

3.2 ELECTROCHEMICAL SERIES (e.m.f series)

A series in which elements are arranged in the ascending (increasing) order of their standard reduction potential is called emf series.

Significance of EMF series

Half cell reaction	E° (V)
$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$	- 3.04
$\text{Mg}^{2+} + 2\text{e}^{-} \rightarrow \text{Mg}$	- 2.37
$\text{Al}^{3+} + 3\text{e}^{-} \rightarrow \text{Al}$	- 1.66
$\text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn}$	- 0.76
$\text{Fe}^{2+} + 2\text{e}^{-} \rightarrow \text{Fe}$	- 0.44
$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2 (\text{g})$	0.00
$\text{Hg}_2^{2+} + 2\text{e}^{-} \rightarrow \text{Hg} (\text{l})$	0.2422
$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$	0.34
$\text{Cu}^{+} + \text{e}^{-} \rightarrow \text{Cu}$	0.52
$\text{Pt, Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}$	0.77
$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	0.80
$\text{Au}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	1.69
$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	2.8

Application / Significance of electrochemical series

(i) Relative ease of oxidation or reduction

- The metals which lie above hydrogen in the series undergo spontaneous oxidation and the metals which lie below SHE undergo reduction spontaneously (ie. Acts as Anodes and Cathodes respectively)
- The metals which lie above hydrogen are good reducing agents and which lies below hydrogen will act as good oxidizing agents

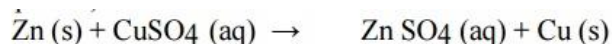
(ii) Replacement tendency

The metal lying above in emf series displaces the metal lying below it from an electrolyte of the later.

Example 1: Ni spatula cannot be used to stir copper sulphate solution due to the following reaction



Example 2: when zinc is dipped in copper sulphate solution copper gets deposited (displaced)



(iii) Liberation of Hydrogen

- The metal with negative reduction potential will displace H_2 from an acid solution



Hence acids cannot be stored in galvanized steel containers.

For exactly the same reason galvanized steels are not used to store food stuffs containing vinegar. (Vinegar is used as food preservative- vinegar is acetic acid)

(iv) Calculation of equilibrium constant (K_{eq})

$$\begin{aligned} \Delta G^{\circ} &= n F E^{\circ} \\ -\Delta G^{\circ} &= 2.303 RT \log K(\text{eq}) \text{ Therefore} \\ \log K(\text{eq}) &= \frac{n F E^{\circ}}{2.303 RT} \end{aligned}$$

$\log K(\text{eq}) = \frac{nE^{\circ}}{0.0591}$

(v) Calculation of Standard emf of the cell

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

(if both reduction potentials are considered)

$$E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

(if oxidation potential of anode and the reduction potential of cathode are considered)

(vi) Corrosion

The metals higher in the series are anodic and are more prone to corrosion.

The metals lower in the series are noble metals (cathodic) and they are less prone to corrosion.

(vii) Predicting the spontaneity of cell reaction

Spontaneity of the redox reaction can be predicted from the emf value of complete cell reaction.

If the value of E_{cell} is positive, the reaction is feasible. as ΔG will be negative (i.e. it is an electrochemical cell)

If the value of E_{cell} is negative, the reaction is not feasible. as ΔG will be positive (i.e. it is an electrolytic cell)

3.2.1 Conductometric titrations

- 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.

Principle

- 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 dependent upon the occurrence of a chemical reaction in the electrolytic solution.

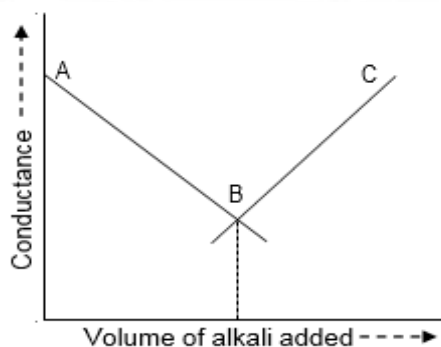
Types of conductometric titrations:

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:



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.

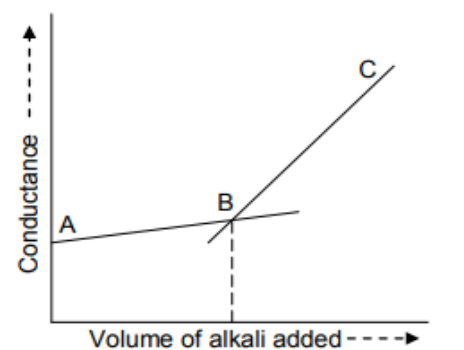


2) **Weak acid against strong base: (CH_3COOH against $NaOH$)**

When acid is weak, conductance is low, on addition of strong base poorly conducting acid is converted into highly ionized 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.

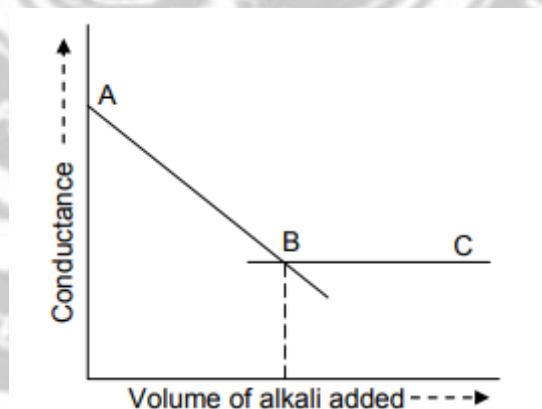


The graph is represented as:



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.



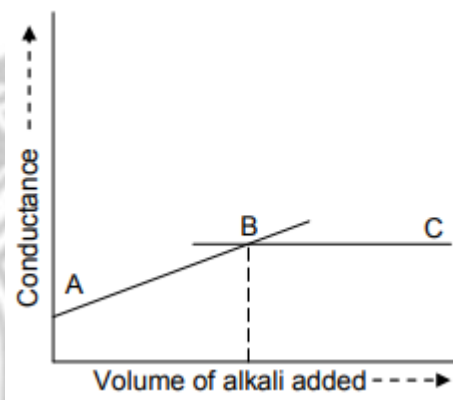
Beyond end point, further addition of weakly ionized NH_4OH will not cause any appreciable change in conductance. The point of intersection of curves is the end point of titration.

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.

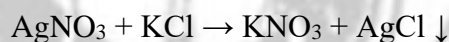


The graph is shown in fig.

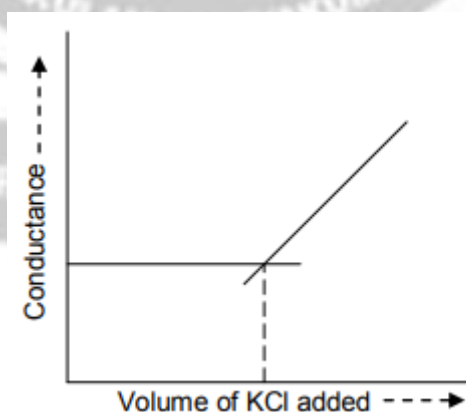


5) **Precipitation titration: ($AgNO_3$ against KCl)**

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



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:

- Small quantity of solutions is required for titrations.
- As end point is determined graphically, no special precautions are necessary.
- Indicator is not required, so conductometric titrations are used in titration of coloured and turbid solutions. Volume of alkali added Conductance A B C
Volume of KCl added Conductance
- Conductometric titrations are used for analysis of dilute solutions as well as for weak acids.
- Conductometric titrations can be applied to mixture of acids, precipitation & other types of titrations.
- Conductometric measurements give more accurate results.

Disadvantages of conductometric titrations:

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

Applications of conductometric titrations:

- 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.