

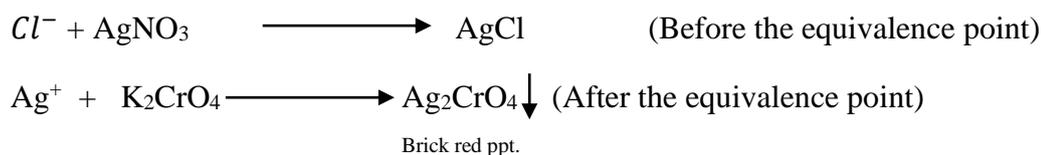
ARGENTOMETRIC/ PRECIPITATION TITRATIONS

Q.1. What are precipitation Titrations?

Ans. Those chemical reactions that involves the formation of precipitates or sparingly soluble salt are known as precipitation Titrations. These reactions are not numerous as compared to acid base or oxidation-reduction reactions. These are limited to those involving the precipitation of silver ions with anions like Halogens or thiocyanate (SCN⁻), because there is lack of suitable indicators to detect end point and due to slow rate of reaction. The composition of precipitate is not exactly known due to co-precipitation.

Q.2. Explain the end point detection in precipitation titration by Mohr's Method.

Ans. In this method the end point detection is marked with formation of colored precipitates. It is used for determination of Cl^- & Br^- . In the titration of for example Cl^- with $AgNO_3$ solution, a small quantity of K_2CrO_4 (potassium chromate) is added as indicator. At end point chromate ions combine with Ag^+ to form brick red colored Ag_2CrO_4 precipitates.



Explanation:

In the titration, we have two sparingly soluble salts that are produced.

One is $AgCl$ with solubility ($K_{sol} = 1.2 \times 10^{-10}$) & other one Ag_2CrO_4 with solubility ($K_{sol} = 1.7 \times 10^{-12}$).

In titration of 0.1M $NaCl$ with 0.1M $AgNO_3$ in presence of few ml of K_2CrO_4 solution, $AgCl$, a low solubility salt is produced. Since initially concentration of chloride (Cl^-) solution is high, therefore $AgCl$ is precipitated first. At the first point where red Ag_2CrO_4 is just precipitated both the salts (i.e. $AgCl$ & Ag_2CrO_4) will be in equilibrium with the solution.

Therefore, $[Ag^+][Cl^-] = (K_{sol}(AgCl) = 1.2 \times 10^{-10}$
& $[Ag^+]^2 [CrO_4^{2-}] = K_{sol} (Ag_2CrO_4) = 1.7 \times 10^{-12}$.

$$\begin{aligned} [Ag^+] &= \frac{K_{sol}(AgCl)}{[Cl^-]} = \sqrt{\frac{K_{sol}(Ag_2CrO_4)}{[CrO_4^{2-}]}} \\ \frac{[Cl^-]}{\sqrt{[CrO_4^{2-}]}} &= \frac{K_{sol}(AgCl)}{\sqrt{K_{sol}(Ag_2CrO_4)}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 9.2 \times 10^{-5}. \end{aligned}$$

Now, at equilibrium or equivalent point

$$[Cl^-] = \sqrt{K_{sol.AgCl}} = 1.1 \times 10^{-5}$$

So if Ag_2CrO_4 is to be precipitated at above Cl^- concentration

$$[CrO_4^{2-}] = \left(\frac{[Cl^-]}{9.2 \times 10^{-5}}\right)^2 = \left(\frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}}\right)^2 = 1.4 \times 10^{-2} \quad \text{OR} \quad 0.014M$$

Therefore, Concentration of K_2CrO_4 should be 0.014M. Generally for practical purposes more dilute solutions of K_2CrO_4 (0.003-0.005 M) is used. Because chromate solution of 0.01-0.02M concentration will give deep orange color to solution & it will be very difficult to detect first appearance of Ag_2CrO_4 . Titration error can be minimized by performing a blank titration by measuring volume of standard $AgNO_3$ solution required to give the precipitable color when added to distilled water containing same quantity of indicator. This volume is subtracted from volume of standard solution used. This method is not successful with iodide or thiocyanate because AgI or $AgSCN$ adsorb chromate ions so strongly that a false & indistinct end point is obtained.