{175}\right]$$

$$P^{H =} 0.84$$

Adding 90ml of titrant

$$P^H = -\log \left[\frac{10}{190}\right]$$

$$P^H = 0.1927$$

Adding 99ml of titrant

$$P^H = -\log \left[\frac{1}{199}\right]$$

$$P^H = 2.27$$

After addition of 100ml of titrant the p^H will sharply change to 7 (end point).

After this the addition of 101ml of titrant

$$[OH^-] = [\frac{1}{101}]$$

$$P^{OH} = -\log [\frac{1}{101}]$$

$$P^H = 11.70$$

As the titration proceed the p^H change slowly until the end point, after that the p^H changes very sharply so any indicator which is effective in p^H range 3-10.5 may be used.

2. Titration of weak acid against strong base

This type of titration involves the neutralization of a weak acid with a strong base, such as the reaction between acetic acid and sodium hydroxide. The pH of the solution changes more gradually near the equivalence point.

3. Titration of strong acid against weak base

This type of titration involves the neutralization of a strong acid with a weak base, such as the reaction between hydrochloric acid and ammonia. The pH of the solution changes more gradually near the equivalence point than in a strong acid-strong base titration.

4. Titration of weak acid against weak base

The reaction between a weak acid and weak base is very very slow in nature that no steep rise occurs near the equivalence point nor the rise of pH encompasses an interval equal to pH transition range. Hence no indicator can be used to detect the end point. If we try to do it then the result will be full of error.

Theories of Acid Base titration indicators

Indicator: An indicator is a substance which is used to determine the end point in a titration. In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range.

Theory of acid-base indicators:

Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.

1. **Ostwald's theory:**

According to this theory: (a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form. (b) The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H+ ions while it is fairly ionised in alkalies. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH- ions.

Considering two important indicators phenolphthalein (a weak acid) and methyl orange (a weak base), Ostwald theory can be illustrated as follows:

Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as: $HPh \leftrightarrow H^{+} + Ph^{-}$ Colourless Pink

Applying law of mass action, K = [H+][Ph-]/[HpH]

The undissociated molecules of phenolphthalein are colourless while Ph- ions are pink in colour. In presence of an acid the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph- ions increases in solution and they impart pink colour to the solution.

2. Quinonoid Theory

According to this theory:

(a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

(b) The two forms have different colors. The color change in due to the interconversation of one tautomeric form into other.

(c) One form mainly exists in acidic medium and the other in alkaline medium.

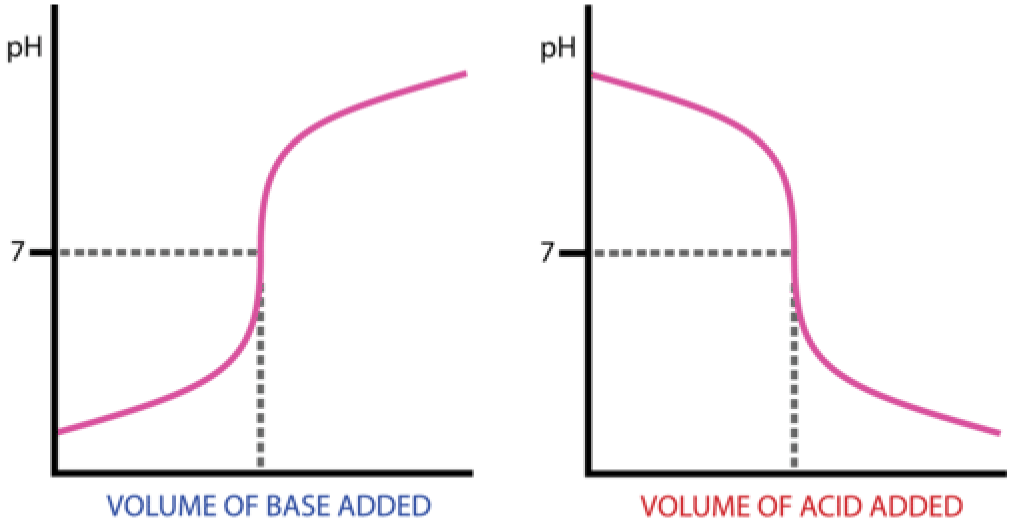
Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.

Phenolphthalein has benziod form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red.

Titration curve / Neutralization curve:

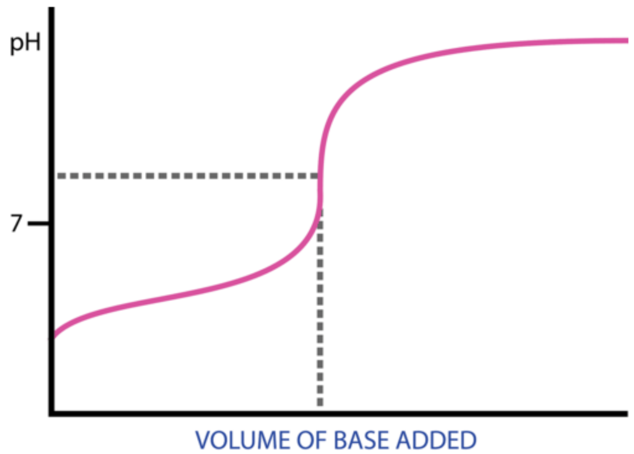
As base is added to acid at the beginning of a titration, the pH rises very slowly. Nearer to the equivalence point, the pH begins to rapidly increase. If the titration is a strong acid with a strong base, the pH at the equivalence point is equal to 7. A bit past the equivalence point, the rate of change of the pH again slows down. A **titration curve** is a graphical representation of the pH of a solution during a titration. The figure below shows two different examples of a strong acid-strong base titration curve. On the left is a titration in which the base is added to the acid, and so the pH progresses from low to high. On the right is a titration in which the acid is added to the base. In this case, the pH starts out high and decreases during the titration. In both cases, the equivalence point is reached when the moles of acid and base are equal and the pH is 7. This also corresponds to the color change of the indicator**.**



Titration curve of a strong acid (HCl) with a strong base (NaOH)

Titration curve of a strong base (NaOH) with a strong acid (HCl)

Titration curves can also be generated in the case of a weak acid-strong base titration or a strong acid-weak base titration. The general shape of the titration curve is the same, but the pH at the equivalence point is different. In a weak acid-strong base titration, the pH is greater than 7 at the equivalence point. In a strong acid-weak base titration, the pH is less than 7 at the equivalence point.



Titration curve of a weak acid (CH_3COOH) with a strong base (NaOH)

Summary

- A titration curve is a graphical representation of the pH of a solution during a titration.
- In a strong acid-strong base titration, the equivalence point is reached when the moles of acid and base are equal and the pH is 7.
- In a weak acid-strong base titration, the pH is greater than 7 at the equivalence point.
- In a strong acid-weak base titration, the pH is less than 7 at the equivalence point.

Non-aqueous solution titration:

The need for non aqueous titration arises because water can behave as a weak base and a weak acid as well, and can hence compete in proton acceptance or proton donation with other weak acids and bases dissolved in it.

The procedure of non aqueous titration is very useful because:

- it satisfies two different requirements, namely – suitable titration of very weak acids or bases
- along with providing a solvent with an ability to dissolve organic compounds. An example of a reaction in which water is not a suitable solvent is the reaction given by:

$$R\text{-}NH_2 + H^+ \rightleftharpoons R\text{-}NH_3^+$$

which is competed with in an aqueous solvent by the reaction given by:

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

This type of competition provided by water towards weak bases or weak acids makes it difficult to detect the end point of the titration.

Therefore, these substances which have very sharp end points when titrated in aqueous solutions due to their weakly basic or weakly acidic nature generally need to be titrated in non aqueous solvents.

Many reactions which occur in non aqueous titration procedures can be explained via the Bronsted-Lowry Theory and its definition of acids and bases. Basically, acids can be thought of as proton donors, whereas bases can be thought of as proton acceptors.

Limitation of aqueous acid-base titrations :

Titration in water solutions is limited by factors:

- It is impossible to titrate for a mix of acids or the bases
- It is impossible to titrate separately for a mix of acids (bases)
- It is impossible to titrate for a mix of strong and weak acids (bases) near constants of dissociation
- It is impossible to define substances which are insoluble in water**.**

Non-aqueous titrations have the following advantages

- Organic acids and bases that are insoluble in water are soluble in nonaqueous solvent.
- A non-aqueous solvent may help two are more acids in mixture. The individual acid can give separate end point in different solvent.
- Enlargement of solubility range: many substances that are not soluble in water can be easily titrated in water-free media (e.g. fats and oils)
- Enlargement of application range: weak bases and acids can be easily titrated
- Non-aqueous solvents are useful for the titration of very weak acids or bases that cannot be titrated in water.

    - Non aqueous titrations are simple and accurate.

- **Next Topic-**

➢ Pharmaceutical Analysis – (Solvents)

- **Academic Day ends with-**

  National song 'Vande Mataram'