Dichromatometry

Redox titrations with potassium dichromate as oxidant are known as dichromatometry.

In acid medium $K_2Cr_2O_7$ has higher standard reduction potential and so it acts as a powerful oxidant. However, it is a weaker oxidant than $KMnO_4$ for its comparatively lower standard reduction potential.

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O, \quad E^\circ = 1.33V$$

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O, \quad E^\circ = 1.51V$$

1) Potassium dichromate can be obtained in very high purity.

2) Its solutions are stable for a long time if they are properly protected from evaporation.

3) Its solutions are stable towards light and organic matter.

4) $K_2Cr_2O_7$ is not reduced by cold dilute HCl or Chloride.

Therefore, $K_2Cr_2O_7$ is used as an excellent primary standard.

Equivalent Weight of $K_2Cr_2O_7$

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3O$$

Or ionically,

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

During reduction of $Cr_2O_7^{2-}$ to Cr^{3+}, a molecule of $K_2Cr_2O_7$ accepts 6 electrons.

Hence, according to the definition of equivalent weight of oxidising agents,

$$\text{Equivalent weight of } K_2Cr_2O_7 = \frac{\text{Molecular weight}}{6}$$

$$= \frac{294}{6}$$

$$= 49$$

pH of dichromate solution

The half reaction of the reduction of dichromate is — $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

This equation reveals that oxidation potential this above reaction must be strongly influenced by the concentration of the acid.

Therefore, the volumetric titrations with dichromate are to be carried out in 1-2 (N) acid.

Redox Indicators for titrations with $K_2Cr_2O_7$

Sodium or Barium diphenylamine sulfonate (BaDS) is usually used as the indicator.

Freshly prepared diphenylamine may also be used as indicator.

But BaDS works better as its solution can resist aerial oxidation and can be stored for a long time.

BaDS gives a very sharp colour change from colourless through green to red-violet.

To use BaDS or diphenylamine as indicator, H_3PO_4 or F^- (NH_4HF_2) should be added prior to the start of the titration to lower the reduction potential of Fe^{3+}/Fe^{2+} system and makes the idicator suitable for the titration.

For an indicator to be suitable for redox titration, its standard reduction potential should be higher than that of the reductant and lower than that of the oxidation.

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O, \quad E^\circ = 1.33V$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}, \quad E^\circ = 0.77V$$

$$In_{ox} + ne \rightleftharpoons In_{red}, \quad E^\circ = 0.83V$$

The standard reduction potential of Fe^{3+}/Fe^{2+} system is

lowered by addition of H_3PO_4 or F^- prior to the start of titration. H_3PO_4 or F^- (NH_4HF_2) reduces the standard reduction potential of Fe^{3+}/Fe^{2+} system by removing Fe^{3+} as $[Fe(HPO_4)]^+$ or FeF_6^{3-} complex to about 0.61 V.