

## Chapter 26

### Sections 26.1, 26.2, 26.3, 26.5, 26.6, and 26.8

## Gravimetric Analysis, Precipitation Titrations, and Combustion Analysis

In gravimetric analysis, the mass of a product used to calculate the quantity of the original analyte through a process of precipitation of the analyte, isolation of the precipitate, and weighing the isolated product.

Analyte  $\rightarrow$  insoluble form  $\rightarrow$  dry or ignite ppt.  $\rightarrow$  weigh the ppt.

Uses of gravimetric analysis...

- Chemical analysis of ores and industrial materials
  - Calibration of instrumentation
  - Elemental analysis of inorganic compounds
1. A weighed sample is dissolved
  2. An excess of a precipitating agent is added to this solution
  3. The resulting precipitate is filtered, dried (or ignited) and weighed
  4. From the mass and known composition of the precipitate, the amount of the original ion can be determined

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### 26.1 Examples of Gravimetric Analysis

Example 1) A 10.00-mL solution containing  $\text{Cl}^-$  was treated with excess  $\text{AgNO}_3$  to precipitate 0.4368 g of  $\text{AgCl}$  (143.321 g/mol). What was the molarity of  $\text{Cl}^-$  in the unknown?



$$\text{mol AgCl} = \frac{0.4368 \text{ g AgCl}}{143.321 \text{ g AgCl/mol AgCl}} = 3.048 \times 10^{-3} = \text{mol Cl}^-$$

$$[\text{Cl}^-] = \frac{3.048 \times 10^{-3} \text{ mol}}{0.01000 \text{ L}} = 0.3048 \text{ M}$$

Q) How many grams of  $\text{Br}^-$  (FM = 79.904 g/mol) were in a sample that produced 1.000 g of AgBr precipitate (FM = 187.77 g/mol)? (Answer: 0.425 5 g)

Example 2) When 0.091 92 g of pure  $\text{RaCl}_2$  was dissolved and treated with excess  $\text{AgNO}_3$ , 0.088 90 g of AgCl precipitated. How many moles of  $\text{Cl}^-$  were in the  $\text{RaCl}_2$ ? From this measurement, find the atomic mass of Ra.

$$\text{mol AgCl} = \frac{0.08890 \text{ g AgCl}}{143.321 \text{ g AgCl/mol AgCl}} = 6.202_9 \times 10^{-4} = \text{mol Cl}^-$$

$$\text{mol RaCl}_2 = 6.202_9 \times 10^{-4} \text{ mol Cl}^- \times \frac{1 \text{ mol RaCl}_2}{2 \text{ mol Cl}^-} = 3.101_4 \times 10^{-4}$$

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$$\text{molar mass of RaCl}_2 = \frac{0.09192 \text{ g}}{3.101_4 \times 10^{-4} \text{ mol}} = 296.3_8 \text{ g/mol}$$

$$\text{Formula mass of RaCl}_2 = \text{atomic mass of Ra} + 2 \left( 35.453 \frac{\text{g}}{\text{mol}} \right) = 296.3_8$$

$$\text{atomic mass of Ra} = 296.3_8 - 70.906 = 225.5 \text{ g/mol}$$

Q) How many grams of AgBr (FM = 187.77 g/mol) would have been formed from 0.100 g of  $\text{RaBr}_2$  (FM = 385.808 g/mol)? (Answer: 0.097 g)

Representative analytical precipitations are listed in **Table 26-1**. A few common organic precipitants (agents that cause precipitation) are listed in **Table 26-2**.

Conditions must be controlled to selectively precipitate one species. Potentially interfering substances may need to be removed prior to analysis.

**TABLE 26-1** Representative gravimetric analyses

| Species analyzed              | Precipitated form  | Form weighed   | Interfering species   |
|-------------------------------|--|--|---|
| K <sup>+</sup>                | KB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>  | KB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>                      | NH <sub>4</sub> <sup>+</sup> , Ag <sup>+</sup> , Hg <sup>2+</sup> , Tl <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup>   |
| Mg <sup>2+</sup>              | Mg(NH <sub>4</sub> )PO <sub>4</sub> · 6H <sub>2</sub> O  | Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>                        | Many metals except Na <sup>+</sup> and K <sup>+</sup>   |
| Ca <sup>2+</sup>              | CaC <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O   | CaCO <sub>3</sub> or CaO   | Many metals except Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup>  |
| Ba <sup>2+</sup>              | BaSO <sub>4</sub>  | BaSO <sub>4</sub>  | Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> , Cu <sup>2+</sup> , Al <sup>3+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> , Sr <sup>2+</sup> , Pb <sup>2+</sup> , NO <sub>3</sub> <sup>-</sup>                               |
| Ti <sup>4+</sup>              | TiO (5,7-dibromo-8-hydroxyquinoline) <sub>2</sub>  | Same   | Fe <sup>3+</sup> , Zr <sup>4+</sup> , Cu <sup>2+</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , citrate, HF  |
| VO <sub>4</sub> <sup>3-</sup> | Hg <sub>3</sub> VO <sub>4</sub>  | V <sub>2</sub> O <sub>5</sub>  | Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , CrO <sub>4</sub> <sup>2-</sup> , AsO <sub>4</sub> <sup>3-</sup> , PO <sub>4</sub> <sup>3-</sup>  |
| Cr <sup>3+</sup>              | PbCrO <sub>4</sub>   | PbCrO <sub>4</sub>   | Ag <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>  |
| Mn <sup>2+</sup>              | Mn(NH <sub>4</sub> )PO <sub>4</sub> · H <sub>2</sub> O   | Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>                        | Many metals   |
| Fe <sup>3+</sup>              | Fe(HCO <sub>2</sub> ) <sub>3</sub>   | Fe <sub>2</sub> O <sub>3</sub>                                       | Many metals   |
| Co <sup>2+</sup>              | Co(1-nitroso-2-naphtholate) <sub>2</sub>   | CoSO <sub>4</sub> (by reaction with H <sub>2</sub> SO <sub>4</sub> ) | Fe <sup>3+</sup> , Pd <sup>2+</sup> , Zr <sup>4+</sup>  |
| Ni <sup>2+</sup>              | Ni(dimethylglyoximate) <sub>2</sub>  | Same   | Pd <sup>2+</sup> , Pt <sup>2+</sup> , Bi <sup>3+</sup> , Au <sup>3+</sup>   |
| Cu <sup>2+</sup>              | CuSCN (after reduction of Cu <sup>2+</sup> to Cu <sup>+</sup> with HSO <sub>3</sub> <sup>-</sup> ) | CuSCN  | NH <sub>4</sub> <sup>+</sup> , Pb <sup>2+</sup> , Hg <sup>2+</sup> , Ag <sup>+</sup>  |
| Zn <sup>2+</sup>              | Zn(NH <sub>4</sub> )PO <sub>4</sub> · H <sub>2</sub> O   | Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>                        | Many metals   |
| Ce <sup>4+</sup>              | Ce(IO <sub>3</sub> ) <sub>4</sub>  | CeO <sub>2</sub>   | Th <sup>4+</sup> , Ti <sup>4+</sup> , Zr <sup>4+</sup>  |
| Al <sup>3+</sup>              | Al(8-hydroxyquinolate) <sub>3</sub>  | Same   | Many metals   |
| Sn <sup>4+</sup>              | Sn(cuperron) <sub>4</sub>  | SnO <sub>2</sub>   | Cu <sup>2+</sup> , Pb <sup>2+</sup> , As(III)   |
| Pb <sup>2+</sup>              | PbSO <sub>4</sub>  | PbSO <sub>4</sub>  | Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Hg <sup>2+</sup> , Ag <sup>+</sup> , HCl, HNO <sub>3</sub>   |
| NH <sub>4</sub> <sup>+</sup>  | NH <sub>4</sub> B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>                                     | NH <sub>4</sub> B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>       | K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup>  |
| Cl <sup>-</sup>               | AgCl   | AgCl   | Br <sup>-</sup> , I <sup>-</sup> , SCN <sup>-</sup> , S <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , CN <sup>-</sup>   |
| Br <sup>-</sup>               | AgBr   | AgBr   | Cl <sup>-</sup> , I <sup>-</sup> , SCN <sup>-</sup> , S <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , CN <sup>-</sup>   |
| I <sup>-</sup>                | AgI  | AgI  | Cl <sup>-</sup> , Br <sup>-</sup> , SCN <sup>-</sup> , S <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , CN <sup>-</sup>  |
| SCN <sup>-</sup>              | CuSCN  | CuSCN  | NH <sub>4</sub> <sup>+</sup> , Pb <sup>2+</sup> , Hg <sup>2+</sup> , Ag <sup>+</sup>  |
| CN <sup>-</sup>               | AgCN   | AgCN   | Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , SCN <sup>-</sup> , S <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>   |
| F <sup>-</sup>                | (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnF  | (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnF                    | Many metals (except alkali metals), SiO <sub>4</sub> <sup>4-</sup> , CO <sub>3</sub> <sup>2-</sup>  |
| ClO <sub>4</sub> <sup>-</sup> | KClO <sub>4</sub>  | KClO <sub>4</sub>  |   |
| SO <sub>4</sub> <sup>2-</sup> | BaSO <sub>4</sub>  | BaSO <sub>4</sub>  | Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> , Cu <sup>2+</sup> , Al <sup>3+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> , Sr <sup>2+</sup> , Pb <sup>2+</sup> , NO <sub>3</sub> <sup>-</sup>                               |
| PO <sub>4</sub> <sup>3-</sup> | Mg(NH <sub>4</sub> )PO <sub>4</sub> · 6H <sub>2</sub> O  | Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>                        | Many metals except Na <sup>+</sup> , K <sup>+</sup>   |
| NO <sub>3</sub> <sup>-</sup>  | Nitron nitrate   | Nitron nitrate   | ClO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> , SCN <sup>-</sup> , CrO <sub>4</sub> <sup>2-</sup> , ClO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , Br <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> |
| CO <sub>3</sub> <sup>2-</sup> | CO <sub>2</sub> (by acidification)   | CO <sub>2</sub>  | (The liberated CO <sub>2</sub> is trapped with Ascarite and weighed.)   |

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**TABLE 26-2** Common organic precipitating agents

| Name   | Structure   | Ions precipitated   |
|--|---|---|
| Dimethylglyoxime   |   | $\text{Ni}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Pt}^{2+}$  |
| Cupferron  |   | $\text{Fe}^{3+}$ , $\text{VO}_2^+$ , $\text{Ti}^{4+}$ , $\text{Zr}^{4+}$ , $\text{Ce}^{4+}$ , $\text{Ga}^{3+}$ , $\text{Sn}^{4+}$   |
| 8-Hydroxyquinoline (oxine)                               |   | $\text{Mg}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Bi}^{3+}$ , $\text{Ga}^{3+}$ , $\text{Th}^{4+}$ , $\text{Zr}^{4+}$ , $\text{UO}_2^{2+}$ , $\text{TiO}^{2+}$     |
| Salicylaldoxime  |   | $\text{Cu}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Zn}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pd}^{2+}$   |
| 1-Nitroso-2-naphthol                                     |   | $\text{Co}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Pd}^{2+}$ , $\text{Zr}^{4+}$   |
| Nitron   |   | $\text{NO}_3^-$ , $\text{ClO}_4^-$ , $\text{BF}_4^-$ , $\text{WO}_4^{2-}$   |
| Sodium tetraphenylborate<br>Tetraphenylarsonium chloride | $\text{Na}^+ \text{B}(\text{C}_6\text{H}_5)_4^-$<br>$(\text{C}_6\text{H}_5)_4\text{As}^+ \text{Cl}^-$ | $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{NH}_4^+$ , $\text{Ag}^+$ , organic ammonium ions<br>$\text{Cr}_2\text{O}_7^{2-}$ , $\text{MnO}_4^-$ , $\text{ReO}_4^-$ , $\text{MoO}_4^{2-}$ , $\text{WO}_4^{2-}$ , $\text{ClO}_4^-$ , $\text{I}_3^-$ |

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## 26.2 Precipitation

The ideal product of a gravimetric analysis should be:

1. Insoluble
2. Easily filterable
3. Very pure
4. Possess a known composition.

→ We need to control precipitation conditions:

### **Solubility:**

\* Solubility depends on the temperature and the solvent.

\* The solubility of a precipitate is usually decreased by cooling the solution.

**Filterability:**

\* Particles of precipitate should not be so small that they clog or pass through the filter.

\* Large crystals are easily filterable and also have less surface area to which foreign species may attach.

\* At the other extreme is a colloidal suspension of particles that have diameter in the range 1-500 nm and pass through most filters.

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**Crystal Growth:**

\* Crystallization occurs in two phases: nucleation and particle growth.

During nucleation: molecules in solution come together randomly and form small aggregates.

Particle growth: involves the addition of more molecules to the nucleus to form a crystal.

In a highly supersaturated solution: nucleation precedes faster than particle growth → the results a suspension of tiny particles or, worse, a colloid.

**Techniques that promote particle growth include:**

1. Raising the temperature to increase solubility and thereby decrease supersaturation

2. Adding precipitant slowly with vigorous mixing, to prevent a local, highly supersaturated condition where the stream of precipitant first enters the analyte

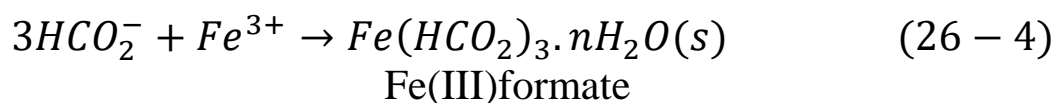
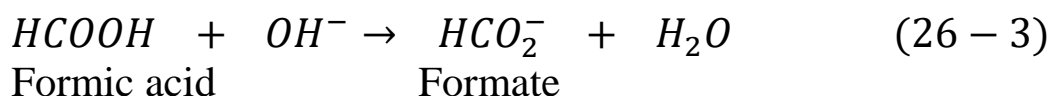
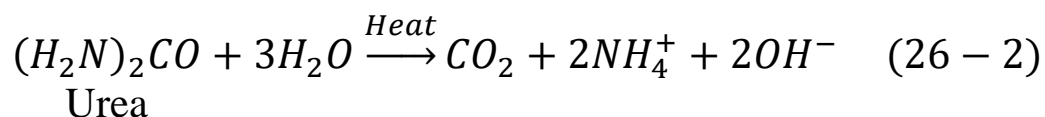
3. Using a large volume of solution so that concentrations of analyte and precipitant are low

## Homogenous Precipitation:

Is a technique used for controlling supersaturation. In this technique the precipitant is generated slowly by a chemical reaction (Table 26-3).

Particle size of ferric formate is enhanced by using urea to generate  $\text{OH}^-$  ions slowly.

For example, urea decomposes slowly in boiling water to produce  $\text{OH}^-$ :



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Table 27-3 Common reagents used for homogeneous precipitation

| Precipitant                 | Reagent                    | Reaction   | Some elements precipitated     |
|-----------------------------|----------------------------|--|--------------------------------|
| $\text{OH}^-$               | Urea                       | $(\text{H}_2\text{N})_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$  | Al, Ga, Th, Bi, Fe, Sn, Cr, Fe |
| $\text{OH}^-$               | Potassium cyanate          | $\text{HOCN} + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{CO}_2 + \text{OH}^-$<br>Hydrogen cyanate  | Cr, Fe                         |
| $\text{S}^{2-}$             | Thioacetamide <sup>a</sup> | $\begin{array}{c} \text{S} \\    \\ \text{CH}_3\text{CNH}_2 \end{array} + \text{H}_2\text{O} \rightarrow \begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CNH}_2 \end{array} + \text{H}_2\text{S}$  | Sb, Mo, Cu, Cd                 |
| $\text{SO}_4^{2-}$          | Sulfamic acid              | $\text{H}_3\text{NSO}_3^- + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{SO}_4^{2-} + \text{H}^+$  | Ba, Ca, Sr, Pb                 |
| $\text{C}_2\text{O}_4^{2-}$ | Dimethyl oxalate           | $\begin{array}{c} \text{OO} \\     \\ \text{CH}_3\text{OCCOCH}_3 \end{array} + 2\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{C}_2\text{O}_4^{2-} + 2\text{H}^+$  | Ca, Mg, Zn                     |
| $\text{PO}_4^{3-}$          | Trimethyl phosphate        | $(\text{CH}_3\text{O})_3\text{P}=\text{O} + 3\text{H}_2\text{O} \rightarrow 3\text{CH}_3\text{OH} + \text{PO}_4^{3-} + 3\text{H}^+$  | Zr, Hf                         |
| $\text{CrO}_4^{2-}$         | Chromic ion plus bromate   | $2\text{Cr}^{3+} + \text{BrO}_3^- + 5\text{H}_2\text{O} \rightarrow 2\text{CrO}_4^{2-} + \text{Br}^- + 10\text{H}^+$   | Pb                             |
| 8-Hydroxyquinoline          | 8-Acetoxyquinoline         | $\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CO} \end{array} \text{C}_8\text{H}_6\text{N}_2 + \text{H}_2\text{O} \rightarrow \begin{array}{c} \text{OH} \\   \\ \text{C}_8\text{H}_6\text{N}_2 \end{array} + \text{CH}_3\text{CO}_2\text{H}$ | Al, U, Mg, Zn                  |

*a. Hydrogen sulfide is volatile and toxic; it should be handled only in a well-vented hood. Thioacetamide is a carcinogen that should be handled with gloves. If thioacetamide contacts your skin, wash yourself thoroughly immediately. Leftover reagent is destroyed by heating at 50°C with 5 mol of NaOCl per mole of thioacetamide. [H. Elo, J. Chem. Ed. 1987, 64, A144.]*

## Precipitation in the Presence of Electrolyte

Ionic compounds are usually precipitated in the presence of an electrolyte. To understand why, we must discuss how tiny colloidal crystallites *coagulate* (come together) into larger crystals.

Figure 26-2 shows a colloidal particle of AgCl growing in a solution containing excess  $\text{Ag}^+$ ,  $\text{H}^+$ , and  $\text{NO}_3^-$ . The surface of the particle has excess positive charge due to the **adsorption** of extra silver ions on exposed chloride ions. (To be adsorbed means to be attached to the surface. In contrast, **absorption** means penetration beyond the surface, to the inside.) The positively charged surface attracts anions and repels cations from the *ionic atmosphere* (Figure 26-2) surrounding the particle. The positively charged particle and the negatively charged ionic atmosphere together are called the **electric double layer**.

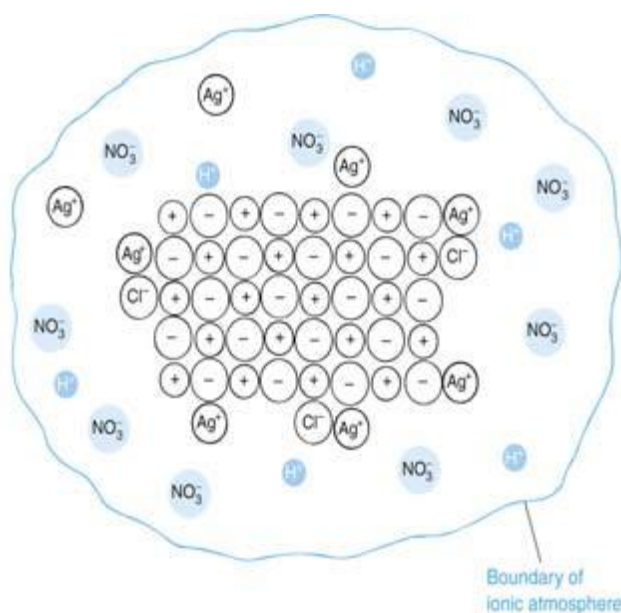


Figure 26-2

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Colloidal particles must collide with one another to coalesce. However, the negatively charged ionic atmospheres of the particles repel one another. Particles must have enough kinetic energy to overcome electrostatic repulsion before they can coalesce.

Heating promotes coalescence by increasing the kinetic energy.

Increasing electrolyte concentration ( $\text{HNO}_3$  for AgCl) decreases the

volume of the ionic atmosphere and allows particles to come closer together before electrostatic repulsion becomes significant. For this reason, most gravimetric precipitations are done in the presence of an electrolyte.

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## **Digestion:**

Liquid from which a substance precipitates or crystallizes is called the mother liquor. After precipitation, most procedures call for a period of standing in the presence of the hot mother liquor. This treatment, called digestion, promotes slow recrystallization of the precipitate. Particle size increases and impurities tend to be expelled from the crystal.

## **Purity:**

Contamination of the precipitate by impurities can be classified as:

1) **Coprecipitation** and 2) **Postprecipitation**

1) **Coprecipitation**: Precipitation of impurities along with the desired product, even though the solubility of the impurity has not been exceeded

- **Coprecipitation** occurs to some degree in every gravimetric analysis and cannot be avoided, but can be minimized by careful precipitation and a thorough washing of the precipitate.

- **Coprecipitation** can occur by

A) **Adsorption**: impurities are bound to the surface of a crystal.

B) **Absorption**: impurities are held within the crystal.

Absorbed impurities within the crystal are classified as **inclusions** or **occlusions**:

B1) **inclusions**: are impurity ions that randomly occupy sites in the crystal lattice normally occupied by ions that belong in the crystal. The chance of inclusions increases when the impurity ion has a similar size and charge to one of the ions that belong to the product (precipitate).

Example:  $K^+$  in  $NH_4MgPO_4$  ( $K^+$  is similar to  $NH_4^+$ )



B2) **occlusions**: are impurities trapped (sometimes with solvent) in pockets inside the growing crystal.

Coprecipitation tends to be worst in colloidal precipitates such as  $\text{BaSO}_4$ ,  $\text{Al}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_3$ , which all have a large surface area. Many procedures call for washing away the mother liquor, redissolving the precipitate, and *reprecipitating* the product. During the second precipitation, the concentration of impurities in solution is lower than during the first precipitation, and the degree of coprecipitation therefore tends to be lower.

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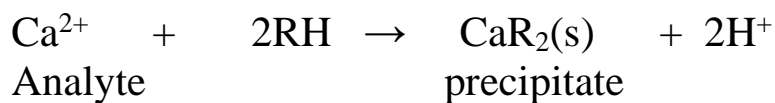
*There is an advantage for coprecipitation to gather the trace components.*

\* The precipitate used to collect the trace component is called a **gathering agent** and the process is called **gathering**.

- Toxic metals such as natural arsenic in drinking water in Bangladesh can be removed from wastewater by coprecipitation with  $\text{Fe}(\text{OH})_3$ .  $\text{Fe}(\text{II})$  or  $\text{Fe}(\text{s})$  is added to the water and oxidized in air for several hours to precipitate  $\text{Fe}(\text{OH})_3$ . After filtration through sand to remove solids, the water is drinkable.

## Masking agents

- Some impurities can be treated with a **masking agent** to prevent them from reacting with the precipitant.
- In the gravimetric analysis of  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , or  $\text{Ba}^{2+}$  with the reagent *N-p*-chlorophenylcinnamohydroxamic acid (RH), impurities such as  $\text{Mn}^{2+}$ ,  $\text{Ag}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ga}^{3+}$  are kept in solution by excess KCN.  $\text{Pb}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{5+}$ , and  $\text{Mo}^{6+}$  are masked with a mixture of citrate and oxalate.



2) Postprecipitation: adsorption (collection) of impurities on the precipitate while it standing in the mother liquor (after the precipitation is over).

An example is the crystallization of  $MgC_2O_4$  on  $CaC_2O_4$ .

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## Washing of precipitates:

After collection of the precipitate on the filter, it has to be washed to remove any droplets of the mother liquor that contain excess solute.

Some precipitates can be washed with water, but many require electrolyte to maintain coherence. For these precipitates, the ionic atmosphere is required to neutralize the surface charge of the tiny particles. If electrolyte is washed away with water, the charged solid particles repel one another and the product breaks up. This breaking up, called **peptization**, results in loss of product through the filter.

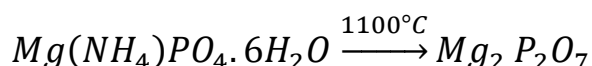
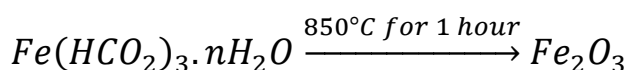
$AgCl$  will peptize if washed with water, so it is washed with dilute  $HNO_3$  instead. Electrolyte used for washing must be volatile so that it will be lost during drying. Volatile electrolytes include  $HNO_3$ ,  $HCl$ ,  $NH_4NO_3$ ,  $NH_4Cl$ , and  $(NH_4)_2CO_3$ .



## Product Composition:

- \* The final product must have a stable and known composition
- \* A **hygroscopic substance** is one that picks up water from the air and is therefore difficult to weigh accurately.
- \* Many precipitates contain a variable quantity of water and must be dried under conditions that give a known (possibly zero) stoichiometry of  $H_2O$ .
- \* Ignition (strong heating) is often used to change the chemical form of some precipitates.

Examples:



**In thermogravimetric analysis**, a substance is heated, and its mass is measured as a function of temperature. Figure 26-4 shows how the composition of calcium salicylate changes in four stages:

Figure 26-4 shows how the composition of calcium salicylate changes in four stages:

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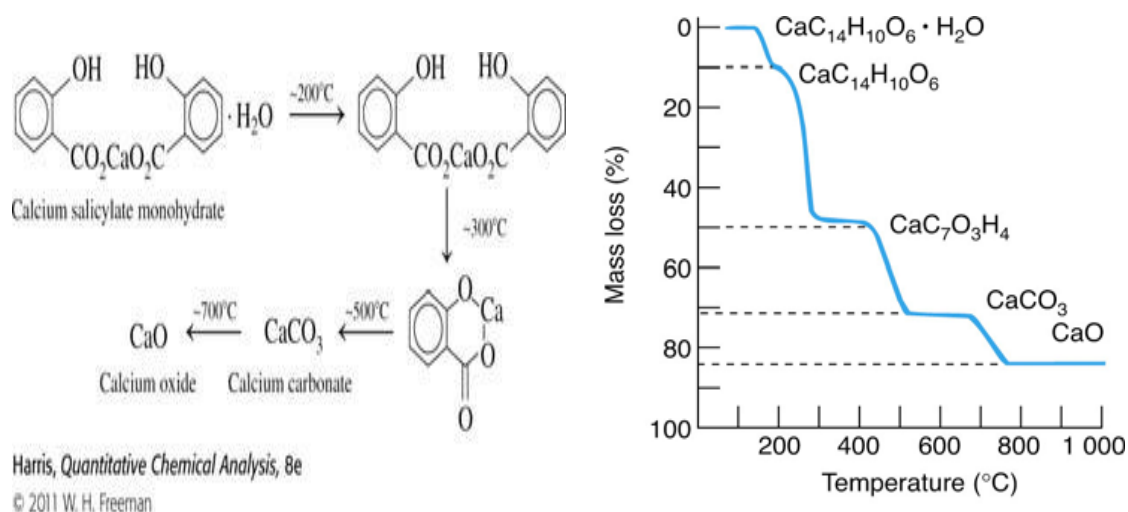
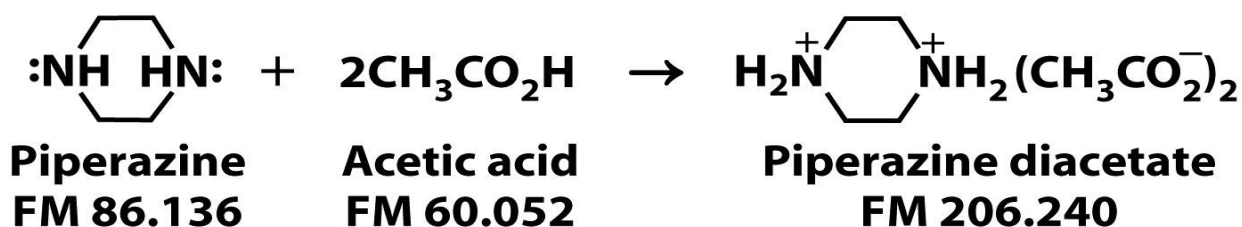


Figure 26-4 Thermogravimetric curve for calcium salicylate

The composition of the product depends on the temperature and duration of heating.

## 26.3 Examples of Gravimetric Calculations



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**Example 1:** The piperazine content of an impure commercial material can be determined by precipitating and weighing the diacetate. In one experiment, 0.3126 g of sample was dissolved in 25 mL of acetone, and 1 mL of acetic acid was added. After 5 min, the precipitate was filtered, washed with acetone, dried at 110°C, and found to weigh 0.7121 g. Find the wt% of piperazine in the sample.

For each mole of piperazine in the impure material, 1 mol of product is formed.

$$\begin{aligned} \text{moles of piperazine diacetate} &= \frac{0.7121 \text{ g}}{206.240} = 3.453 \times 10^{-3} \text{ mol} \\ &= \text{moles of piperazine} \end{aligned}$$

$$\text{mass of piperazine} = (3.453 \times 10^{-3} \text{ mol}) \left( 86.136 \frac{\text{g}}{\text{mol}} \right) = 0.2974 \text{ g}$$

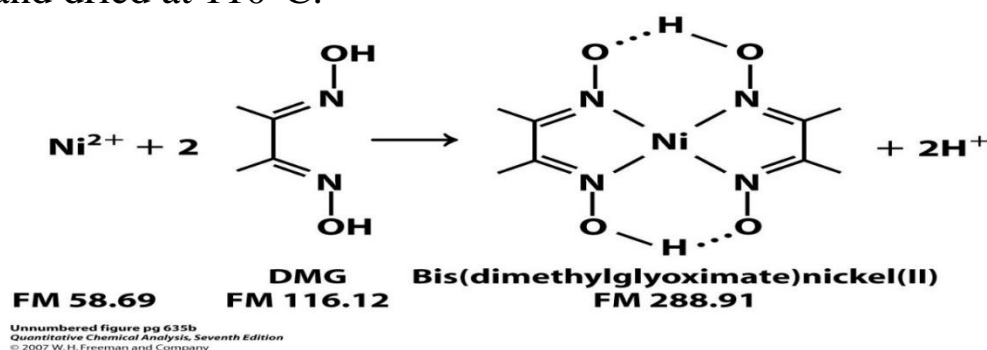
$$\text{Percentage of piperazine} = \frac{0.2974 \text{ g}}{0.3126 \text{ g}} \times 100 = 95.14\%$$

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Q) A 0.3854 g sample gave 0.8000 g of product. Find the wt% of piperazine in the sample.

Answer: 86.69%

Example 2: (a) To measure the nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in solution. The slightly basic solution is warmed, and dimethylglyoxime (DMG) is added to precipitate the red DMG-nickel complex quantitatively. The product is filtered, washed with cold water, and dried at 110°C.



If the nickel content is known to be near 3 wt% and you wish to analyze 1.0 g of steel, what volume of 1.0 wt% alcoholic DMG solution should be used to give a 50% excess of DMG for the analysis? Assume that the density of the alcohol solution is 0.79 g/mL.

Because the Ni content is about 3%, 1.0 g of steel will contain about 0.03 g of Ni

$$\text{moles of Ni} = \frac{0.03 \text{ g}}{58.69 \text{ g/mol}} = 5.11 \times 10^{-4} \text{ mol}$$

$$\text{moles of DMG} = 2 \times 5.11 \times 10^{-4} \text{ mol} = 1.02 \times 10^{-3}$$

$$\text{mass of DMG} = 1.02 \times 10^{-3} \times 116.12 \frac{\text{g}}{\text{mol}} = 0.118 \text{ g}$$

$$\begin{array}{ll} 100 \text{ g solution} & \rightarrow 1 \text{ g DMG} \\ ? & \rightarrow 0.118 \text{ g} \end{array}$$

$$\text{mass of solution needed} = \frac{100 \times 0.118 \text{ g}}{1 \text{ g}} = 11.8 \text{ g}$$

$$\text{volume of solution needed} = \frac{11.8 \text{ g}}{0.79 \text{ g/mL}} = 15 \text{ mL}$$

$$\begin{aligned} \text{volume of solution needed to give 50\% excess} &= 1.5 \times 15 \text{ mL} \\ &= 23 \text{ mL} \end{aligned}$$

**(b)** If 1.1634 g of steel gives 0.1795 g of precipitate, what is the percentage of Ni in the steel?

$$\begin{aligned} \text{moles of Ni(DMG)}_2 &= \frac{0.1795 \text{ g}}{288.91 \text{ g/mol}} = 6.213 \times 10^{-4} \\ &= \text{moles of Ni} \end{aligned}$$

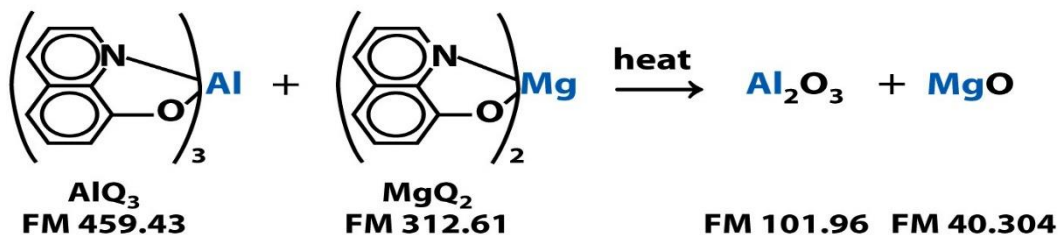
$$\text{mass of Ni} = 6.213 \times 10^{-4} \text{ mol} \times 58.69 \frac{\text{g}}{\text{mol}} = 0.03646 \text{ g}$$

$$\text{Percentage of Ni in steel} = \frac{0.03646 \text{ g}}{1.1634 \text{ g}} \times 100 = 3.134\%$$

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**Example 3:** A problem with two components

A mixture of the 8-hydroxyquinoline complexes of Al and Mg weighed 1.0843 g. When ignited in a furnace open to the air, the mixture decomposed, leaving a residue of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  weighing 0.1344 g. Find the weight percent of  $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$  in the original mixture.



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We will abbreviate the 8-hydroxyquinoline anion as Q. Letting the mass of  $\text{AlQ}_3$  be  $x$  and the mass of  $\text{MgQ}_2$  be  $y$ , we can write

$$\begin{array}{c} x \\ \text{Mass of} \\ \text{AlQ}_3 \end{array} + \begin{array}{c} y \\ \text{Mass of} \\ \text{MgQ}_2 \end{array} = 1.0843 \text{ g}$$

$$\text{moles of AlQ}_3 = \frac{x}{459.43}$$

$$\text{moles of MgQ}_2 = \frac{y}{312.61}$$

$$\text{moles of Al}_2\text{O}_3 = \left(\frac{1}{2}\right) \left(\frac{x}{459.43}\right)$$

$$\text{moles of MgO} = \frac{y}{312.61}$$

$$\text{Mass of Al}_2\text{O}_3 + \text{mass of MgO} = 0.1344 \text{ g}$$

$$\left(\frac{1}{2}\right) \left(\frac{x}{459.43}\right) (101.96) + \frac{y}{312.61} (40.304) = 0.1344 \text{ g}$$

$$\left(\frac{1}{2}\right) \left(\frac{x}{459.43}\right) (101.96) + \left(\frac{1.0843 - x}{312.61}\right) (40.304) = 0.1344 \text{ g}$$

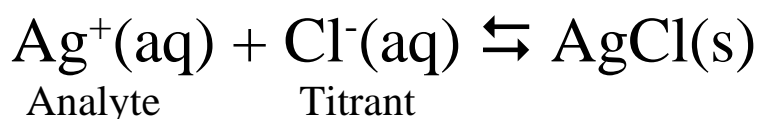
$$X = 0.3003 \text{ g}$$

$$\text{mass\% of AlQ}_3 = \frac{0.3003 \text{ g}}{1.0843} \times 100 = 27.70\%$$

## 26.5 Precipitation Titration Curves

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- Precipitation titrations are used in very limited instances, but are widely used to explain titration theory.
- Usually in a precipitation titration, we are determining some analyte that the titrant forms a precipitate with.
- For example, one can determine the concentration of many anions (especially halides) using silver as a titrant.



- The **titration curve** is a plot of how the concentration of a reactant varies with titrant
- Concentration varies over orders of magnitude, so it is useful to plot the p function

**P Function:**  $pX = -\log_{10}[X]$

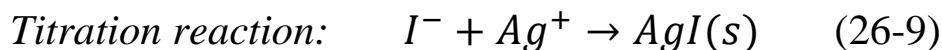
where [X] is the concentration of X.

- A titration curve has three distinct regions: before, at, and after the equivalence point

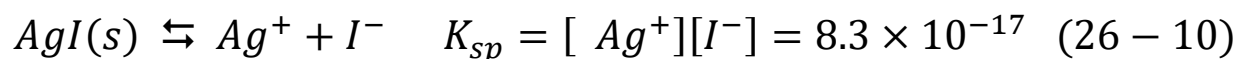
Steps....

- Write a balanced equation
- Write the  $K_{sp}$  equilibrium expression
- Calculate  $V_{eq}$  (volume of equivalence point)
- Determine where in the titration curve you are (Before, At, After  $V_{eq}$ )
- Solve
- Plot Titration Curve if necessary
- Let's sketch the titration curve

Consider the titration of 25.00 mL of 0.1000 M  $I^-$  with 0.05000 M  $Ag^+$ ,



and suppose that we are monitoring  $[Ag^+]$  with an electrode. Reaction 26-9 is the reverse of the dissolution of  $AgI(s)$ , whose solubility product is rather small:



The equilibrium constant for the titration reaction 26-9 is large ( $K = \frac{1}{K_{sp}} = 1.2 \times 10^{16}$ ), so the equilibrium lies far to the right. Each aliquot of  $Ag^+$  reacts nearly completely with  $I^-$ , leaving only a tiny amount of  $Ag^+$  in solution. At the equivalence point, there will be a sudden increase in  $[Ag^+]$  because there is no  $I^-$  left to consume the added  $Ag^+$ .

What volume of  $Ag^+$  titrant is needed to reach the equivalence point? We calculate this volume, designated  $V_e$ , with the fact that 1 mol of  $Ag^+$  reacts with 1 mol of  $I^-$

At the equivalence point ( $V_e$ ):

$$\text{moles of } Ag^+ = \text{moles of } I^-$$

$$0.05000 \times V_e = 0.1000 \times 25.00$$

$$V_e = \frac{0.1000 \times 25.00}{0.05000} = 80.00 \text{ mL}$$

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## Before the Equivalence Point

Suppose that 10.00 mL of  $Ag^+$  have been added. There are more moles of  $I^-$  than  $Ag^+$  at this point, so virtually all  $Ag^+$  is “used up” to make  $AgI(s)$ . We want to find the small concentration of  $Ag^+$  remaining in solution after reaction with  $I^-$ . Imagine that Reaction 26-9 has gone to



completion and that some AgI redissolves (Reaction 26-10). The solubility of  $Ag^+$  is determined by the concentration of free  $I^-$  remaining in the solution:

$$[Ag^+] = \frac{K_{sp}}{[I^-]} \quad (26 - 11)$$

Free  $I^-$  is overwhelmingly from the  $I^-$  that has not been precipitated by 10.00 mL of  $Ag^+$ . By comparison,  $I^-$  from dissolution of AgI(s) is negligible. So let's find the concentration of unprecipitated  $I^-$ :

$$\begin{aligned} \text{Moles of } I^- &= \text{original mols of } I^- - \text{moles of } Ag^+ \text{ added} \\ &= (0.02500 \text{ L})(0.100 \text{ mol/L}) - (0.01000 \text{ L})(0.05000 \text{ mol/L}) \\ &= 0.002000 \text{ mol } I^- \end{aligned}$$

The volume is 0.03500 L (25.00 mL + 10.00 mL), so the concentration is

$$[I^-] = \frac{0.002000 \text{ mol } I^-}{0.03500 \text{ L}} = 0.05714 \text{ M} \quad (26 - 12)$$

The concentration of  $Ag^+$  in equilibrium with this much  $I^-$  is

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{0.05714} = 1.45 \times 10^{-15} \text{ M} \quad (26 - 13)$$

$$p^{Ag^+} = -\log[Ag^+] = -\log 1.45 \times 10^{-15} = 14.84 \quad (26 - 14)$$

## Shortcut Calculations

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The preceding step-by-step calculation is a tedious way to find the concentration of  $I^-$ . Here is a streamlined procedure that is well worth learning. Bear in mind that  $V_e = 50.00 \text{ mL}$ . When 10.00 mL of  $Ag^+$  have been added, the reaction is **one-fifth** complete because 10.00 mL out of the 50.00 mL of  $Ag^+$  needed for complete reaction have been added. Therefore, **four-fifths** of the  $I^-$  is unreacted. If there were no dilution,  $[I^-]$  would be four-fifths of its original value. However, the original volume of 25.00 mL has been increased to 35.00 mL. If no  $I^-$

had been consumed, the concentration would be the original value of  $[I^-]$  times  $(25.00/35.00)$ . Accounting for both the reaction and the dilution, we can write

$$[I^-] = \underbrace{\left(\frac{40}{50}\right)}_{\text{Fraction remaining}} \underbrace{(0.1000\text{ M})}_{\text{Original concentration}} \underbrace{\left(\frac{25.00}{35.00}\right)}_{\text{Dilution factor}} = 0.05714\text{ M}$$

**This is the same result found in Equation 26-12.**

25.00 mL is the original volume of  $I^-$

35.00 mL is the total volume of solution

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**EXAMPLE** Using the Streamlined Calculation

Let's calculate  $pAg^+$  when (the volume added from the buret) is 49.00 mL.

$$[I^-] = \left(\frac{1}{50}\right)(0.1000\text{ M})\left(\frac{25.00}{74.00}\right) = 6.76 \times 10^{-4}\text{ M}$$

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{6.76 \times 10^{-4}\text{ M}} = 1.2 \times 10^{-13}\text{ M}$$

$$pAg^+ = -\log[Ag^+] = -\log[1.2 \times 10^{-13}] = 12.91$$

The concentration of  $Ag^+$  is negligible compared with the concentration of unreacted  $I^-$ , even though the titration is 98% complete.

Question: Find  $pAg^+$  at 49.1 mL. (Answer: 12.86)

## At the Equivalence Point

- At the equivalence point, we have added the exact amount of  $\text{Ag}^+$  needed to react with  $\text{I}^-$
- $p\text{Ag}^+$  is found by solving for  $x$  from  $K_{sp}$

$$[\text{Ag}^+][\text{I}^-] = K_{sp}$$

$$(x)(x) = 8.3 \times 10^{-17} \rightarrow x = 9.1 \times 10^{-9} \rightarrow p\text{Ag}^+ = -\log 9.1 \times 10^{-9} = 8.04$$

This value of  $p\text{Ag}^+$  is independent of the original concentrations or volumes.

## After the Equivalence Point

- After the equivalence point,  $p\text{Ag}^+$  is simply determined by calculating the excess  $\text{Ag}^+$
- Suppose we have added 52.00 mL of  $\text{Ag}^+$  solution. The volume past the equivalence point is 2.00 mL. The calculation proceeds as follows

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$$\text{mol Ag}^+_{\text{excess}} = (0.00200 \text{ L})(0.050 \text{ M}) = 0.000100 \text{ mol}$$

$$[\text{Ag}^+] = 0.000100 \text{ mol} / 0.07700 \text{ L} = 1.30 \times 10^{-3} \text{ M}$$

$$p\text{Ag}^+ = -\log[\text{Ag}^+] = -\log[1.30 \times 10^{-3}] = 2.89$$

For a streamlined calculation, the concentration of  $\text{Ag}^+$  in the burette is 0.050 00 M, and 2.00 mL of titrant are being diluted to  $(25.00 + 52.00) = 77.00$  mL. Hence,  $[\text{Ag}^+]$  is

$$[\text{Ag}^+] = \underbrace{(0.05000 \text{ M})}_{\substack{\text{Original} \\ \text{concentration} \\ \text{of } \text{Ag}^+}} \underbrace{\left(\frac{2.00}{77.00}\right)}_{\substack{\text{Dilution} \\ \text{factor}}} = 1.3 \times 10^{-3} \text{ M}$$

2.00 mL is the volume of excess  $\text{Ag}^+$

77.00 mL is the total volume of solution

### The Shape of the Titration Curve

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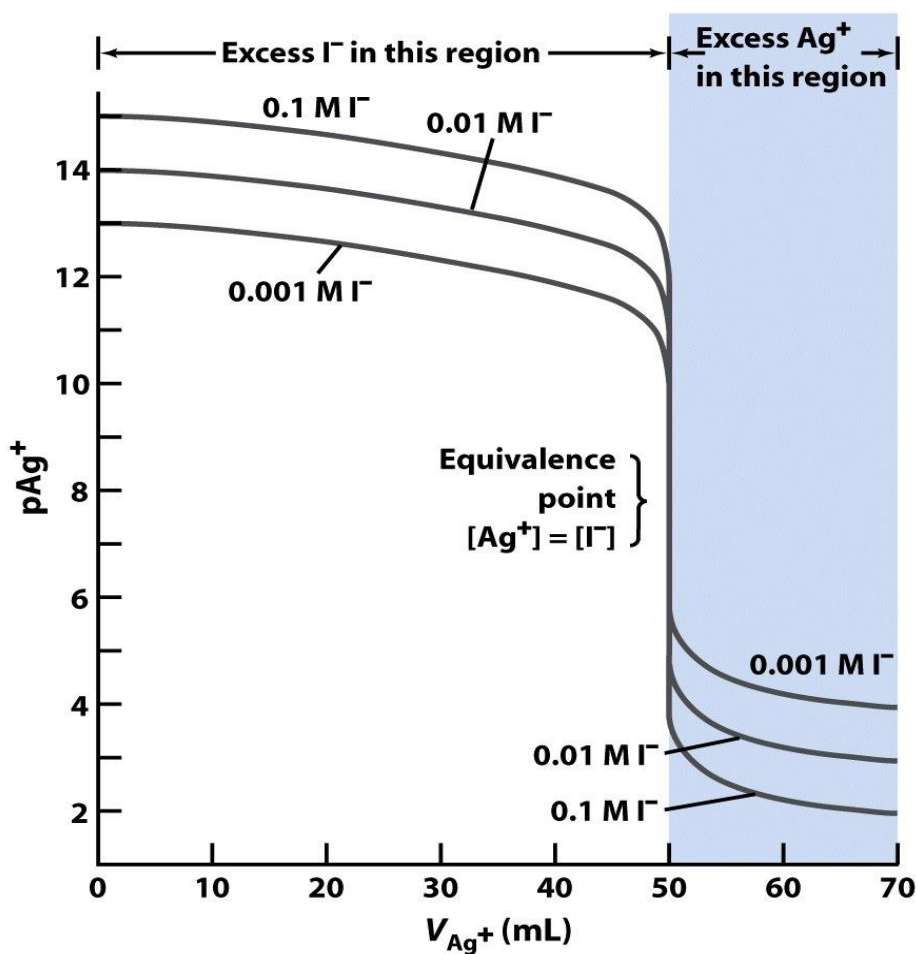


Figure 7-6  
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Figure 26-8

Titration curves in Figure 26-8 illustrate the effect of **reactant concentration**. The equivalence point is the steepest point of the curve. In titrations involving 1:1 stoichiometry of reactants, the equivalence point is the steepest point of the titration curve. For stoichiometries other than 1:1, such as  $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4(s)$ , the curve is not symmetric. The equivalence point is not at the center of the steepest section of the curve, and it is not an inflection point.

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### Effect of $K_{sp}$ on the Curve

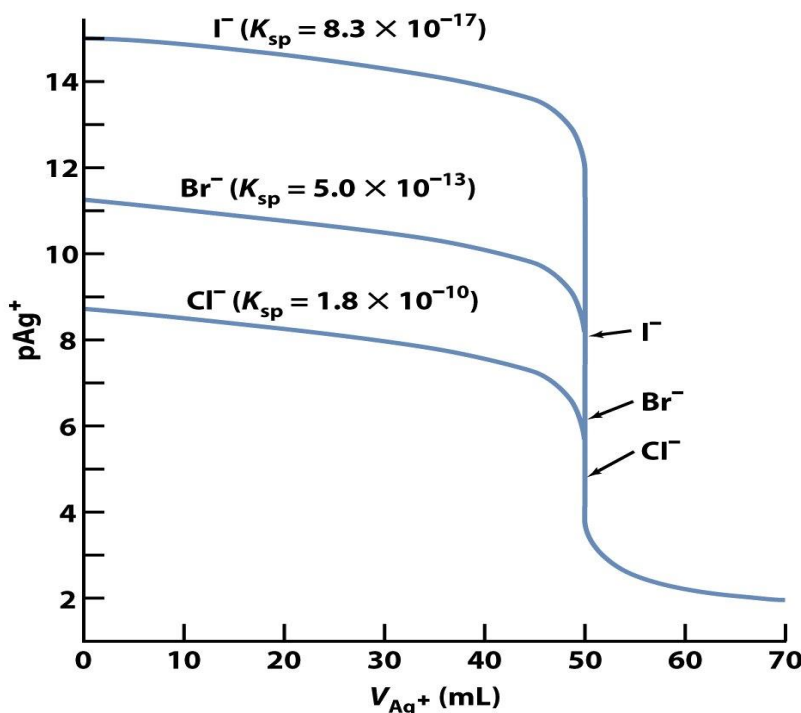


Figure 7-7  
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**Figure 26-9: Titration curves showing the effect of  $K_{sp}$ .** Each curve is calculated for 25.00 mL of 0.100 0 M halide titrated with 0.050 00 M  $Ag^+$ . Equivalence points are marked by arrows.

Figure 26-9 illustrates how  $K_{sp}$  affects the titration of halide ions. The least soluble product, AgI, gives the sharpest change at the equivalence point. However, even for AgCl, the curve is steep enough to locate the equivalence point accurately. The larger the equilibrium constant for a titration reaction, the more pronounced will be the change in concentration near the equivalence point.

## Example

- 25.00 mL of 0.04132 M  $\text{Hg}_2(\text{NO}_3)_2$  was titrated with 0.05789 M  $\text{KIO}_3$ :



$K_{sp}$  for  $\text{Hg}_2(\text{NO}_3)_2$  is  $1.3 \times 10^{-18}$

Calculate the concentration of  $\text{Hg}_2^{2+}$  in solution

- after addition of 34.00 mL  $\text{KIO}_3$ ,
- after addition of 36.00 mL  $\text{KIO}_3$ , and
- at the equivalence point

The volume of iodate needed to reach the equivalence point is found as follows:

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$$\begin{aligned} \text{moles of } \text{IO}_3^- &= 2 \text{ moles of } \text{Hg}_2^{2+} \\ (0.05789 \text{ M}) \times (V_e) &= 2(0.04132 \text{ M})(25.00 \text{ mL}) \\ V_e &= 35.69 \text{ mL} \end{aligned}$$

(A) After addition of 34.00 mL  $\text{KIO}_3$

## Example A

- If  $V=34.00$  mL,  $\text{Hg}_2^{2+}$  precipitation is not complete

$$[\text{Hg}_2^{2+}] = \left( \frac{35.69 - 34.00}{35.69} \right) (0.04132 \text{ M}) \left( \frac{25.00}{25.00 + 34.00} \right) = 8.29 \times 10^{-4} \text{ M}$$

From Remaining
Conc.
Dilution Factor

(B) After addition of 36.00 mL  $\text{KIO}_3$

### Example B

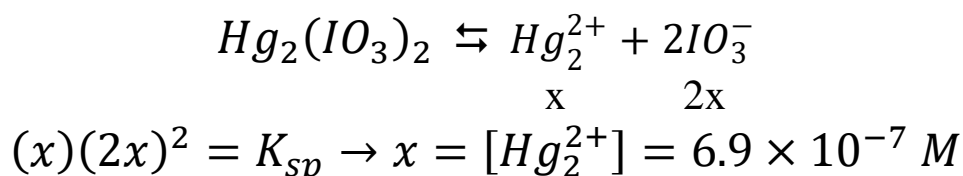
- If  $V=36.00$  mL, the precipitation is complete and we have gone past the equivalence point

$$[\text{IO}_3^-] = \left( \frac{36.00 - 35.69}{25.00 + 36.00} \right) (0.05789 \text{ M}) = 2.9 \times 10^{-4} \text{ M}$$

Dilution Factor
Conc<sub>i</sub>

$$[\text{Hg}_2^{2+}] = \frac{K_{sp}}{[\text{IO}_3^-]^2} = \frac{1.3 \times 10^{-18}}{(2.9 \times 10^{-4})^2} = 1.5 \times 10^{-11} \text{ M}$$

(C) At the equivalence point, there is exactly enough  $\text{IO}_3^-$  to react with all  $\text{Hg}_2^{2+}$ . We can imagine that all of the ions precipitate and then some  $\text{Hg}_2(\text{IO}_3)_2(\text{s})$  redissolves, giving two moles of iodate for each mole of mercurous ion:



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Q) Find  $[\text{Hg}_2^{2+}]$  at 34.50 and 36.50 mL. (Answer:  $5.79 \times 10^{-4} \text{ M}$ ,  $2.2 \times 10^{-12} \text{ M}$ )

## 26.6 Titration of a Mixture

If a mixture of two ions is titrated, the less soluble precipitate forms first. If the solubilities are sufficiently different, the first precipitation is nearly complete before the second commences.

Consider the addition of  $\text{AgNO}_3$  to a solution containing  $\text{KI}$  and  $\text{KCl}$ .

Because  $K_{sp}(\text{AgI}) \ll K_{sp}(\text{AgCl})$ ,  $\text{AgI}$  precipitates first. When precipitation of  $\text{I}^-$  is almost complete, the concentration of  $\text{Ag}^+$  abruptly increases and  $\text{AgCl}$  begins to precipitate. When  $\text{Cl}^-$  is consumed,

another abrupt increase in  $[Ag^+]$  occurs. We expect two breaks in the titration curve, first at  $V_e$  for AgI and then at  $V_e$  for AgCl.

Figure 26-10 shows an experimental curve for this titration. The apparatus used to measure the curve is shown in Figure 26-11.

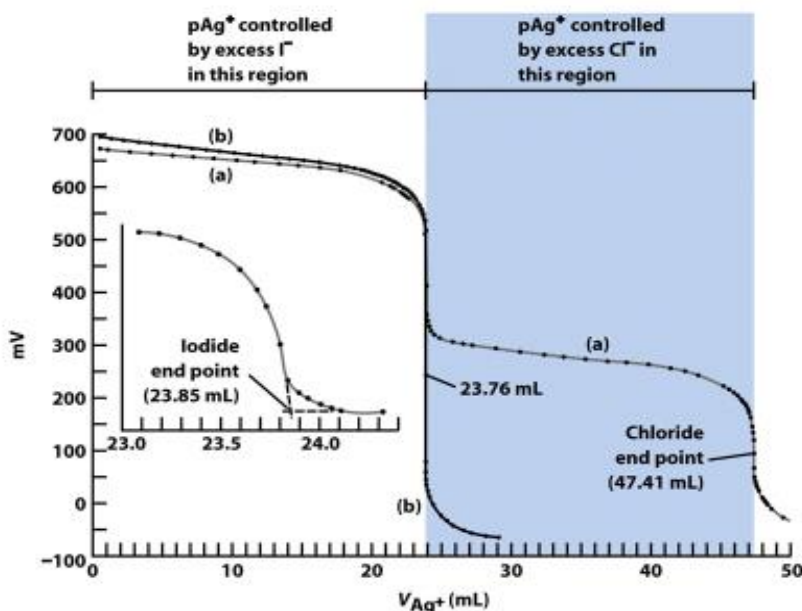
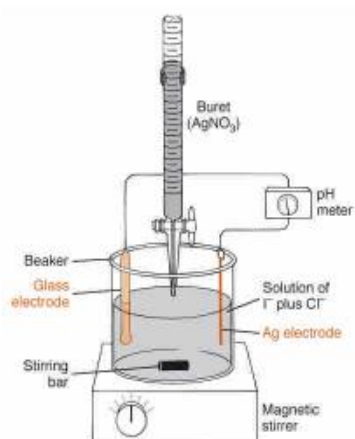


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Figure 26-10

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## Technique to Monitor Titration



The technique used to monitor the mixture titration of  $Ag^+$  with  $I^-$  and  $Cl^-$  was electrochemistry. An electrode specific to  $Ag^+$  was used to monitor  $[Ag^+]$

The principles of electrochemistry and electrode operation will be discussed in Chs. 14-15. As discussed, this is just one method of monitoring a titration. Spectroscopy is another.

Figure 26-11



The  $I^-$  end point is taken as the intersection of the steep and nearly horizontal curves shown in the inset of Figure 26-10. Precipitation of  $I^-$  is not quite complete when  $Cl^-$  begins to precipitate. (The way we know that  $I^-$  precipitation is not complete is by a calculation. That's what these obnoxious calculations are for!) Therefore, the end of the steep portion (the intersection) is a better approximation of the equivalence point than is the middle of the steep section. The  $Cl^-$  end point is taken as the midpoint of the second steep section, at 47.41 mL. The moles of  $Cl^-$  in the sample equal the moles of  $Ag^+$  delivered between the first and second end points. That is, it requires 23.85 mL of  $Ag^+$  to precipitate  $I^-$ , and  $(47.41 - 23.85) = 23.56$  mL of  $Ag^+$  to precipitate  $Cl^-$ .

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## 26.8 End-Point Detection

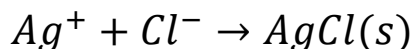
Precipitation titration end points are commonly found with electrodes (Figure 26-11) or indicators. We now describe two indicator methods for the titration of  $Cl^-$  with  $Ag^+$ :

**Volhard titration:** formation of a soluble, colored complex at the end point

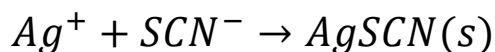
**Fajans titration:** adsorption of a colored indicator on the precipitate at the end point

### Volhard Titration

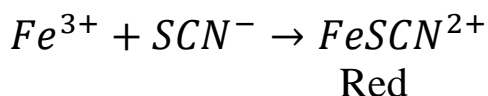
The Volhard titration is a titration of  $Ag^+$  in  $HNO_3$  solution. For  $Cl^-$ , a back titration is necessary. First,  $Cl^-$  is precipitated by a known, excess quantity of standard  $AgNO_3$ .



The  $AgCl$  is filtered and washed, and excess  $Ag^+$  in the combined filtrate is titrated with standard  $KSCN$  (potassium thiocyanate) in the presence of  $Fe^{3+}$ .



When all  $Ag^+$  has been consumed,  $SCN^-$  reacts with  $Fe^{3+}$  to form a red complex.



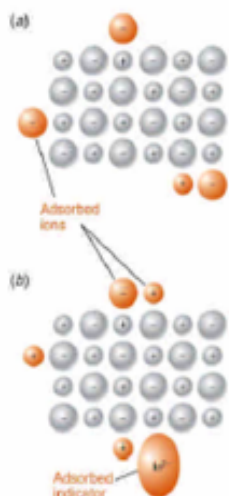
The appearance of red color is the end point. Knowing how much  $SCN^-$  was required for the back titration tells us how much  $Ag^+$  was left over from the reaction with  $Cl^-$ . The total amount of  $Ag^+$  is known, so the amount consumed by  $Cl^-$  can be calculated.

In the analysis of  $Cl^-$  by the Volhard method, the end point would slowly fade if the  $AgCl$  were not filtered off, because  $AgCl$  is more soluble than  $AgSCN$ . The  $AgCl$  slowly dissolves and is replaced by  $AgSCN$ . To eliminate this secondary reaction, we filter the  $AgCl$  and titrate only the  $Ag^+$  in the filtrate.  $Br^-$  and  $I^-$ , whose silver salts are less soluble than  $AgSCN$ , can be titrated by the Volhard method without isolating the silver halide precipitate.

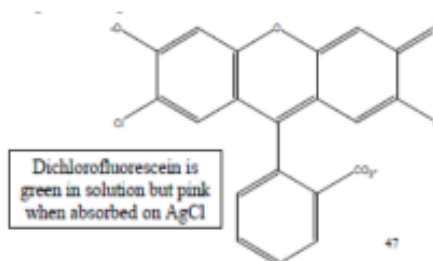
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## Fajans Titration

### 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



## Common Precipitation Titrations

**Table 7-1** Applications of precipitation titrations

| Species analyzed  | Notes   |
|---|---|
| <b>VOLHARD METHOD</b>   |   |
| $\text{Br}^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{CNO}^-$ , $\text{AsO}_4^{3-}$  | Precipitate removal is unnecessary.   |
| $\text{Cl}^-$ , $\text{PO}_4^{3-}$ , $\text{CN}^-$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{CO}_3^{2-}$ , $\text{S}^{2-}$ , $\text{CrO}_4^{2-}$ | Precipitate removal required.   |
| $\text{BH}_4^-$   | Back titration of $\text{Ag}^+$ left after reaction with $\text{BH}_4^-$ :<br>$\text{BH}_4^- + 8\text{Ag}^+ + 8\text{OH}^- \rightarrow 8\text{Ag}(s) + \text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O}$   |
| $\text{K}^+$  | $\text{K}^+$ is first precipitated with a known excess of $(\text{C}_6\text{H}_5)_4\text{B}^-$ . Remaining $(\text{C}_6\text{H}_5)_4\text{B}^-$ is precipitated with a known excess of $\text{Ag}^+$ . Unreacted $\text{Ag}^+$ is then titrated with $\text{SCN}^-$ . |
| <b>FAJANS METHOD</b>  |   |
| $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{Fe}(\text{CN})_6^{4-}$   | Titration with $\text{Ag}^+$ . Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromophenol blue.   |
| $\text{F}^-$  | Titration with $\text{Th}(\text{NO}_3)_4$ to produce $\text{ThF}_4$ . End point detected with alizarin red S.   |
| $\text{Zn}^{2+}$  | Titration with $\text{K}_3\text{Fe}(\text{CN})_6$ to produce $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ . End-point detection with diphenylamine.  |
| $\text{SO}_3^{2-}$  | Titration with $\text{Ba}(\text{OH})_2$ in 50 vol % aqueous methanol using alizarin red S as indicator.   |
| $\text{Hg}_2^{2+}$  | Titration with $\text{NaCl}$ to produce $\text{Hg}_2\text{Cl}_2$ . End point detected with bromophenol blue.  |
| $\text{PO}_4^{3-}$ , $\text{C}_2\text{O}_4^{2-}$  | Titration with $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ to give $\text{Pb}_3(\text{PO}_4)_2$ or $\text{PbC}_2\text{O}_4$ . End point detected with dibromofluorescein ( $\text{PO}_4^{3-}$ ) or fluorescein ( $\text{C}_2\text{O}_4^{2-}$ ).                             |

**Table 26-5**

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Applications of precipitation titrations are listed in Table 26-5. Whereas the Volhard method is an argentometric titration, the Fajans method has wider applications. Because the Volhard titration is carried out in acidic solution (typically 0.2 M  $\text{HNO}_3$ ), it avoids certain interferences that affect other titrations. Silver salts of  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ , and  $\text{AsO}_4^{3-}$  are soluble in acidic solution, so these anions do not interfere.