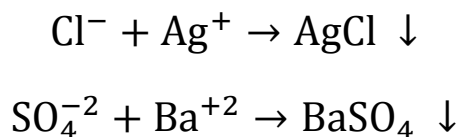


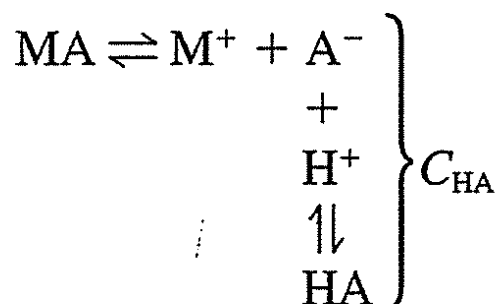
Precipitation Reactions and Titrations

A number of anions form slightly precipitates with certain ions and can be titrated with the metal solutions.



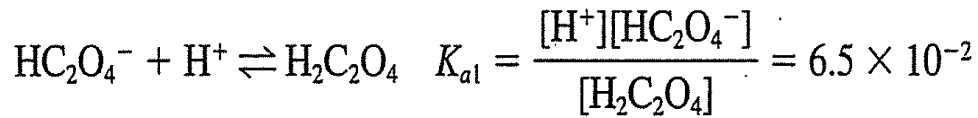
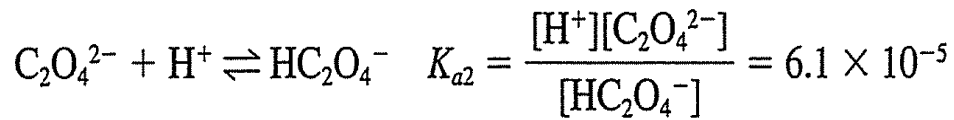
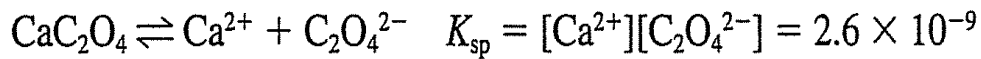
Effect of acidity on solubility of precipitates: conditional solubility product.

The solubility of a precipitate whose anion is derived from a weak acid will increase in the presence of added acid because the acid will lead to combine with the anion and thus remove the anion from solution for example the precipitate MA that partially dissolves to give M^+ and A^- ions will exhibit the following.



The anion A^- can combine with protons to increase the solubility of the precipitates. The combined equilibrium concentrations of A^- and HA make up the total analytical concentration, C_{HA} , which will be equal to $[\text{M}^+]$ from the dissolved precipitate (M^+ or A^- excess).

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad \text{Effect of acidity on solubility of precipitates}$$



The solubility s of CaC_2O_4 is equal to $[\text{Ca}^{2+}] = C_{\text{H}_2\text{C}_2\text{O}_4}$, where $C_{\text{H}_2\text{C}_2\text{O}_4}$ represents the concentrations of all the oxalate species in equilibrium ($= [\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]$). We can substitute $C_{\text{H}_2\text{C}_2\text{O}_4}\alpha_2$ for $[\text{C}_2\text{O}_4^{2-}]$ in the K_{sp} expression:

$$K_{\text{sp}} = [\text{Ca}^{2+}]C_{\text{H}_2\text{C}_2\text{O}_4}\alpha_2$$

where α_2 is the fraction of the oxalate species present as $\text{C}_2\text{O}_4^{2-}$ ($\alpha_2 = [\text{C}_2\text{O}_4^{2-}]/C_{\text{H}_2\text{C}_2\text{O}_4}$).

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

We can write, then, that

$$\frac{K_{\text{sp}}}{\alpha_2} = K'_{\text{sp}} = [\text{Ca}^{2+}]C_{\text{H}_2\text{C}_2\text{O}_4} = s^2$$

where K'_{sp} is the **conditional solubility product**

Note: The conditional solubility product value holds for only a specified pH.

Example 11.1: Calculate the solubility of CaC_2O_4 in a solution containing 0.001M HCl?

$$\alpha_2 = \frac{(6.5 \times 10^{-2})(6.1 \times 10^{-5})}{(1.0 \times 10^{-3})^2 + (6.5 \times 10^{-2})(1.0 \times 10^{-3}) + (6.5 \times 10^{-2})(6.1 \times 10^{-5})}$$
$$= 5.7 \times 10^{-2}$$
$$s = \sqrt{K_{\text{sp}}/\alpha_2} = \sqrt{2.6 \times 10^{-9}/5.7 \times 10^{-2}} = 2.1 \times 10^{-4} \text{ M}$$

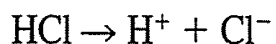
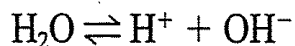
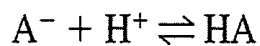
This compares with a calculated solubility in water using $K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$ of $5.1 \times 10^{-5} \text{ M}$ (a 400% increase in solubility).

Mass Balance Approach for Multiple Equilibria:

The systematic approach is well suited for competing equilibria calculations.

Example 11.2: How many moles of MA will dissolve in 1L of 0.1M HCl if K_{sp} for MA is 1.0×10^{-8} and K_a for HA is 1.0×10^{-6} ?

The equilibria are



The equilibrium expressions are

$$K_{sp} = [M^+][A^-] = 1.0 \times 10^{-8} \quad (1)$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = 1.0 \times 10^{-6} \quad (2)$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (3)$$

The mass balance expressions are

$$[M^+] = [A^-] + [HA] = C_{HA} \quad (4)$$

$$[H^+] = [Cl^-] + [OH^-] - [HA] \quad (5)$$

$$[Cl^-] = 0.10 \text{ M} \quad (6)$$

The charge balance expression is

$$[H^+] + [M^+] = [A^-] + [Cl^-] + [OH^-] \quad (7)$$

Number of expressions versus number of unknowns:

There are six unknowns ($[H^+]$, $[OH^-]$, $[Cl^-]$, $[HA]$, $[M^+]$, and $[A^-]$) and six independent equations (the charge balance equation can be generated as a linear combination of the others, and is not used here).

Simplifying assumptions:

(1) In an acid solution, dissociation of HA is suppressed, making $[A^-] \ll [HA]$, so from (4):

$$[M^+] = [A^-] + [HA] \approx [HA]$$

(2) In an acid solution $[OH^-]$ is very small, so from (5) and (6):

$$[H^+] = 0.10 + [OH^-] - [HA] \approx 0.10 - [HA]$$

Calculate:

We need to calculate $[M^+]$ in order to obtain the moles of MA dissolved in a liter.

From (1)

$$[M^+] = \frac{K_{sp}}{[A^-]} \quad (8)$$

From (2)

$$[A^-] = \frac{K_a[HA]}{[H^+]} \quad (9)$$

So, dividing (8) by (9):

$$[M^+] = \frac{K_{sp}[H^+]}{K_a[HA]} = 1.0 \times 10^{-2} \frac{[H^+]}{[HA]} \quad (10)$$

From assumption (1),

$$[M^+] \approx [HA]$$

From assumption (2),

$$[H^+] \approx 0.10 - [HA] \approx 0.10 - [M^+]$$

$$[M^+] = \frac{(1.0 \times 10^{-2})(0.10 - [M^+])}{[M^+]}$$

$$\frac{[M^+]^2}{0.10 - [M^+]} = 1.0 \times 10^{-2}$$

Use of the quadratic equation gives $[M] = 0.027 M$.

So, in 1 L, 0.027 mol of MA will dissolve. This compares with 0.00010 mol in water. Check

$$(1) \quad [HA] \approx [M^+] = 0.027 M$$

$$[A^-] = \frac{K_{sp}}{[M^+]} = \frac{1.0 \times 10^{-8}}{0.027} = 3.7 \times 10^{-7} M$$

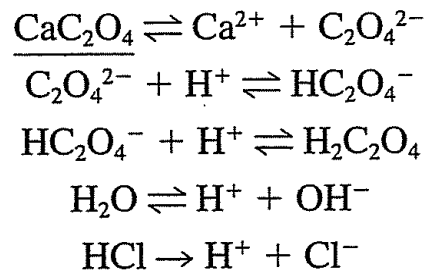
Assumption (1) is acceptable because $[A^-] \ll [HA]$.

$$(2) \quad [H^+] \approx 0.10 - [M^+] = 0.073 M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.073} = 1.4 \times 10^{-13}$$

Assumption (2) is acceptable because $[OH^-] \ll [Cl^-]$ or $[HA]$.

Example 11.3: calculate the solubility of CaC_2O_4 in a solution of 0.001M HCl by systematic approach?



The equilibrium constant expressions are

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.6 \times 10^{-9} \quad (1)$$

$$K_{a1} = \frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = 6.5 \times 10^{-2} \quad (2)$$

$$K_{a2} = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = 6.1 \times 10^{-5} \quad (3)$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (4)$$

The mass balance expressions are

$$[\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] = C_{\text{H}_2\text{C}_2\text{O}_4} \quad (5)$$

$$[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-] - [\text{HC}_2\text{O}_4^-] - [\text{H}_2\text{C}_2\text{O}_4] \quad (6)$$

$$[\text{Cl}^-] = 0.0010 \text{ M} \quad (7)$$

The charge balance expression is

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = 2[\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{Cl}^-] + [\text{OH}^-] \quad (8)$$

There are seven unknowns ($[\text{H}^+]$, $[\text{OH}^-]$, $[\text{Cl}^-]$, $[\text{Ca}^{2+}]$, $[\text{C}_2\text{O}_4^{2-}]$, $[\text{HC}_2\text{O}_4^-]$, and $[\text{H}_2\text{C}_2\text{O}_4]$) and seven independent equations.

Simplifying assumptions:

(1) K_{a1} is rather large and K_{a2} is rather small, so assume $[\text{HC}_2\text{O}_4^-] \gg [\text{H}_2\text{C}_2\text{O}_4]$, $[\text{C}_2\text{O}_4^{2-}]$.

(2) In an acid solution, $[\text{OH}^-]$ is very small, so from (6) and (7):

$$[\text{H}^+] = 0.0010 + [\text{OH}^-] - [\text{H}_2\text{C}_2\text{O}_4^-] - [\text{H}_2\text{C}_2\text{O}_4] \approx 0.0010 - [\text{HC}_2\text{O}_4^-] \quad (9)$$

Calculate:

We need to calculate $[\text{Ca}^{2+}]$ in order to obtain the moles of CaC_2O_4 dissolved in a liter.

From (1)

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}}}{[\text{C}_2\text{O}_4^{2-}]} \quad (10)$$

From (3)

$$[\text{C}_2\text{O}_4^{2-}] = \frac{K_{a2}[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]} \quad (11)$$

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}}[\text{H}^+]}{K_{a2}[\text{HC}_2\text{O}_4^-]} \quad (12)$$

From assumption (1),

$$[\text{Ca}^{2+}] = [\text{HC}_2\text{O}_4^-] \quad (13)$$

From assumption (2),

$$[\text{H}^+] \approx 0.0010 - [\text{HC}_2\text{O}_4^-] \approx 0.0010 - [\text{Ca}^{2+}] \quad (14)$$

Substitute (13) and (14) in (12):

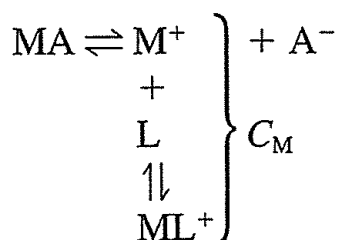
$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}}(0.0010 - [\text{Ca}^{2+}])}{K_{a2}[\text{Ca}^{2+}]} = \frac{(2.6 \times 10^{-9})(0.0010 - [\text{Ca}^{2+}])}{(6.1 \times 10^{-5})[\text{Ca}^{2+}]}$$
$$[\text{Ca}^{2+}] = \frac{(4.6 \times 10^{-5})(0.0010 - [\text{Ca}^{2+}])}{[\text{Ca}^{2+}]}$$

Solving the quadratic equation gives $[\text{Ca}^{2+}] = 1.9 \times 10^{-4} \text{M}$. This is the same as that calculated in Example 11.1.

Effect of Complexation on Solubility:

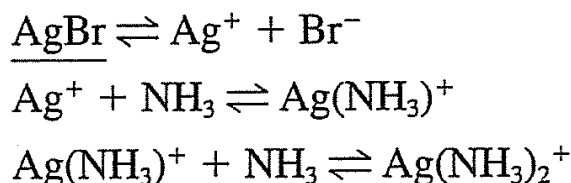
Conditional Solubility Product

Complexing agents can compete for the metal ion in a precipitate, just as acids compete for the anion. A precipitate MA that dissociates to give M^+ and A^- and whose metal complexes with the ligand L to form ML^+ would have the following equilibria:



The sum of $[M^+]$ and $[ML^+]$ is the analytical concentration C_M in equilibrium, which is equal to $[A^-]$. Calculations for such a situation are handled in a manner completely analogous to those for the effects of acids on solubility.

Consider the solubility of AgBr in the presence of NH_3 . The equilibria are



$$K_{sp} = [Ag^+][Br^-] = C_{Ag}\beta_0[Br^-] = 4 \times 10^{-13}$$

$$\boxed{\frac{K_{sp}}{\beta_0} = K'_{sp} + C_{Ag}[Br^-] = s^2}$$

The solubility s of AgBr is equal to $[Br^-] = C_{Ag}$, where C_{Ag} represents the concentrations of all the silver species in equilibrium $[= [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+]$. As before, we can substitute $C_{Ag}\beta_0$ for $[Ag^+]$ in the K_{sp} expression, where β_0 is the fraction of silver species present as Ag^+

where K'_{sp} is again the **conditional solubility product**, whose value depends on the concentration of ammonia.

Example 11.4: Calculate the molar solubility of silver bromide in 0.1M ammonia solution.

$$\beta_0 = \frac{1}{K_{f1}K_{f2}[\text{NH}_3]^2 + K_{f1}[\text{NH}_3] + 1}$$

$$\beta_0 = \frac{1}{(2.5 \times 10^3)(1.0 \times 10^4)(0.10)^2 + (2.5 \times 10^3)(0.10) + 1} = 4.0 \times 10^{-6}$$

$$s = \sqrt{\frac{K_{sp}}{\beta_0}} = \sqrt{4 \times 10^{-13} / 4.0 \times 10^{-6}} = 3.2 \times 10^{-4} M$$

This compares with a solubility in water of $6 \times 10^{-7} M$ (530 times more soluble).

Precipitation Titrations: (Argentometric Titration)

Example 11.5: Calculate pCl for the titration of 100mL of 0.10M Cl^- with 0.1M AgNO_3 after addition of 0.0, 20.0, 99.0, 99.50, 100.0, 100.50 and 110.0mL AgNO_3 ?

At 0.00 mL:

$$\text{pCl} = -\log 0.1000 = 1.000$$

At 20.00 mL:

$$\text{mmol Cl}^- = 100.0 \text{ mL} \times 0.1000 \text{ mmol/mL} = 10.00 \text{ mmol}$$

$$\text{mmol Ag}^+ = 20.00 \text{ mL} \times 0.1000 \text{ mmol/mL} = 2.000 \text{ mmol}$$

$$\text{Cl}^- \text{ left} = 10.00 - 2.00 = 8.00 \text{ mmol} / 120.0 \text{ mL} = 0.0667 M$$

$$\text{pCl} = -\log 0.0667 = 1.18$$

At 99.00 mL:

$$\text{mmol Ag}^+ = 99.00 \text{ mL} \times 0.1000 \text{ mmol/mL} = 9.900 \text{ mmol}$$

$$\text{Cl}^- \text{ left} = 10.00 - 9.90 = 0.10 \text{ mmol} / 199.0 \text{ mL} = 5.0 \times 10^{-4} M$$

$$\text{pCl} = -\log 5.0 \times 10^{-4} = 3.26$$

At 99.50 mL:

$$\text{mmol Ag}^+ = 99.50 \text{ mL} \times 0.1000 \text{ mmol/mL} = 9.950 \text{ mmol}$$

$$\text{Cl}^- \text{ left} = 10.00 - 9.95 = 0.05 \text{ mmol}/199.5 \text{ mL} = 2.5 \times 10^{-4} \text{ M}$$

$$\text{pCl} = -\log 2.5 \times 10^{-4} = 3.60$$

At 100.00 mL, all the Cl^- is reacted with Ag^+ :

$$[\text{Cl}^-] = \sqrt{K_{\text{sp}}} = \sqrt{1.0 \times 10^{-10}} = 1.0 \times 10^{-5} \text{ M}$$

$$\text{pCl} = -\log 1.0 \times 10^{-5} = 5.00$$

At 100.50 mL:

$$\text{mmol Ag}^+ = 100.50 \text{ mL} \times 0.1000 \text{ mmol/mL} = 10.05 \text{ mmol}$$

$$\text{Ag}^+ \text{ left} = 10.05 - 10.00 = 0.05 \text{ mmol}/200.5 \text{ mL} = 0.02_4 \text{ M}$$

$$[\text{Cl}^-] = K_{\text{sp}}/[\text{Ag}^+] = 1.0 \times 10^{-10}/2.4 \times 10^{-2} = 4.2 \times 10^{-9} \text{ M}$$

$$\text{pCl} = -\log 4.2 \times 10^{-9} = 8.38$$

At 110.00 mL:

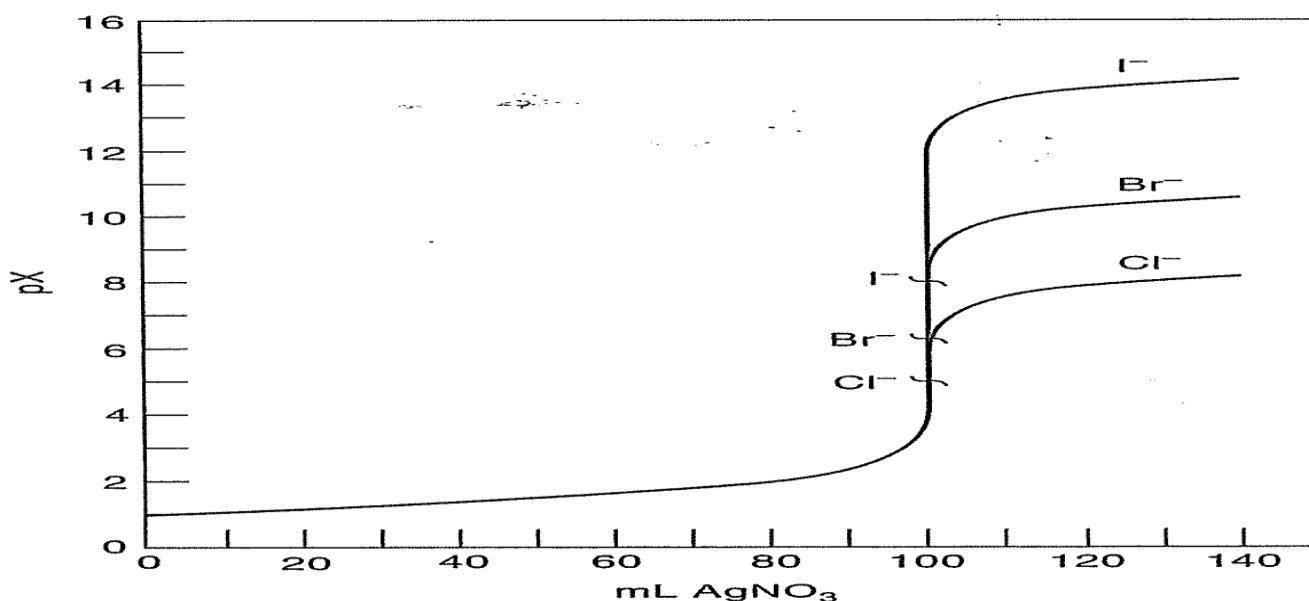
$$\text{mmol Ag}^+ = 110.00 \text{ mL} \times 0.1000 \text{ mmol/mL} = 11.00 \text{ mmol}$$

$$\text{Ag}^+ \text{ left} = 11.00 - 10.00 = 1.00 \text{ mmol}/210 \text{ mL} = 4.76 \times 10^{-3} \text{ M}$$

$$[\text{Cl}^-] = 1.0 \times 10^{-10}/4.76 \times 10^{-3} = 2.1 \times 10^{-8} \text{ M}$$

$$\text{pCl} = -\log 2.1 \times 10^{-8} = 7.67$$

Titration curves for 100mL 0.1M Cl^- , Br^- , and I^- solutions versus 0.1M AgNO_3 .



Note: The smaller the K_{sp} , the sharper the endpoint (or the smaller the K_{sp} , the larger the break at the equivalence point).

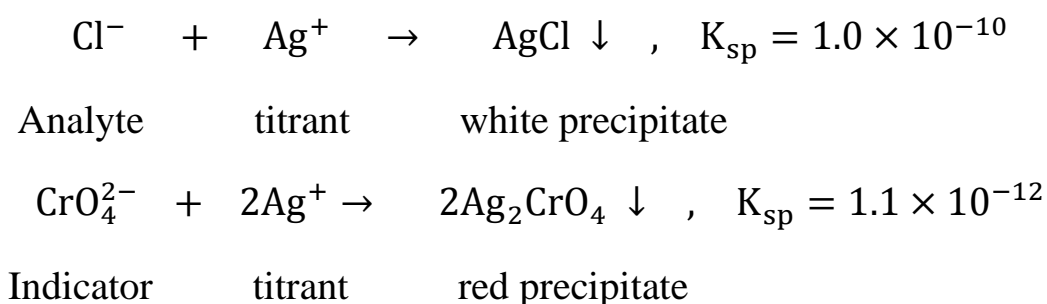
The detection of the endpoint (indicators):

We can detect the endpoint by measuring either pCl or pAg with two types of indicators:

(1) Indicators Reacting with the Titrant:

There are several examples of an indicator forming a colored compound with a titrant, two common method were:

(a) Mohr Method: used for determining chloride ion, after chloride ion consumed by reacting with equal mmol of AgNO_3 , the excess (after drops) of AgNO_3 than reacting with the indicator (K_2CrO_4) to form red precipitate Ag_2CrO_4 .



The concentration of the indicator is important. The Ag_2CrO_4 should just start precipitating at the equivalence point, where we have a saturated solution of AgCl . From K_{sp} , the concentration of Ag^+ at the equivalence point is $10^{-5} M$. (It is less than this before the equivalence point.) So, Ag_2CrO_4 should precipitate just when $[\text{Ag}^+] = 10^{-5} M$. The solubility product of Ag_2CrO_4 is 1.1×10^{-12} . By inserting the Ag^+ concentration in the K_{sp} equation for Ag_2CrO_4 , we calculate that, for this to occur, $[\text{CrO}_4^{2-}]$ should be $0.011 M$:

$$\begin{aligned} (10^{-5})^2[\text{CrO}_4^{2-}] &= 1.1 \times 10^{-12} \\ [\text{CrO}_4^{2-}] &= 1.1 \times 10^{-2} M \end{aligned}$$

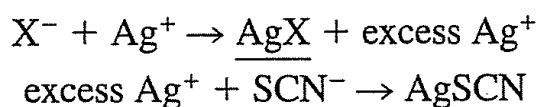
If the concentration is greater than this, Ag_2CrO_4 will begin to precipitate when $[\text{Ag}^+]$ is less than $10^{-5} M$ (before the equivalence point). If it is less than $0.011 M$, then the $[\text{Ag}^+]$ will have to exceed $10^{-5} M$ (beyond the equivalence point) before precipitation of Ag_2CrO_4 begins.

In actual practice, the indicator concentration is kept at 0.002 to $0.005 M$. If it is much higher than this, the intense yellow color of the chromate ion obscures the red Ag_2CrO_4 precipitate color, and an excess of Ag^+ is required to produce enough precipitate to be seen. An indicator blank should always be run and subtracted from the titration to correct for errors.

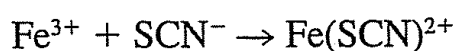
The Mohr titration must be performed at a pH of about 8. If the solution is too acid ($\text{pH} < 6$), then part of the indicator is present as HCrO_4^- , and more Ag^+ will be required to form the Ag_2CrO_4 precipitate. Above pH 8, silver hydroxide may be precipitated (at $\text{pH} > 10$). The pH is properly maintained by adding solid calcium carbonate to the solution. (While the carbonate ion is a fairly strong Brønsted base, the concentration in a saturated calcium carbonate solution is just sufficient to give a pH about 8.) The Mohr titration is useful for determining chloride in neutral or unbuffered solutions, such as drinking water.

(b) Volhard Titration (Back Titration):-

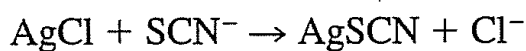
This is an indirect titration procedure for determining anions that precipitate with silver (Cl^- , Br^- , SCN^-), and it is performed in acid (HNO_3) solution. In this procedure, we add a measured excess of AgNO_3 to precipitate the anion and then determine the excess Ag^+ by back-titration with standard potassium thiocyanate solution:



We detect the end point by adding iron(III) as a ferric alum (ferric ammonium sulfate), which forms a soluble red complex with the first excess of titrant:



If the precipitate, AgX , is less soluble than AgSCN , we do not have to remove the precipitate before titrating. Such is the case with I^- , Br^- , and SCN^- . In the case of I^- , we do not add the indicator until all the I^- is precipitated, since it would be oxidized by the iron(III). If the precipitate is more soluble than AgSCN , it will react with the titrant to give a high and diffuse end point. Such is the case with AgCl :



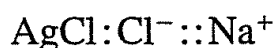
Therefore, we remove the precipitate by filtration before titrating.

Obviously, these indicators must not form a compound with the titrant that is more stable than the precipitate, or the color reaction would occur when the first drop of titrant is added.

(2) Adsorption Indicators (Fajan's Method):

With adsorption indicators, the indicator reaction takes place on the surface of the precipitate. The fluorescein indicators such as fluorescein, methyl violet, Rhodamine and Bromphenol blue are dyes, exists in solution as ionized form, usually anion In^- .

Consider the titration of Cl^- with Ag^+ . Before the equivalence point, Cl^- is in excess, and the *primary adsorbed layer* is Cl^- . This repulses the indicator anion, and the more loosely held *secondary (counter) layer* of adsorbed ions is cations, such as Na^+ :



Beyond the equivalence point, Ag^+ is in excess, and the surface of the precipitate becomes positively charged, with the primary layer being Ag^+ . This will now attract the indicator anion and adsorb it in the counterlayer:



The colour of the adsorbed indicator is different from that of the unadsorbed indicators, and the difference signals the completion of the titration. The more insoluble precipitates can be titrated in more strongly adsorbed indicators. We want the maximum surface area for adsorption in contrast to gravimetry. Coagulate decreases the surface area for absorption of the indicator, which in turn decreases the sharpness of the end point, we can prevent coagulation of silver chloride by adding some dextrin to solution.

1. Explain the Volhard titration of chloride. The Fajan titration. Which is used for acid solutions? Why?
2. Explain the principles of adsorption indicators.

EFFECT OF ACIDITY ON SOLUBILITY

3. Calculate the solubility of AgIO_3 in 0.100 M HNO_3 . Also calculate the equilibrium concentrations of IO_3^- and HIO_3 .
4. Calculate the solubility of CaF_2 in 0.100 M HCl . Also calculate the equilibrium concentrations of F^- and HF .

5. Calculate the solubility of PbS in 0.0100 *M* HCl. Also calculate the equilibrium concentrations of S²⁻, HS⁻, and H₂S.

EFFECT OF COMPLEXATION ON SOLUBILITY

6. Silver ion forms a stepwise 1 : 2 complex with ethylenediamine (en) with formation constants of $K_{f1} = 5.0 \times 10^4$ and $K_{f2} = 1.4 \times 10^3$. Calculate the solubility of silver chloride in 0.100 *M* ethylenediamine. Also calculate the equilibrium concentrations of Ag(en)⁺ and Ag(en)₂⁺.

MASS BALANCE CALCULATIONS

7. Calculate the solubility of AgIO₃ in 0.100 *M* HNO₃, using the mass balance approach. Compare with Problem 3.
8. Calculate the solubility of PbS in 0.0100 *M* HCl, using the mass balance approach. Compare with Problem 5.
9. Calculate the solubility of AgCl in 0.100 *M* ethylenediamine. Compare with Problem 6. The formation constant is given in Problem 6.

QUANTITATIVE PRECIPITATION DETERMINATIONS

10. Chloride in a brine solution is determined by the Volhard method. A 10.00-mL aliquot of the solution is treated with 15.00 mL of standard 0.1182 *M* AgNO₃ solution. The excess silver is titrated with standard 0.101 *M* KSCN solution, requiring 2.38 mL to reach the red Fe(SCN)²⁺ end point. Calculate the concentration of chloride in the brine solution, in g/L.
11. In a Mohr titration of chloride with silver nitrate, an error is made in the preparation of the indicator. Instead of 0.011 *M* chromate indicator in the titration flask at the end point, there is only 0.0011 *M*. If the flask contains 100 mL at the end point, what is the error in the titration in milliliters of 0.100 *M* titrant? Neglect errors due to the color of the solution.

SPREADSHEET PROBLEM

12. Prepare a spreadsheet to plot the titration curve of 100 mL 0.1 *M* chloride titrated with 0.1 *M* silver nitrate (Figure 11.1). See your CD for a suggested setup. Use the spreadsheet to change the concentrations of chloride and silver (e.g., 0.2 *M* each, 0.05 *M* each), and notice how the titration curve changes. Note that there is a limit to how low the concentrations can go in these calculated plots because eventually the solubility of the AgCl at 99.9 and 100.1 mL titrant becomes appreciable.