

Lecture- 10

Titration Based on Precipitation Reactions

Precipitation Titrations

Thus far we have examined titrimetric methods based on acid-base reactions. A reaction in which the analyte and titrant form an insoluble precipitate also can form the basis for a titration. We call this type of titration a **precipitation titration**.

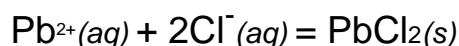
One of the earliest precipitation titrations, developed at the end of the eighteenth century, was for the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $Ca(NO_3)_2$, was used as a titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$. The end point was signaled by noting when the addition of titrant ceased to generate additional precipitate.

The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag^+ and halide ions.

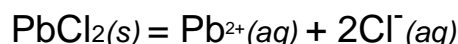
Precipitation Reactions

A precipitation reaction occurs when two or more soluble species combine to form an insoluble product that we call a **precipitate**. The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. When a solution of lead nitrate is added to a solution of potassium chloride, for example, a precipitate of lead chloride forms. We usually write the balanced reaction as a net ionic equation, in which only the precipitate and those ions involved in the reaction are included.

Thus, the precipitation of $PbCl_2$ is written as



In the equilibrium treatment of precipitation, however, the reverse reaction describing the dissolution of the precipitate is more frequently encountered.



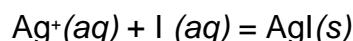
The equilibrium constant for this reaction is called the **solubility product**, K_{sp} , and is given as

$$K_{sp} = [Pb^{2+}] [Cl^{-}]^2 = 1.7 \times 10^{-5}$$

Note that the precipitate, which is a solid, does not appear in the K_{sp} expression. It is important to remember, however, that equation is valid only if $PbCl_2(s)$ is present and in equilibrium with the dissolved Pb^{2+} and Cl^{-} .

Titration Curves

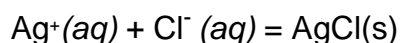
The titration curve for a precipitation titration follows the change in either the analyte's or titrant's concentration as a function of the volume of titrant. For example, in an analysis for I using Ag⁺ as a titrant



the titration curve may be a plot of pAg or pI as a function of the titrant's volume. As we have done with previous titrations, we first show how to calculate the titration curve.

Calculating the Titration Curve

As an example, let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M Cl⁻ with 0.100 M Ag⁺. The reaction in this case is



The equilibrium constant for the reaction is

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9$$

Since the equilibrium constant is large, we may assume that Ag⁺ and Cl⁻ react completely.

By now you are familiar with our approach to calculating titration curves. The first task is to calculate the volume of Ag⁺ needed to reach the equivalence point. The stoichiometry of the reaction requires that

$$\text{Moles Ag}^+ = \text{moles Cl}^-$$

$$M_{\text{Ag}}V_{\text{Ag}} = M_{\text{Cl}}V_{\text{Cl}}$$

Solving for the volume of Ag⁺

$$V_{\text{Ag}} = \frac{M_{\text{Cl}}V_{\text{Cl}}}{M_{\text{Ag}}} = \frac{(0.050 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 25.0 \text{ mL}$$

shows that we need 25.0 mL of Ag⁺ to reach the equivalence point.

Before the equivalence point Cl⁻ is in excess. The concentration of unreacted Cl⁻ after adding 10

$$[\text{Cl}^-] = \frac{\text{moles excess Cl}^-}{\text{total volume}} = \frac{M_{\text{Cl}}V_{\text{Cl}} - M_{\text{Ag}}V_{\text{Ag}}}{V_{\text{Cl}} + V_{\text{Ag}}}$$

$$= \frac{(0.050 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 2.50 \times 10^{-2} \text{ M}$$

.0 mL of Ag⁺,

for example, is

If the titration curve follows the change in concentration for Cl⁻, then we calculate pCl as

$$\text{pCl} = -\log[\text{Cl}^-] = -\log(2.50 \times 10^{-2}) = 1.60$$

However, if we wish to follow the change in concentration for Ag⁺ then we must first calculate its concentration. To do so we use the K_{sp} expression for AgCl

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

Solving for the concentration of Ag⁺

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9} \text{ M}$$

gives a pAg of 8.14.

At the equivalence point, we know that the concentrations of Ag⁺ and Cl⁻ are equal. Using the solubility product expression

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+]^2 = 1.8 \times 10^{-10}$$

gives

$$[\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ M}$$

At the equivalence point, therefore, pAg and pCl are both 4.89.

After the equivalence point, the titration mixture contains excess Ag⁺. The concentration of Ag⁺ after adding 35.0 mL of titrant is

$$[\text{Ag}^+] = \frac{\text{moles excess Ag}^+}{\text{total volume}} = \frac{M_{\text{Ag}}V_{\text{Ag}} - M_{\text{Cl}}V_{\text{Cl}}}{V_{\text{Cl}} + V_{\text{Ag}}}$$

$$= \frac{(0.10 \text{ M})(35.0 \text{ mL}) - (0.050 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}} = 1.18 \times 10^{-2} \text{ M}$$

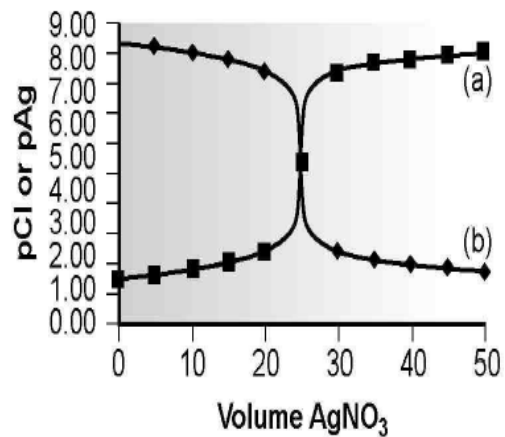
or a pAg of 1.93. The concentration of Cl⁻ is

$$[\text{Cl}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M}$$

or a pCl of 7.82.

| Volume AgNO ₃ (mL) | pCl | pAg |
|-------------------------------|------|------|
| 0.00 | 1.30 | — |
| 5.00 | 1.44 | 8.31 |
| 10.00 | 1.60 | 8.14 |
| 15.00 | 1.81 | 7.93 |
| 20.00 | 2.15 | 7.60 |
| 25.00 | 4.89 | 4.89 |
| 30.00 | 7.54 | 2.20 |
| 35.00 | 7.82 | 1.93 |
| 40.00 | 7.97 | 1.78 |
| 45.00 | 8.07 | 1.68 |
| 50.00 | 8.14 | 1.60 |

Data for Titration of 50.0 mL of 0.0500 M Cl⁻ with 0.100 M Ag⁺

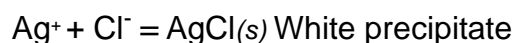


Precipitation titration curve for 50.0 mL of 0.0500 M Cl⁻ with 0.100 M Ag⁺. (a) pCl versus volume of titrant; (b) pAg versus volume of titrant

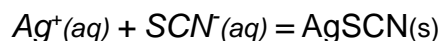
Methods for finding the end point in Precipitation Titration:

1- Finding the End Point with a Visual Indicator

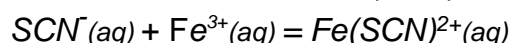
There are three methods to find the end point in precipitation titration with a visual indicator. **First** important visual indicator to be developed was the **Mohr method** for Cl^- using Ag^+ as a titrant. By adding a small amount of K_2CrO_4 to the solution containing the analyte, the formation of a precipitate of reddish-brown Ag_2CrO_4 signals the end point.



A second end point is the **Volhard method** in which Ag^+ is titrated with SCN^- in the presence of Fe^{3+} . The end point for the titration reaction



is the formation of the reddish colored $\text{Fe}(\text{SCN})^{2+}$ complex.



The titration must be carried out in a strongly acidic solution to achieve the desired end point.

A third end point is evaluated with **Fajans' method**, which uses an adsorption indicator whose color when adsorbed to the precipitate is different from that when it is in solution.

For example, when titrating Cl^- with Ag^+ the anionic dye dichloro-fluorescein is used as the indicator. Before the end point, the precipitate of AgCl has a negative surface charge due to

the adsorption of excess Cl^- . The anionic indicator is repelled by the precipitate and remains in solution where it has a greenish yellow color. After the end point, the precipitate has a positive surface charge due to the adsorption of excess Ag^+ . The anionic indicator now adsorbs to the precipitate's surface where its color is pink. This change in color signals the end point.

2- Finding the End Point Potentiometrically.

