Potentiometric titration

❖ In a titration, there is a change in ionic concentration which can be followed by measuring the potential of a suitable electrode.

❖ The potential of an electrode depends upon the concentration of the ions in accordance to Nernst equation,
e.g. $O^{n+} + n\ e^- \longrightarrow R$

$E = E^0 - (RT/nF) \ln [R/O^{n+}]$
E^0 is standard reduction potential

❖ The potentiometric titrations are those titrations which involve the measurement of electrode potentials with the addition of the titrant.

Types of potentiometric titration

The potentiometric titrations are of three categories

1. Acid-base titrations

2. Redox titrations

3. Precipitation titrations

Advantages:

❖ This can be carried out in coloured solutions where indicators can not be used

❖ No information about the relative strength of acids and bases for the selection of a proper indicator is required

Acid-base titrations

Requirement of two electrodes

1. Indicator electrode (e.g., Hydrogen electrode) $H^+ + e^- \rightarrow \frac{1}{2} H_2$

2. Reference electrode (whose potential does not change)

The galvanic cell may be represented as

Pt, H_2 (1 atm), H^+ (c= unknown) $\|$ KCl sat. soln.; Hg_2Cl_2 (s), Hg

EMF of the cell :
$$E = E_R - E_L = E_{calomel} - E_{hydrogen}$$
$$= 0.2422 - 0.0591 \log H^+$$
$$= 0.2422 + 0.0591 \text{ pH}$$
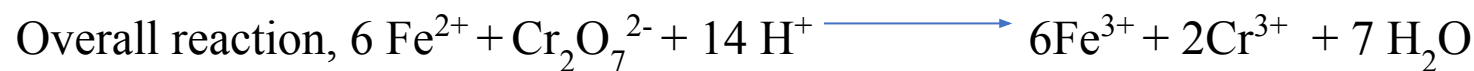
Redox titrations

Requirement of two electrodes

1. Indicator electrode (Here Pt electrode)

2. Reference electrode (whose potential does not change)

In this case, the hydrogen electrode (reversible w.r.t. H^+ ions)
is replaced by an inert metal such as Pt wire immersed in a solution
containing both the oxidized and the reduced forms of the same species

The galvanic cell may be represented as

Hg, Hg_2Cl_2 (s), KCl sat. soln. $\parallel$ Fe^{2+}, Fe^{3+}; Pt

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} + 14\ H^+ + 6e- \longrightarrow 2Cr^{3+} + 7\ H_2O$

Overall reaction, $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7\ H_2O$

Before the equivalence point, the EMF of the cell will be given by,

$E = E_R - E_L$

$= E^0_{el} + 0.0591\ \log\ \{[Fe^{3+}] / [Fe^{2+}]\}\ -\ E_{calomel}$

$= 0.77 + 0.0591\ \log\ \{[Fe^{3+}] / [Fe^{2+}]\}\ -\ 0.2422$

At the equivalent point, the EMF of the cell is given by,

$E = (0.77 + E^0_{Cr}{}^{6+/3+})/2\ -\ 0.2422$ $E_{Cr}{}^{6+/3+} = E^0_{Cr}{}^{6+/3+} - (0.0591/6)\ \log\ \{[Cr^{3+}]^2/[Cr^{6+}]\ [H^+]^{14}\}$

The EMF of the cell is measured potentiometrically at each stage of titration and the EMF data
thus obtained are processed for the equivalent point

Precipitation titration

Requirement of two electrodes

1. Indicator electrode (e.g., Ag electrode)

2. Reference electrode (Calomel electrode)

Let us consider the standardization of silver nitrate with NaCl solution

The reaction involved is

$$Ag^+ + NO_3^- + Na^+ + Cl^- \longrightarrow AgCl\ (s) \downarrow + Na^+ + NO_3^-$$

On addition of NaCl, the concentration of Ag^+ ions goes on decreasing and hence, the potential of half-cell Ag^+, Ag electrode given by Nernst equation ;

$$E_{el} = E_{el}^{0} + 0.059 \log [Ag^+]$$

will be decreasing continuously.

❖ The electrode potential will change slowly at first and then more rapidly as the end point approaches.

❖ At the end point, the concentration of Ag^+ ions is very small and the change in electrode potential is maximum

❖ The addition of NaCl beyond the end point will result in a small change in the electrode potential

The cell representation:

Hg, Hg_2Cl_2 (s), KCl sat. soln. ‖ Ag^+, Ag

EMF of the cell (Potentiometer reading):

$$E = E_R - E_L = E_{Ag+,Ag} - E_{calomel}$$
$$= E_{el}^0 + 0.059 \log [Ag^+] - 0.2422 \text{ V}$$
$$= E_{el}^0 + 0.059 \log [Ag^+] - 0.2422 \text{ V}$$
$$= 0.80 \text{ V} + 0.059 \log [Ag^+] - 0.2422 \text{ V}$$
$$= 0.5578 + 0.059 \log [Ag^+]$$