Shri R. L. T. College of Science,

Chapter 6 (Physical chemistry)

B. Electrochemistry

Conductometric titrations:

Principle

The principle of the conductometric titration process can be stated as follows – During a titration process, one ion is replaced with another and the difference in the ionic conductivities of these ions directly impacts the overall electrolytic conductivity of the solution.

It can also be observed that the ionic conductance values vary between cations and anions. Finally, the conductivity is also dependant upon the occurrence of a chemical reaction in the electrolytic solution.

Theory

The theory behind this type of titration states that the end-point corresponding to the titration process can be determined by means of conductivity measurement. For a neutralization reaction between an acid and a base, the addition of the base would lower conductivity of the solution initially. This is because the H+ ions would be replaced by the cationic part of the base.

After the equivalence point is reached, the concentration of the ionic entities will increase. This, in turn, increases the conductance of the solution. Therefore, two straight lines with opposite slopes will be obtained when the conductance values are plotted graphically. The point where these two lines intersect is the equivalence point.

Conductometry is a measurement of electrolytic conductivity

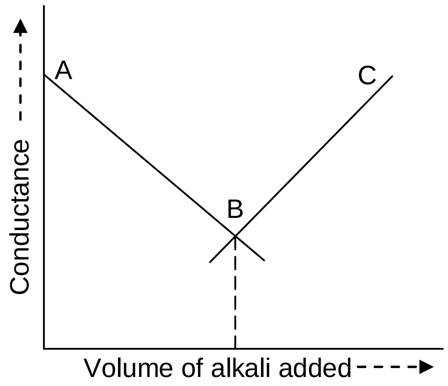
- The titration in which end point is determined by measuring change in conductance of solution upon addition of reagent is called *conductometric titration*.
- The conductance of a solution depends largely on the number of ions and their mobilities. Some examples of conductometric titrations are as given below.

1) Strong acid against strong base: (HCl against NaOH)

Consider the titration of strong acid (HCl) against strong base (NaOH). The acid is taken in conductivity vessel and alkali in burette. The conductance of HCl is due to presence of H^+ and Cl^- ions. As alkali is added, gradually H^+ ions are replaced by slow moving Na^+ ions as given below:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

Until the complete neutralization, conductance decreases on addition of NaOH. Any subsequent addition of alkali after end point will result in introduction of fast moving OH^- ions. The conductance therefore increases on further addition of alkali. The variation of conductance is plotted against volume of alkali added, we get two straight lines meeting at point 'B' which represents end point of titration.

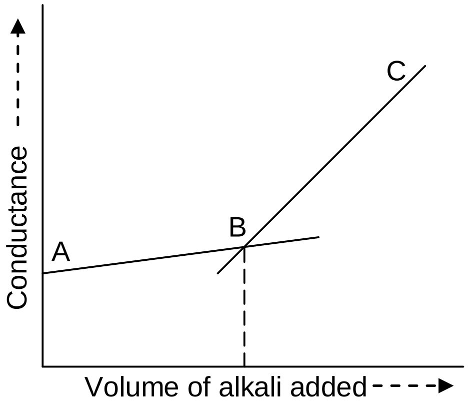


2) Weak acid against strong base: (CH_3COOH against NaOH)

When acid is weak, conductance is low, on addition of strong base poorly conducting acid is converted into highly ionsed salt and hence conductance increases slowly up to the equivalence point. Beyond the equivalence point, addition of alkali causes sharp increase in conductance due to excess of hydroxide ions.

- $CH_3COO^- + H^+ + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$

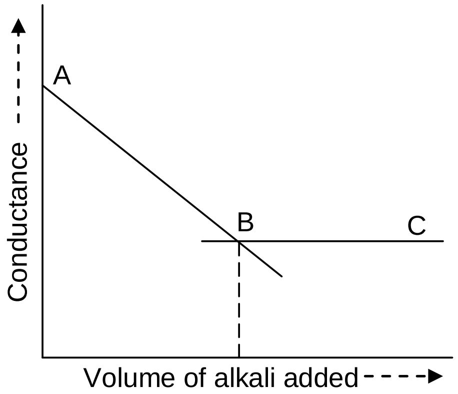
The graph is represented as:



3) Strong acid against weak base: (HCl against NH_4OH)

In this case conductance initially decreases due to the replacement of fast moving H^+ ions by slow moving NH_4^+ ions.

$H^+ + Cl^- + NH_4^+ + OH^- \rightarrow NH_4^+ + Cl^- + H_2O$



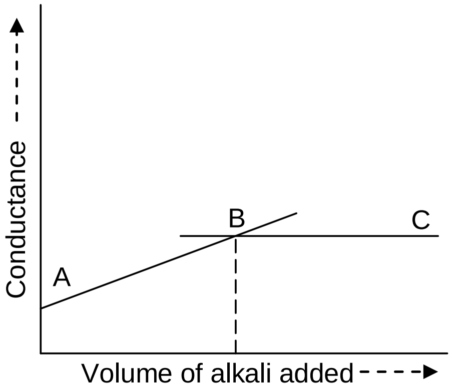
Beyond end point, further addition of weakly ionized NH_4OH will not cause any appreciable change in conductance. The point of intersection of curves is the end point of titration.

4) Weak acid against weak base: (CH_3COOH against NH_4OH)

In this titration, conductance initially increases because of formation of salt (CH_3COONH_4) which is strong electrolyte. This increase continues till end point. Beyond end point, the conductance does not change appreciably.

- $CH_3COO^- + H^+ + NH_4^+ + OH^- \rightarrow CH_3COO^- + NH_4^+ + H_2O$

The graph is shown in fig.

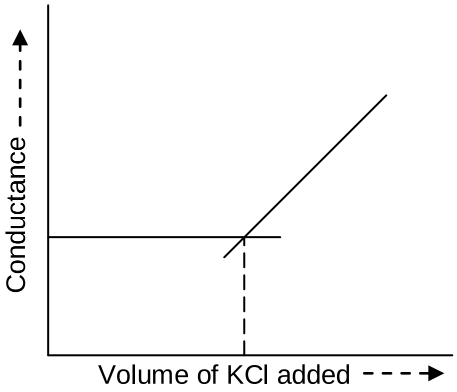


5) Precipitation titration: ($AgNO_3$ against KCl)

The titration of silver nitrate against potassium chloride involves precipitate formation.

$$AgNO_3 + KCl \rightarrow KNO_3 + AgCl\downarrow$$

Since mobility of Ag^+ and K^+ ions is nearly same, the conductance remains almost constant till the equivalence point. After equivalence point, the added KCl, increases the conductance rapidly as shown in graph given below.



Advantages of conductometric titrations:

The conductometric titration has many advantages over ordinary titration:

1) Small quantity of solutions is required for titrations.
2) As end point is determined graphically, no special precautions are necessary.
3) Indicator is not required, so conductometric titrations are used in titration of coloured and turbid solutions.

4) Conductometric titrations are used for analysis of dilute solutions as well as for weak acids.
5) Conductometric titrations can be applied to mixture of acids, precipitation & other types of titrations.
6) Conductometric measurements give more accurate results.

Disadvantages of conductometric titrations:

The conductometric titration has following disadvantages:

- High concentration of salt in the solution does not give accurate results.
- Presence of another electrolytes other than the species to be analysed will not give accurate results.
- Limited use for redox titration .

Applications of conductometric titrations:

The conductometric titration has following applications:

- Pollution in water.
- Quantitative analysis of compounds
- Alkalinity of water.
- Salinity of water.
- Basicity of organic acids.
- Deuterium ion concentration in water.
- Solubility of sparingly soluble salts.