

ARGENTOMETRIC/ PRECIPITATION TITRATIONS

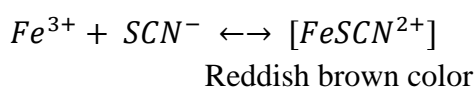
Discuss the principle used in titration of volhard's method.

Ans. In this method there is formation of soluble colored compound. Here titration of Ag^+ in presence of free HNO_3 (0.5-1.5M) with standard potassium (K) or NH_4SCN solution is done. Indicator used is a solution of Iron (III) nitrate or Iron (III) Ammonium sulphate solution.

To Ag^+ solution SCN^- (Thiocyanate) solution is added.



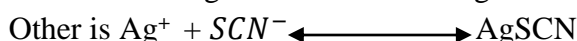
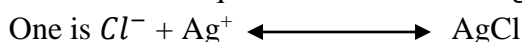
First $AgSCN$ precipitates. When above reaction is complete, slight excess of SCN^- produces a reddish brown coloration due to formation of complex ion.



This method is used for determination of Cl^- , Br^- , I^- in acid solution.

Method:

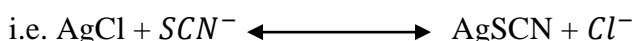
Excess of $AgNO_3$ solution is added and excess is back titrated with standard thiocyanate solution. Two equilibriums exists during the titration of excess of Ag^+ .



$$\therefore \frac{[Cl^-]}{[SCN^-]} = \frac{K_{sol}(AgCl)}{K_{sol}(AgSCN)} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

What problem is encountered in Volhards method and how to overcome it.

A. When excess of Silver has reacted, then SCN^- may react with $AgCl$ because $AgSCN$ is less soluble salt.



The above reaction takes place before the reaction occurs with iron (III) ions in the solution & there is titration error.

Titration error with Cl^- is highest. For Br^- is lower, & for I^- is still more lower, because of solubility of Br^- & I^- .

$$\frac{[Br^-]}{[SCN^-]} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5$$

It is important to prevent the reaction of SCN^- solution with $AgCl$.

Methods to prevent the above problem:

1. **By filtering off $AgCl$** ; produced before back titrating the remaining unreacted Ag^+ against SCN^- solution. But at this stage precipitates of $AgCl$ will be contaminated with adsorbed Ag^+ . Therefore, the suspension of $AgCl$ is boiled for few minutes. This boiling results in coagulation of $AgCl$ & this removes the adsorbed ions of Ag^+ before filtration. Then the cooled filtrate is titrated.

2. **By use of coagulant:** After the addition of AgNO_3 to halide solution, KNO_3 is added as coagulant & then suspension is boiled for 3 minutes. Then cooled & titrated immediately. This results in desorption of Ag^+ that are adsorbed & on cooling re-adsorption is prevented by presence of KNO_3 .

3. Use of Immiscible liquid:

An immiscible liquid is added to coat AgCl particles & thereby protect them from interaction with SCN^- solution. Eg. Liquid like nitrobenzene (1 ml for each 50 mg of Cl^-) is added to suspension & is shaken well to coagulate precipitate before back titration.