

Precipitation Titration

5-6

Precipitation titration is a titration in which the reaction between the analyte and titrant involves a precipitation. The matter responsible for precipitation is called precipitating agent or precipitant. So, it must determine the volume of a standardized titrant needed to just precipitate the entire ion and also need an indicator or electrode to determine when the precipitation is complete.

Precipitation titrations are based upon reactions that yield ionic compounds of limited solubility.

Important conditions of this group of reactions:

1. The precipitate must be slightly soluble
2. The precipitation process must be done as fast.
3. Avoid any adsorption which causing the co-precipitation and precipitate pollution
4. Clear endpoint during the titration.

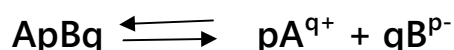
The application of the precipitation reactions in volumetric analysis is easier than in gravimetric analysis in which the precipitant should be free from the entire soluble matter and separated by filtration. While in volumetric analysis, the separation of precipitate is not a must especially if the precipitant reacts quantitatively with analyte.

Comparing to acid-base or reduction-oxidation titrations the precipitometric titration has no much more methods because;

- ✓ Difficult to select a suitable indicator
- ✓ Difficult to obtain an accurate precipitate composition, the co-precipitation effect is often occurred.

When the precipitates are start to form?

It depends on the chemical equilibrium law, precipitate dissociation constant and solubility product K_{sp}

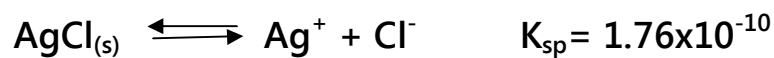


$$K_{sp} = [A^{q+}]^p [B^{p-}]^q$$

While,

- If $K_{sp} > [A^{q+}]^p [B^{p-}]^q$ the precipitation was not formed
- If $K_{sp} < [A^{q+}]^p [B^{p-}]^q$ the precipitation was formed

The most important precipitation processes in titrimetric analysis utilize $AgNO_3$ as the reagent (argentometric processes). To determine the concentration of chloride ion, one could titrate this solution with a solution of a silver nitrate whose concentration is known. The chemical reaction occurring is:



- ✓ Reverse of the K_{sp} reaction for the of $AgCl(s)$ equilibrium ($K = 1/K_{sp}[AgCl(s)] = 5.68 \times 10^9$)
- ✓ Large K value means that the equilibrium lies to the right for this reaction, that is means each aliquot addition of Ag^+ titrant reacts directly to form $AgCl(s)$

Example 1: In a precipitation titration of 46mL of a chloride solution of unknown concentration, 31mL of 0.6973M $AgNO_3$ were required to reach the equivalence point. Calculate the concentration of chloride.

Solution:

In this case the M concentration of the unknown solution (Cl^-) is calculated as follows:

$$31.00 \text{ mL} \times 0.6973 \text{ molar} = 21.62 \text{ mmol } Ag^+ = 21.62 \text{ mmol } Cl^-$$

$$21.62 \text{ mmol } Cl^- / 46.00 \text{ mL } Cl^- = 0.4700 \text{ molar } Cl^-$$

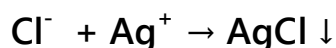
The endpoint of this titration can be detected if the rapid change in either the concentration of Ag^+ or the concentration of Cl^- which occurs at the endpoint can be made apparent to an observer. There are three common chemical indicators that are associated with argentometric titrations:

- 1) The chromate ion, CrO_4^{2-} (the Mohr method; *formation of a colored precipitate*).
- 2) The ferric ion, Fe^{3+} (the Volhard method; *formation of a soluble colored compound*).
- 3) Adsorption indicators such as fluorescein (the Fajans method; *use of adsorption indicators*).

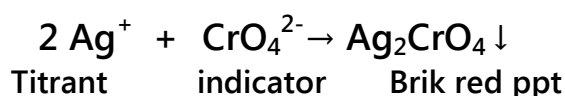
Mohr method

It depends on the titration of NaCl sample with standard AgNO_3 using potassium chromate (K_2CrO_4) as indicator.

Titration reaction:



End point reaction:



In this method, Cl^- sample is titrated with Ag^+ in presence of CrO_4^{2-} indicator where AgCl is precipitated as a white ppt before Ag_2CrO_4 then at the end point (when Cl^- is completely reacted with Ag^+). The first slight excess of Ag^+ will react with CrO_4^{2-} indicator giving Ag_2CrO_4 (brick red ppt) leading to darkening of the yellow colour of the solution.

Notes:

1. Effect of pH: Mohr's method should be done in neutral or slightly alkaline medium (pH \approx 6.5 -9) because:

At pH > 9: Ag^+ will be precipitated as $\text{AgOH} \downarrow$ (brown to black ppt) leading to Consumption of the titrant & Masking of the E.P. color.



While at pH <6.5: The chromate ion (CrO_4^{2-}) changes into acid chromate (HCrO_4^-) then to dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Both HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ form soluble salts with Ag^+ & so no colored ppt will be formed at the E.P.



2. Ag_2CrO_4 is more soluble than AgCl so that no Ag_2CrO_4 will be precipitated until all Cl^- ions have been precipitated as AgCl provided that the CrO_4^{2-} concentration should be adjusted to make Ag_2CrO_4 formed only at the end point and so prevent error in the end point. 1 ml of 5% K_2CrO_4 solution is suitable.
 - High concentration of $\text{K}_2\text{CrO}_4 \Rightarrow$ gives too soon (early) E.P. because Ag_2CrO_4 will be rapidly precipitated before E.P.
 - Low concentration of $\text{K}_2\text{CrO}_4 \Rightarrow$ gives too late E.P. because CrO_4^{2-} will be insufficient and so a large amount of Ag^+ (titrant) will be needed to precipitate Ag_2CrO_4 and so the E.P. comes too late.
3. I^- & SCN^- cannot be determined by Mohr's method because the formed AgI & AgSCN strongly adsorb CrO_4 on their surfaces and so the ppt formed at the end point will be an adsorption compound which is less colored and so less sharp E.P. will be obtained.
4. BLANK EXPERIMENT should be done because: An additional excess of AgNO_3 (titrant) will be added after the correct E.P. to form enough Ag_2CrO_4 to be seen over the heavy white ppt of AgCl & the yellow color of KCrO_4 indicator leading to error (increase) in the end point. This error can be corrected by performing blank determination to know the volume of the additional excess of AgNO_3 (titrant) that causes error. In blank determination, all steps of the experiment are performed in absence of sample but using 10 ml dist. water instead of it and also using talc or CaCO_3 powder to imitate the white AgCl ppt. i.e. 10 ml dist. water + 1 ml 5% K_2CrO_4 + talc or CaCO_3 powder \rightarrow titrate \neq st. AgNO_3 till the 1st darkening of the yellow chromate color.

The volume consumed of AgNO_3 (titrant) is called Indicator Blank and it should be subtracted from the observed E.P. in the original experiment {i.e. the calculation of concn. involves (E.P. - Ind. Blank)}.

Example 2: Why AgCl was precipitate at first albeit its K_{sp} was greater than that of Ag_2CrO_4 . for example, for the titration of 0.1M NaCl with aq 0.1M AgNO_3 , using a few mL of 0.01 M K_2CrO_4 as indicator.

According to K_{sp} of the reaction its clear that the minimum concentration of Ag^+ required to start to precipitate Cl^- (0.1M) was;

$$[\text{Ag}^+] = K_{sp}/[\text{Cl}^-] = 1.2 \times 10^{-10}/0.1 = 1.2 \times 10^{-9} \text{M}$$

While using 0.01M K_2CrO_4 , the amount of Ag^+ required precipitating it equal to:

$$[\text{Ag}^+] = \sqrt{(1.7 \times 10^{-12}/0.01)} = 1.3 \times 10^{-5} \text{M}$$

AgCl was precipitate at first for two reasons:

1. Ag^+ -present in Ag_2CrO_4 as multiple values.
2. Small volume of dilute (low concentration) indicator was used.

Example 3: A sample containing KCl is analyzed by the Mohr method. A 0.487-g sample is dissolved in 100mL of water and titrated with the Ag_2CrO_4 end point, requiring 35.22mL of 0.12M AgNO_3 . A blank titration requires 0.6mL of titrant to reach the same end point. Report the %w/w KCl in the sample.

Solution:

No. of eq. Of KCl = No. of eq. of AgNO_3

$$\frac{\text{wt. KCl}}{\text{m.wt.KCl}} \times 1000 = V_{\text{AgNO}_3} \times M_{\text{AgNO}_3}$$

$$\begin{aligned} \text{wt. KCl} &= \frac{V_{\text{AgNO}_3} \times M_{\text{AgNO}_3} \times \text{m.wt.KCl}}{1000} \\ &= \frac{(35.22 - 0.6) \times 0.12 \times 74.5}{1000} = 0.306 \text{ g} \end{aligned}$$

$$\% \text{ KCl} = \frac{\text{wt. KCl}}{\text{wt.sample}} \times 100 = \frac{0.306}{0.487} \times 100 = 62.83\%$$

Homework: A mixture containing only KCl and NaBr is analyzed by the Mohr method. A 0.3172-g sample is dissolved in 50mL of water and titrated to the Ag_2CrO_4 end point, requiring 36.85mL of 0.112M AgNO_3 . A blank titration requires 0.71mL of titrant to reach the same end point. Report the %w/w KCl and NaBr in the sample.

Let x= no. of g of KCl obtained

Then 0.3172-x no. of g of NaBr

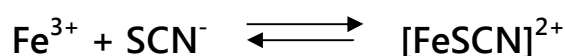
Volhard method

Volhard titration is an indirect (back titration) technique which is used if reaction is too slow or if there is no appropriate indicator selected for determining the equivalent point.

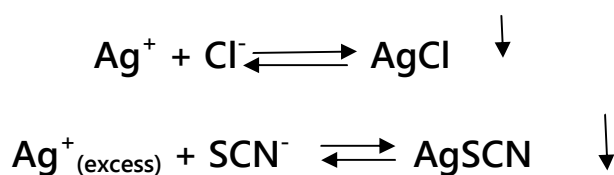
This procedure is exemplified by Volhard's method for the titration of Ag^+ in the presence of free nitric acid (HNO_3) with standard potassium thiocyanate (KSCN) or ammonium thiocyanate (NH_4SCN) solution. The indicator is a solution of iron(III) nitrate or of iron(III) ammonium sulphate. The addition of thiocyanate solution produces first a precipitate of silver thiocyanate ($K_{sp} = 7.1 \times 10^{-13}$).



When this reaction is complete, the slightest excess of SCN^- produces a reddish-brown coloration, due to the formation of a complex ion:



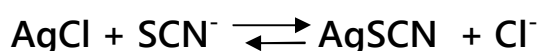
In this titration excess of standard AgNO_3 solution is added, and the excess is back-titrated with standard SCN^- solution. For the Cl^- determination, we have the following two equilibria during the titration of excess of Ag-ions:



The two sparingly soluble salts will be in equilibrium with the solution, hence:

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

When the excess of silver has reacted, the SCN^- may react with the AgCl , since AgSCN is the less soluble salt, until the ratio $[\text{Cl}^-]/[\text{SCN}^-]$ in the solution is 169:



This will take place before reaction occurs with the iron (III) ions in the solution, and there will consequently be a considerable titration error.

It is therefore absolutely necessary to prevent the reaction between the SCN^- and the AgCl . This may be affected in several ways:

- 1- The AgCl is filtered off before back-titrating. Since at this stage the precipitate will be contaminated with adsorbed silver ions, the suspension should be boiled for a few minutes to coagulate the silver chloride and thus remove most of the adsorbed silver ions from its surface before filtration. The cold filtrate is titrated.
- 2- After the addition of AgNO_3 , KNO_3 is added as coagulant; the suspension is boiled for about 3 min., cooled and then titrated

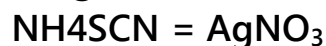
immediately. Desorption of silver ions occurs and, on cooling, reabsorption is largely prevented by the presence of KNO_3 .

- 3- An immiscible liquid is added to 'coat' the AgCl particles and thereby protect them from interaction with the SCN^- . The most successful liquid is nitrobenzene (1.0 mL for each 50 mg of chloride): the suspension is well shaken to coagulate the precipitate before back-titration.

Example 4: A 2-g sample contains KCl (74.5 g/mole) was dissolved and diluted to 100 mL. A 40 mL excess of 0.1 N AgNO_3 was added to 10 mL of this sample solution to precipitate chloride as AgCl . The excess of AgNO_3 was titrated with 0.1N ammonium thiocyanate and required 15 mL by the Volhard method . Calculate the % KCl .

Solution:

- (1) Volume of AgNO_3 that react with thiocyanate



$$0.1 \times 15 = 0.1 \times V_{\text{AgNO}_3}$$

$$V_{\text{AgNO}_3} = 15 \text{ mL}$$

- (2) Calculate the volume of AgNO_3 that reacts with KCl

$$V_{\text{AgNO}_3} = 40 - 15 = 25 \text{ mL}$$

- (3) calculate the weight of KCl

$$\frac{\text{wt. KCl}}{\text{eq. wt}} \times 1000 = V_{\text{AgNO}_3} \times N_{\text{AgNO}_3}$$

$$\text{wt. KCl} = \frac{25 \times 0.1 \times 74.5}{1000} = 0.186 \text{ g}$$

$$\text{wt. KCl in 100 mL} = \frac{0.186 \times 1000}{10} = 1.86 \text{ g}$$

$$\%KCl = \frac{1.86}{2} \times 100 = 93\%$$

Homework: A solution of KBr is titrated with Volhard procedure requires addition of 100 ml of excessed $AgNO_3$ 0,095 M, then titrated with 18,3 ml of KSCN 0,100 M using a Fe^{3+} indicator. Calculate Br^- concentration in the initial solution.

Volhard method can be used as a direct titration of Ag^+ with CNS^- as well as back titration of Cl^- , Br^- and I^- determination. These Br^- and I^- cannot be disturb by the CNS^- as solubility of $AgBr$ is equal to those of $AgCNS$, while solubility of $AgI < solbility$ of $AgCNS$.

Fajan method

In this method at the equivalence point the indicator is adsorbed by the precipitate, and during the process of adsorption a change occurs in the indicator which leads to a substance of different color; they have therefore been termed adsorption indicators.

The theory of the action of these indicators is that;

- 1- When a Cl^- solution is titrated with a solution of $AgNO_3$, the formed precipitated $AgCl$ adsorbs Cl^- (a precipitate has a tendency to adsorb its own ions); this may be termed the primary adsorbed layer. By a process known as secondary adsorption, oppositely charged ions present in solution are held around it these ions called (Counter ions).
- 2- At equivalence point, Ag^+ are present in excess and these now become primarily adsorbed; NO_3^- will be held by secondary adsorption. If fluorescein indicator is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than is the NO_3^- is immediately adsorbed, and will reveal its presence on the precipitate, and changing its Greenish-Yellow colour by the formation of a pink complex of Ag^+ and a modified fluorescein ion on the surface with the first trace of excess of Ag -ions.

Types of Adsorption Indicators

indicator	Analyte	Titrant	Reaction condition
Dichlorofluorescein	Cl^-	Ag^+	pH = 4
Fluorescein	Cl^-	Ag^+	Ag^+ pH = 7 – 8
Eosin	Br, I, SCN	Ag^+	pH = 2
Thorin	SO_4^{2-}	Ba^{2+}	pH = 1,5 – 3,5
Bromcresol green	SCN^-	Ag^+	pH = 4 – 5
Methyl violet	Ag^+	Cl^-	acid solution
Rhodamin 6G	Ag^+	Br^-	HNO_3 upto 0,3 M
Orthochrome T	Pb^{2+}	CrO_4^{2-}	neutral 0,02 M soln
Bromphenol blue	Hg_2^{2+}	Cl^-	solution of 0,1 M

Fajans Titration

The technique uses an adsorption indicator. Prior to the equivalence point, there is excess Cl^- in solution. Some is adsorbed on the surface of the crystal, giving a partial negative charge. After the equivalence point, there is excess Ag^+ in solution. Some adsorbs to the surface imparting a partial positive charge to the precipitate. Choosing an indicator with a partial negative charge will cause it to adsorb to the surface. Dichlorofluorescein is green in solution but pink when absorbed on AgCl

Types of Indicator

1. fluorescein may be used. This indicator is a very weak acid ($K_a = 1 \times 10^{-8}$) hence even a small amount of other acids reduces the ionisation, thus rendering the detection of the end point (which depends essentially upon the adsorption of the free anion) either impossible or difficult to observe. The optimum pH range is between 7 and 10.
2. Dichlorofluorescein is a stronger acid and may be utilized in slightly acid solutions of pH greater than 4.4; this indicator has the further advantage that it is applicable in more dilute solutions.

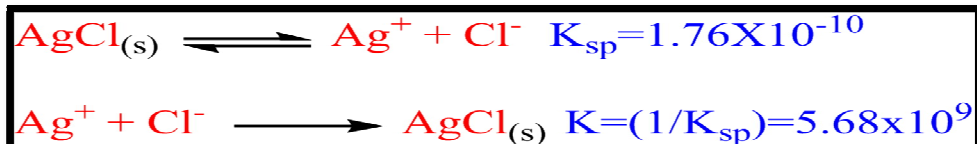
3. Eosin (tetrabromofluorescein) is a stronger acid than dichlorofluorescein and can be used down to a pH of 1-2; the colour change is sharpest in an acetic acid solution (pH < 3).

The factors that must be consider in choosing an adsorption indicator:

1. At the equivalent point, don't let the AgCl precipitate grow too fast to form a big coagulant, for this could sharply decrease adsorptivity of the precipitate surface to indicator molecules. But if it was happened, we can overcome by addition of dextrin molecules (as a protective colloid) into the solution, so that increase particles dispersion, the colour change will be reversible and after equivalent point we can perform back titration using a standardized chloride (Cl^-) solution.
2. Adsorption of indicator should be happen near and more fastly at the equivalent point. A bad indicator performance will result a too strong adsorption process resulting which can substitute ion adsorbed before the equivalent point.
3. The pH must be weel controlled for maintaining indicator ionic concentration a same , in basic or acidic solution. For example, fluorescein ($K_a = 10^{-7}$) in a solution having pH > 7 will release small quantity of fluoreseinate ion, hence we cannot observe color change of the indicator. Fluorescein is used feasibly in a solution of pH 7-10, difluorescein ($K_a=10^{-4}$) is at pH 4-10.
4. It is recommended to choose ionic form of indicator with ionic charge in opposite of titrant ion. Adsorption of indicator can not happen before an excess of titrant ion. In a titration of Ag^+ solution with Cl^- methyl violet (as chloride salt of an organic base) could be used as an indicator of choice. Before an excess of Cl^- in the solution that resulting a negative charge on colloid layer, cation should not be adsorbed. For this condition, we can use dichlorofluorescein, but it must be added just close to the equivalent point.

calculating the Titration Curve in precipitation titration

As an example, let's calculate the titration curve for the titration of 50.0 mL of 0.05 M Cl^- with 0.1M Ag^+ . The reaction in this case is;



Since the equilibrium constant (K) is large, we may assume that Ag^+ and Cl^- react completely.

The first task is to calculate the volume of Ag^+ needed to reach the equivalence point. The stoichiometry of the reaction requires that;

$$\begin{aligned} \text{No. of moles Ag}^+ &= \text{No. of moles Cl}^- \\ M_{\text{Ag}}V_{\text{Ag}} &= M_{\text{Cl}}V_{\text{Cl}} \end{aligned}$$

- Solving for the volume of Ag^+

$$\begin{aligned} V_{\text{Ag}} \text{ at equivalence point} &= (M_{\text{Cl}}V_{\text{Cl}})/M_{\text{Ag}} = (0.05 \times 50)/0.1 \\ V_{\text{Ag}} \text{ at equivalence point} &= 25\text{mL} \end{aligned}$$

1- Before Equivalence point

Before the equivalence point Cl^- is in excess. The concentration of unreacted Cl^- after adding 10.0 mL of Ag^+ , for example, is;

$$\begin{aligned} [\text{Cl}^-] &= \frac{\text{moles excess Cl}^-}{\text{total volume}} = \frac{M_{\text{Cl}}V_{\text{Cl}} - M_{\text{Ag}}V_{\text{Ag}}}{V_{\text{Cl}} + V_{\text{Ag}}} \\ &= \frac{(0.0500 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} \\ &= 2.50 \times 10^{-2} \text{ M} \end{aligned}$$

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 ;

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

Solving for the concentration of Ag^+

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

This gives a pAg of 8.14

2- At Equivalence point

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

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

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

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

2-After Equivalence point

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

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

$$= \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}}$$

$$= 1.18 \times 10^{-2} \text{ M}$$

or a pAg of 1.93. the concentration of Cl^- is

$$[\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M or a pCl} = 7.82$$

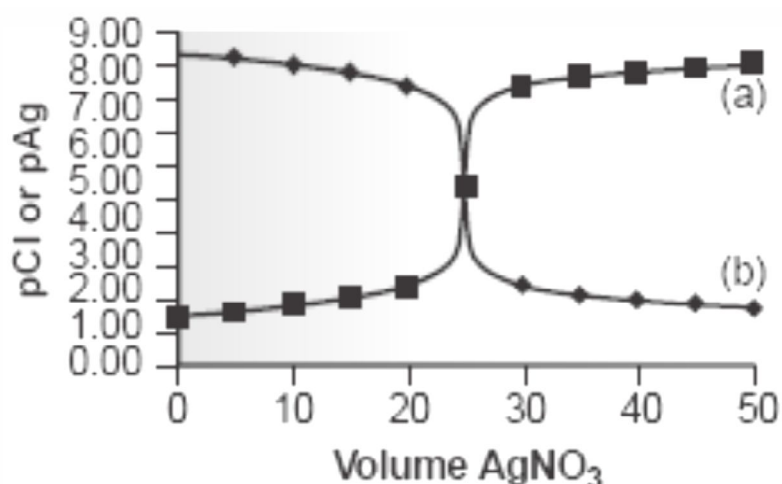
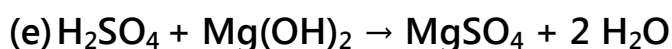
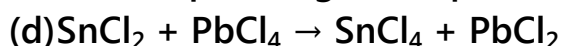
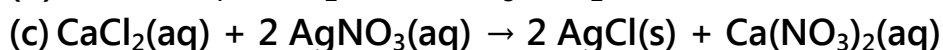
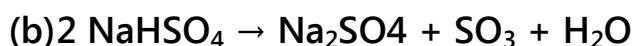


Figure 9.41

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

Exercises No. 3

1. What is the aim of precipitation titration?
2. What is meant by precipitation titration?
3. What are the conditions of Fagan's method in precipitation titration?
4. What are the advantages and limitations of precipitation titration?
5. If a brown precipitate appears during the titration, what does this mean?
6. Complete the following equations:
 - (a) $\text{Ag}^+ + \text{SCN}^- \longrightarrow$
 - (b) $\text{AgCl(s)} + \text{SCN}^-_{(\text{aq})} \longrightarrow$
 - (c) $\text{Fe}^{3+}_{(\text{aq})} + \text{SCN}^-_{(\text{aq})} \longrightarrow$
7. Which of the following will be classified as a precipitation reaction?
 - (a) $\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4$



8. State the conditions for functioning of adsorption indicators.
9. What are the applications of precipitation titrations?
10. Why does the titration curve for Cl^- with Ag^+ show a much smaller, more gradual, sloping break compared to the curve for I^- with Ag^+ .
11. For what purpose Volhard's method is used for?
12. In Fagan's method, for what purpose the dye eosin is used?
13. What are the requirements for an adsorption indicator?
14. Derive a curve for the titration of 50 mL of 0.1 M NaCl with 0.1M AgNO_3 at: (a) 0.00 mL (b) 10.00 mL (c) 49.95 mL (d) 50 mL (e) 52.5 mL ($K_{\text{sp}} = 1.82 \times 10^{-10}$)
15. What is the percentage of silver in a coin if a 0.2000 g sample requires 39.60 mL of potassium thiocyanate solution (0.4103 g of KSCN per 100 mL) for the precipitation of silver (Ans. 90.18%)
16. A sample of impure strontium chloride weighs 0.500 g. after addition of 50.00 mL of 0.210 N AgNO_3 and filtering out of the precipitated AgCl , the filtrate requires 25.50 mL of 0.280 N KSCN to titrate silver. What is the percentage of SrCl_2 in the sample. (Ans: 53.3%).
17. A sample of feldspar weighing 1.50 g is decomposed, and eventually there is obtained a mixture of KCl and NaCl weighing 0.1801 g. these chlorides are dissolved in H_2O , a 50.0 mL of 0.08333 N AgNO_3 is added, and then the precipitate is filtered off. the filtrate requires 16.47 mL of 0.100 N KSCN, with ferric alum as indicator. Calculate the %KCl in the silicate. (Ans: 6.40%)