Chapter 12:

Gravimetric Methods of Analysis

- *Gravimetric methods:* The **quantitative methods** that are based on determining the **mass** of a **pure compound** to which the **analyte** is **chemically related**.
    - **Precipitation gravimetry**: The **analyte** is separated from a solution of the sample as a **precipitate** and is converted to a compound of known composition that can be weighed.
    - **Volatilization gravimetry**: The analyte is separated from other constituents of a sample by converting it to a gas of known chemical composition that can be weighed.
    - **Electrogravimetry**: The analyte is separated by deposition on an electrode by an electrical current.

12A Precipitation gravimetry

- The analyte is converted to a **sparingly soluble precipitate** that is then **filtered**, **washed free of impurities** and converted to a product of **known composition** by suitable **heat** treatment and **weighed**.

Ex. for determining the [Ca^{2+}] in water:

$$2NH_{3(aq)} + H_2C_2O_{4(aq)} \rightarrow 2NH^{+}_{4(aq)} + C_2O^{2-}_{4(aq)}$$

$$Ca^{2+} + C_2O^{2-}_{4(aq)} \rightarrow CaC_2O_{4(s)}$$

filtered, dried, ignited

$$CaC_2O_{4(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{(g)} + CO_{2(g)}$$

After cooling, the precipitate is weighed and the mass is determined.

12A-1 Properties of Precipitates and Precipitating Reagents

✓ A gravimetric **precipitating agent** should react **specifically** or at least **selectively** with the **analyte** and give **precipitates** that is:

1. Enough **particle size** for retaining on filter paper
2. High **purity** (free of contaminants)
3. **Low solubility** that no significant loss of the analyte occurs during filtration and washing
4. Unreactive with air **(stable)**
5. **Known stoichimetric composition** after it is dried or, if necessary, ignited

* **Specific** reagents: react only with a single chemical species.

Selective reagents: react with a limited number of species.

12A-2 Particle Size and Filterability of Precipitates

➢ Characteristics of Ion, colloid and particle

✓The particle size of solids formed by precipitation varies enormously. At one extreme are colloidal suspensions, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution and are difficult to filter.

✓ At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle spontaneously and are easily filtered.

Name	Diameter	Characteristics
Ion	~10^{-8} cm (A°)	Dissolved
Colloid	10^{-7}~10^{-4} cm (nm-μm)	Suspended
Crystalline	>10^{-4}cm (μm)	**Settled from solution (filterable)**

✓Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities.

Factors That Determine the Particle Size of Precipitates

- Precipitate formation has been studied for many years, but the mechanism of the process is still not fully understood. What is certain, however, is that the particle size of a precipitate is influenced by

  * precipitate solubility,
  * temperature,
  * reactant concentrations, and the
  * rate at which reactants are mixed.

The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called **relative supersaturation**, where

$$\mathrm{RSS} = \frac{Q - S}{S}$$

Von Weimarn equation, 1925

Q: the concentration of the solute at **any instant**
S: the concentration solute **at equilibrium**

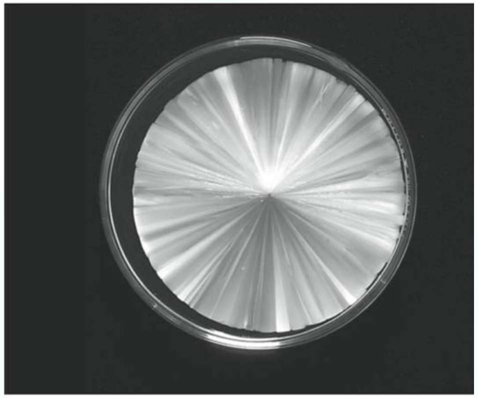
Relative supersaturation (RSS)

$$RSS = \frac{Q - S}{S}$$

- A **supersaturated solution is an** unstable solution that contains a higher solute concentration than a saturated solution. As excess solute precipitates with time, supersaturation decreases to zero.

-Generally, precipitation reactions are slow so that, even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely.

- Experimental evidence indicates that the particle size of a precipitate varies inversely with the average relative supersaturation during the time when the reagent is being introduced. Thus, when *(Q - S)/S is large, the precipitate* tends to be colloidal, and when *(Q - S)/S is small, a crystalline solid is* more likely.



Charlies D. Winters

RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	**Particle growth dominate**	**Larger Particle (Crystalline)**

Mechanism of Precipitate Formation

➢ **Nucleation and Particle growth**

- **Nucleation:** The initial formation process in which a minimum number of atoms, ions, or molecules join together to give a stable solid.
- Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles
- **Particle growth:** The subsequent growth after nucleation.

➢ If nucleation predominates, a precipitate containing a large number of small particles results, and

➢ if growth predominates, a smaller number of larger particles is produced.

RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	**Particle growth dominate**	**Larger Particle (Crystalline)**

Experimental Control of Particle Size

$$RSS = \frac{Q - S}{S}$$

(the lower RSS value the larger particles)

- **Increase S:**
  - ✓ Heating to increase solubility
  - ✓ pH adjustment (If the solubility of the precipitate depends on pH)
  - ✓ Adding complexing agent
- **Decrease Q:**
  - ✓ Using dilute precipitating solution
  - ✓ Adding precipitating agent slowly and stirring
  - ✓ Using homogeneous precipitation technique

12A-3 Colloidal Precipitates

- Individual colloidal particles are so small that they are not retained by ordinary filters. Moreover, Brownian motion prevents their settling out of solution under the influence of gravity.
- Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

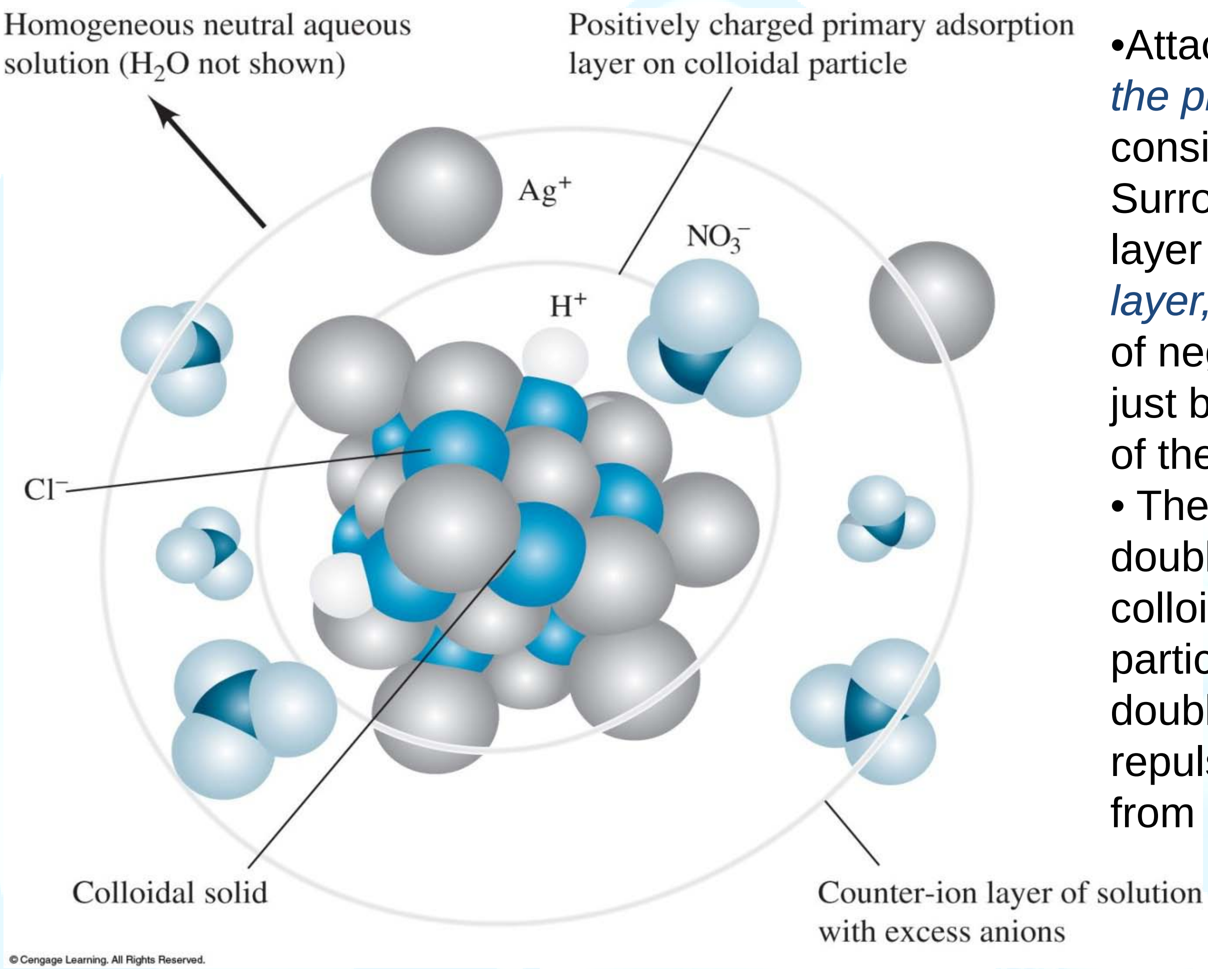
  (When liquid starts to thicken and become solid, it coagulates)

  (agglomeration: a large group of many different things collected or brought together)

Coagulation of Colloids

- Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium. To understand the effectiveness of these measures, we need to look into why colloidal suspensions are stable and do not coagulate spontaneously.
- Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged and thus repel one another. The charge results from cations or anions that are bound to the surface of the particles. We can show that ***colloidal particles are charged*** by placing them between charged plates where some of the particles migrate toward one electrode while others move toward the electrode of the opposite charge. The process by which ions are retained *on the surface of a solid is* known as **adsorption.**

– an *electric double layer*:



- Attached directly to the solid surface is *the primary adsorption layer,* which consists mainly of adsorbed silver ions. Surrounding the charged particle is a layer of solution, called *the counter-ion layer,* which contains sufficient excess of negative ions (principally nitrate) to just balance the charge on the surface of the particle.
- These layers constitute an electric double layer that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.

Figure 12.1 A colloidal silver chloride (AgCl) suspended in a solution of **excess $AgNO_3$**

Adsorption: A process in which a substance (gas, liquid, or solid) is held on the surface of a solid.
Absorption: A process in which a substance within the pores of a solid.

Figure 12-1 p284

The effective charge on two silver chloride particles

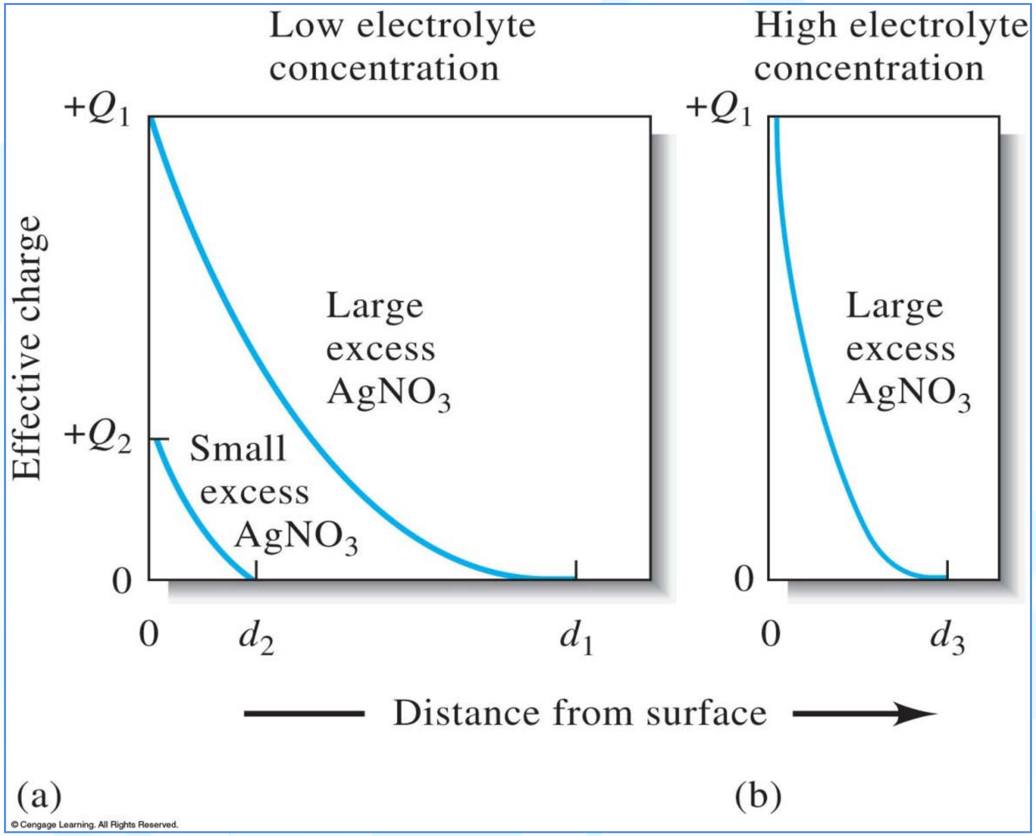


Figure 12-2 Effect of $AgNO_3$ and **electrolyte** concentration on the thickness of double layer surrounding a colloidal AgCl particle in a solution containing excess $AgNO_3$.

In Fig.12(a), The upper curve represents a particle in a solution that contains a reasonably large excess of silver nitrate, and the lower curve depicts a particle in a solution that has a much lower silver nitrate content.

> The effective charge can be thought as a measure of the repulsive force that the particle exerts on like particles in the solution.

Note that the effective charge falls off rapidly as the distance from the surface increases, and it approaches zero at the points *d1 or d2.*

➢ Coagulation of Colloids

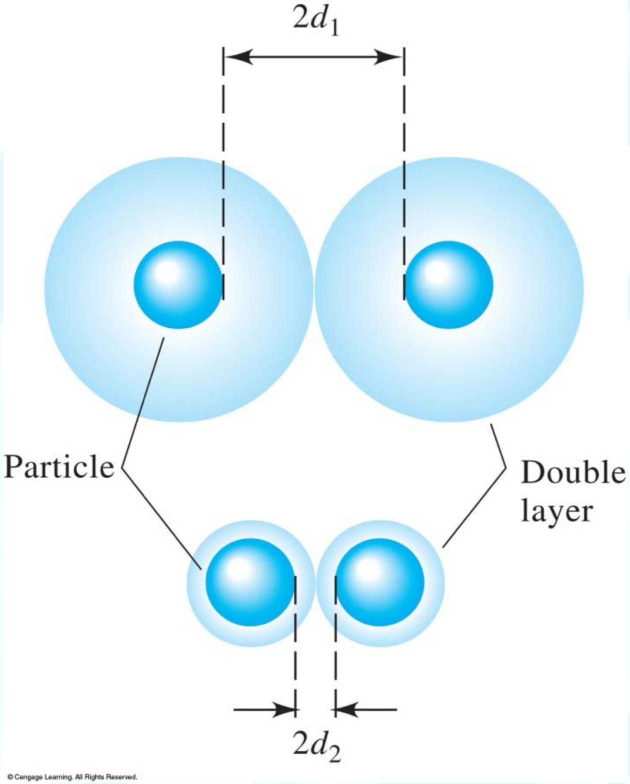
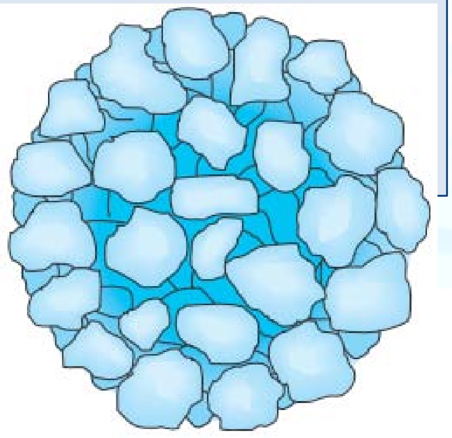


Figure 12-3 The electrical double layer of a colloid consists of a layer of charge adsorbed on the surface of the particle (the primary adsorption layer) and a layer of opposite charge (the counter-ion layer) in the solution surrounding the particle. Increasing the electrolyte concentration has the effect of decreasing the volume of the counter-ion layer, thereby increasing the chances for coagulation.

* The upper portion of Figure 12-3 depicts two silver chloride particles and their counter- ion layers as they approach each other in the concentrated silver nitrate just considered. Note that the effective charge on the particles prevents them from approaching one another more closely than about $2d_1$—*a distance that is too great for* coagulation to occur.

* As shown in the lower part of Figure 12-3, in the more dilute silver nitrate solution, the two particles can approach within $2d_2$ *of one another.* Ultimately, as the concentration of silver nitrate is further decreased, the distance between particles becomes small enough for the forces of agglomeration to take effect And a coagulated precipitate to appear.



A coagulated colloid

Coagulation of a colloidal suspension can often be brought about by a short period of *heating*, particularly if accompanied *by stirring*.

- Heating decreases the number of adsorbed ions and thus the thickness, *of the double layer. The particles may* also gain enough kinetic energy at the higher temperature to overcome the barrier to close approach imposed by the double layer.

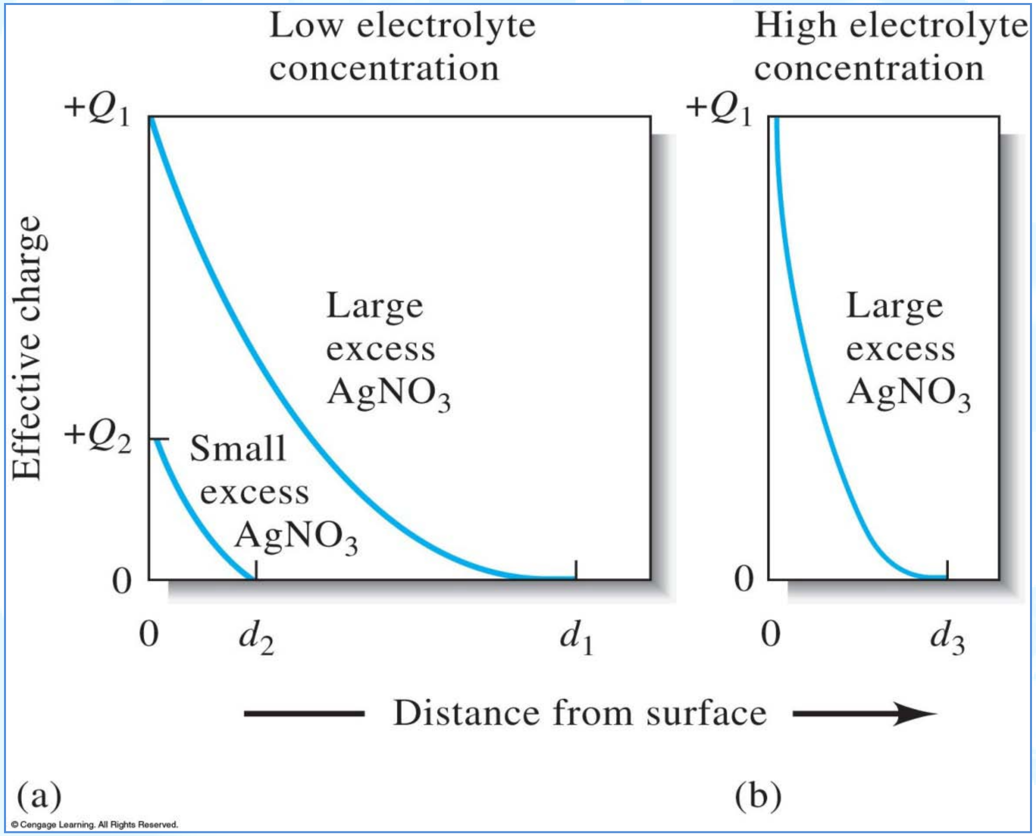


Figure 12-2 Effect of $AgNO_3$ and **electrolyte** concentration on the thickness of double layer surrounding a colloidal AgCl particle in a solution containing excess $AgNO_3$.

- *An even more effective way to coagulate a colloid is to increase the electrolyte concentration of the solution. If we add a suitable ionic compound to a colloidal suspension, the concentration of counter-ions increases in the vicinity of each particle. As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases. The net effect of adding an electrolyte is thus a shrinkage of the counter-ion layer, as shown in Figure 12-2b. The particles can then approach one another more closely and agglomerate.*

➢ *Peptization of Colloids*

Peptization: The process by which a coagulated colloid reverts to its original dispersed colloidal suspension state..

(When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is removed, therefore, the repulsive forces as well as the original colloidal state are reestablished.)

Solution: Use of Volatile electrolyte as washing solution, e.g., HNO_3, NH_4NO_3, to avoid peptization.

Practical Treatment of Colloidal Precipitates

Colloids are best precipitated from hot, stirred solutions containing sufficient electrolyte to ensure coagulation. The filterability of a coagulated colloid often improves if it is allowed to stand for an hour or more in contact with the hot solution from which it was formed. During this process, which is known as **digestion,** weakly bound water appears to be lost from the precipitate. The result is a denser mass that is easier to filter.

Digestion is a process in which a precipitate is heated in the solution from which it was formed (the mother liquor) and allowed to stand in contact with the solution. **Mother liquor** is the solution from which a precipitate was formed.

12A-4 Crystalline Precipitates

- Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids.
- Particle size of crystalline solids can often be improved significantly by
  - minimizing Q (by using dilute solutions, and adding the precipitating reagent slowly, with good mixing) or
  - maximizing S (precipitating from hot solution or by adjusting the pH), or both.
- Digestion improves the purity and filterability of both colloidal and crystalline precipitates.
- The improvement in filterability undoubtedly results from the dissolution and recrystallization that occur continuously and at an enhanced rate at elevated temperatures.
- Recrystallization apparently results in bridging between adjacent particles, a process that yields larger and more easily filtered crystalline aggregates. This view is supported by the observation that little improvement in filtering characteristics occurs if the mixture is stirred during digestion.

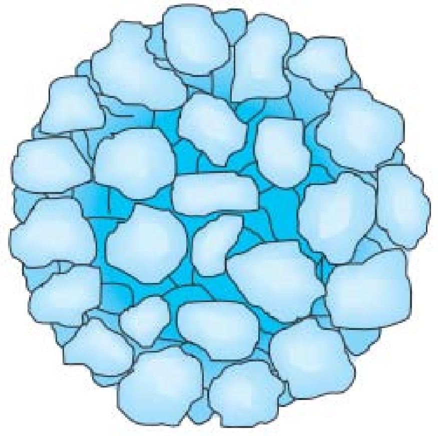
12A-5 Coprecipitation

Coprecipitation:

- ✓ A process in which normally soluble compounds are carried out of solution by a precipitate. It may resulted in **impurities** within the desired precipitates.
- ✓ Coprecipitated impurities may cause either negative or positive errors.
- ✓ There are four types of coprecipitation:
  - ✓surface adsorption,
  - ✓ mixed-crystal formation,
  - ✓occlusion, and
  - ✓mechanical entrapment.

Surface Adsorption:

- The impurity is chemically or physically adsorbed onto the surface of precipitates
- Adsorption is the major source of contamination in coagulated colloids but of no significance in crystalline precipitates.
    - *Minimizing Adsorbed Impurities on Colloids*
        - Washing a coagulated colloid with a solution containing a volatile electrolyte
        - Digestion: during this process, water is expelled from the solid to give a denser mass that has a smaller specific surface area for adsorption.
        - Reprecipitation: In this process, the filtered solid is redissolved and reprecipitated. The solution containing the redissolved precipitate has a significantly lower contaminant concentration than the original, and even less adsorption occurs during the second precipitation.

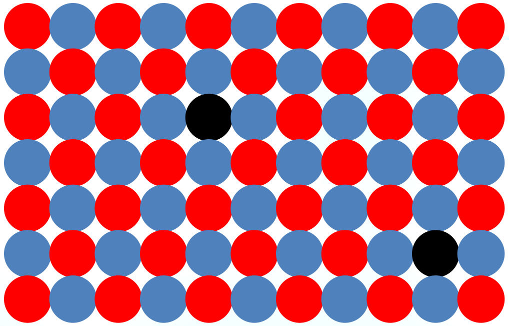


- **Mixed-Crystal Formation:**
  - A type of coprecipitation in which a contaminant ion replaces an ion in the lattice of a crystal.

    Ex. $SrSO_4$ in $BaSO_4$

    MgKPO4 in MgNH4PO4

    MnS in CdS
  - Mixed-crystal formation may occur in both colloidal and crystalline precipitates

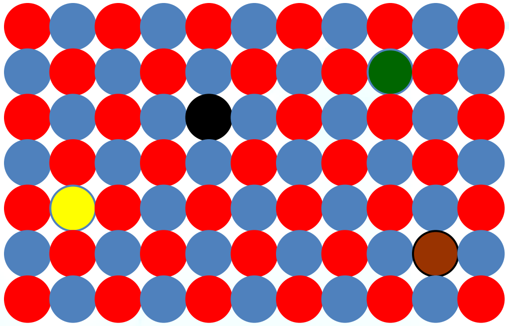


- Problem solving:
  - Change to another more selective precipitating agent
  - Reprecipitation

Occlusion:

- A type of co-precipitation in which *a compound (foreign ions in the counter-ion layer)* is physically trapped within a precipitate during rapid precipitate formation.
- Problem solving: Digestion

Digestion: The process which has a waiting time to achieve desired outcome.
(The **solubility–precipitation** is in a **dynamic equilibrium**, digestion ensures the occluded material is eventually exposed to the supernatant solution.)

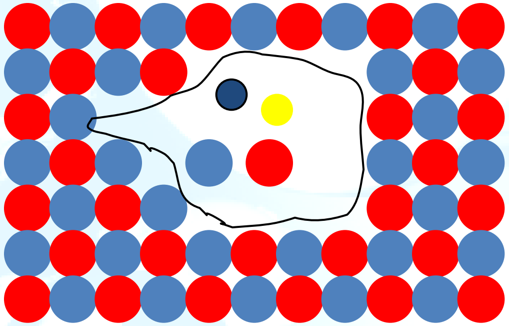


Mechanical Entrapment:

- A type of co-precipitation in which coprecipitated physically trap a *pocket of solution* within a precipitate during rapid precipitate formation.

- Problem solving: Digestion

Mixed-crystal formation may occur in both colloidal and crystalline precipitates, but occlusion and mechanical entrapment are confined to crystalline precipitates.



12A-6 Precipitation from Homogeneous Solution

➢**Homogeneous precipitation** is a process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

- Solids formed by homogeneous precipitation are generally purer and larger in size

Example 1: Urea, for generating OH^- as precipitant (Al(III), Fe(III))

$$CO(NH_2)_{2(aq)} + 3\,H_2O_{(l)} \leftrightarrows CO_{2(g)} + 2\,NH_4{}^+{}_{(aq)} + 2\,OH^-{}_{(aq)}$$

* Generation rate can be controlled by temperature

Example 2: For generating $SO_4{}^{2-}$ as precipitant

$$NH_2SO_3H_{(aq)} + 2H_2O_{(l)} \leftrightarrows NH_4{}^+{}_{(aq)} + H_3O^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

* Generation rate can be controlled by pH

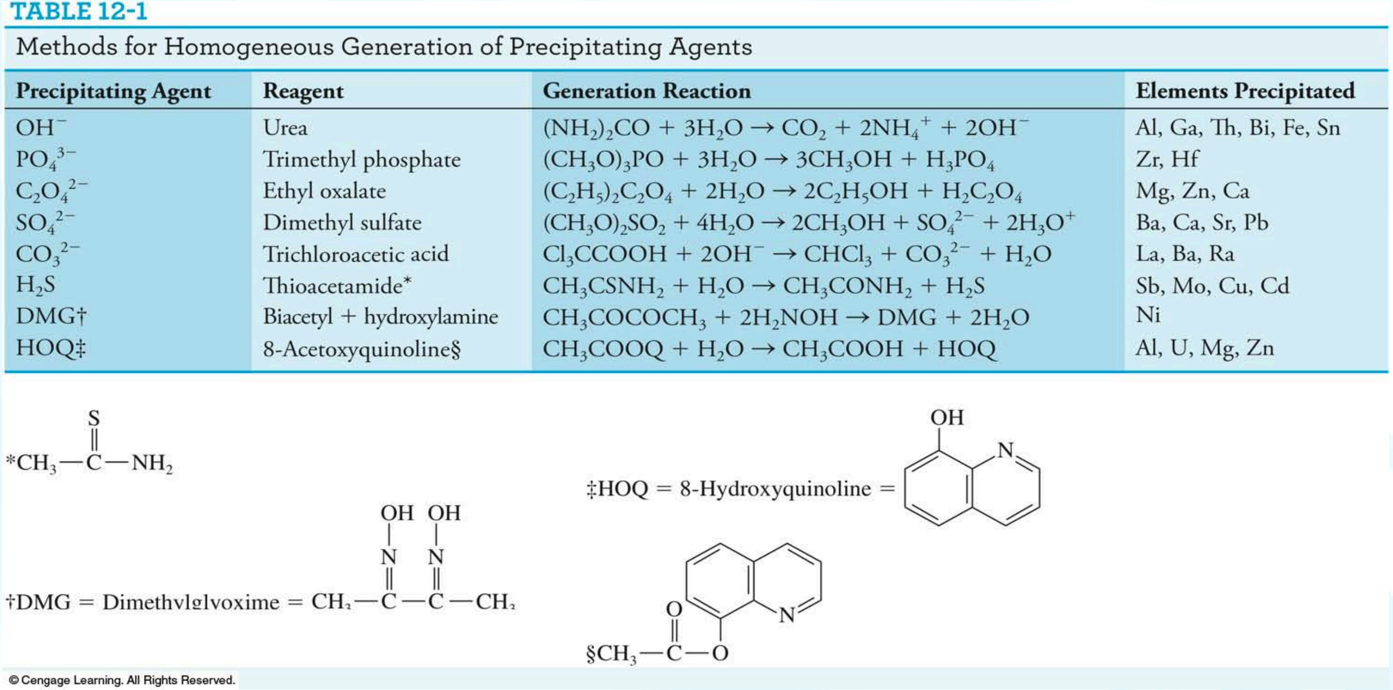


TABLE 12-1

Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4{}^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
$PO_4{}^{3-}$	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4{}^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
$SO_4{}^{2-}$	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4{}^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
$CO_3{}^{2-}$	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3{}^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

*$CH_3—\overset{\overset{\large S}{\|}}{C}—NH_2$

‡HOQ = 8-Hydroxyquinoline =

†DMG = Dimethylglyoxime = $CH_3—\overset{\overset{OH}{|}}{\overset{N}{\|}}{C}—\overset{\overset{OH}{|}}{\overset{N}{\|}}{C}—CH_3$

§$CH_3—\overset{\overset{O}{\|}}{C}—O$

12A-7 Drying and Ignition of Precipitates

- ✓ A gravimetric precipitate is heated until its mass becomes constant.
- ✓ Heating removes the solvent and any volatile species carried down with the ppt.
- ✓ Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the *weighing form.*

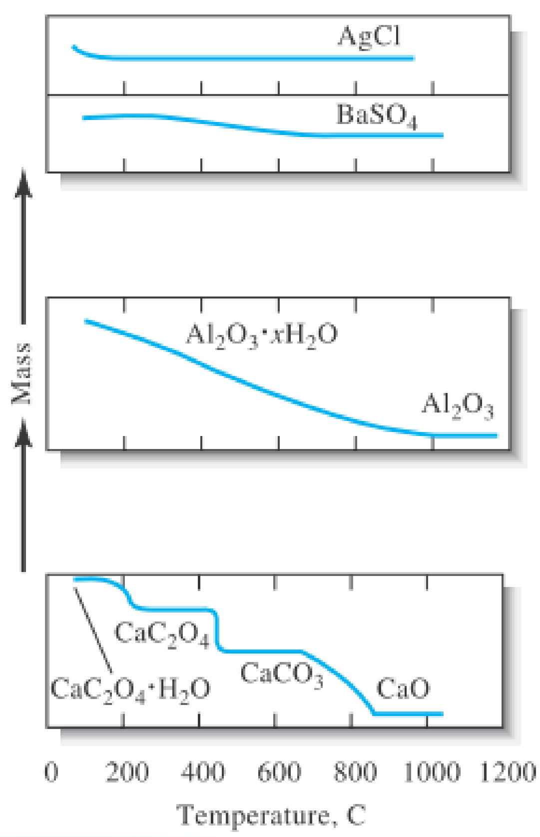


Figure 12-6 Effect of temperature on precipitate mass.

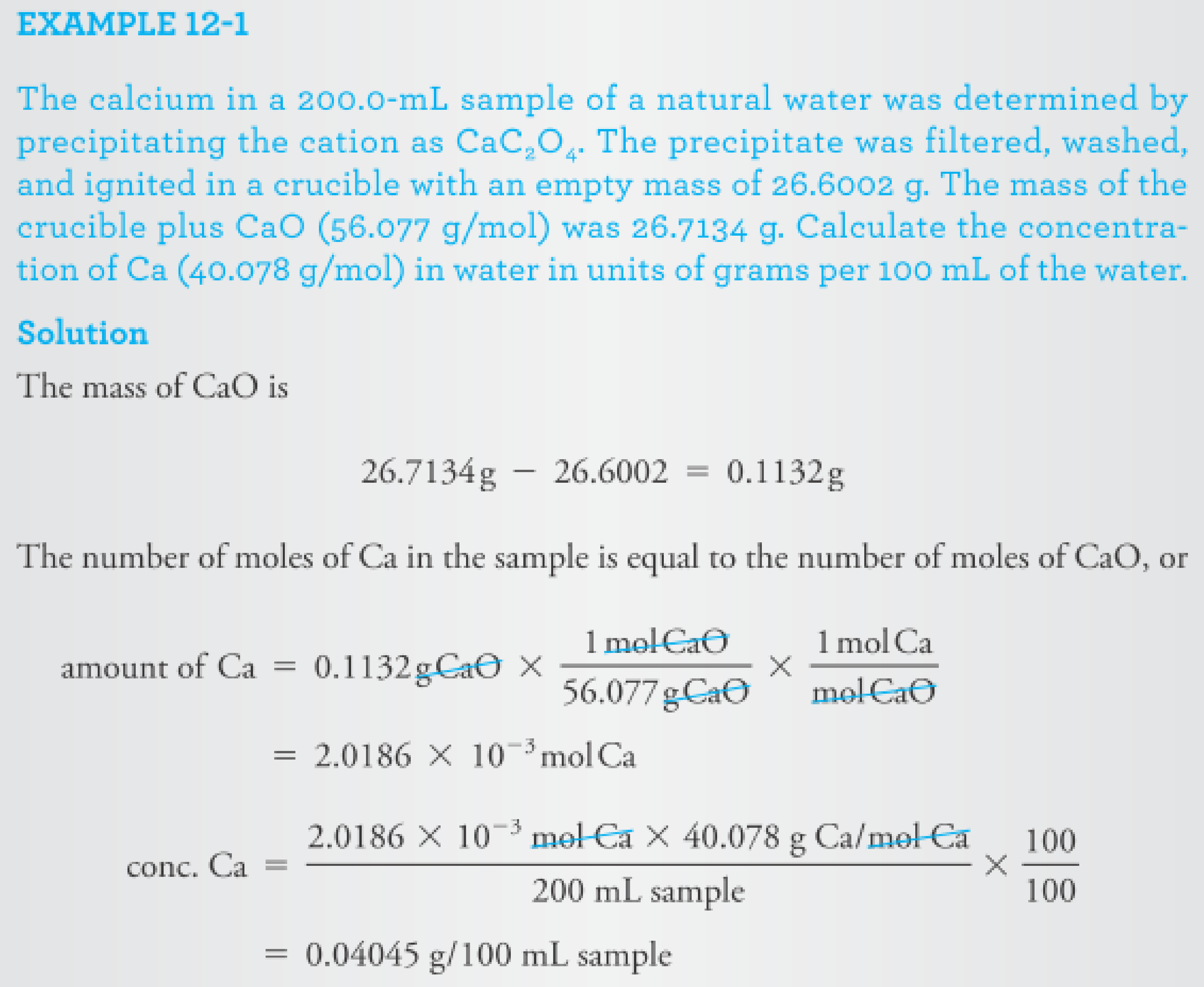
✓The temperature required to dehydrate a precipitate completely may be as low as 100°C or as high as 1000°C

✓ Moisture is completely removed from silver chloride at temperatures higher than 110°C, but dehydration of aluminum oxide is not complete until a temperature greater than 1000°C is achieved.

✓ The thermal curve for calcium oxalate is considerably more complex than the others

✓ Recording thermal decomposition curves is called **thermogravimetric analysis,** and the mass versus temperature curves are termed **thermograms.**

12B Calculation of results from gravimetric data



EXAMPLE 12-1

The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

Solution

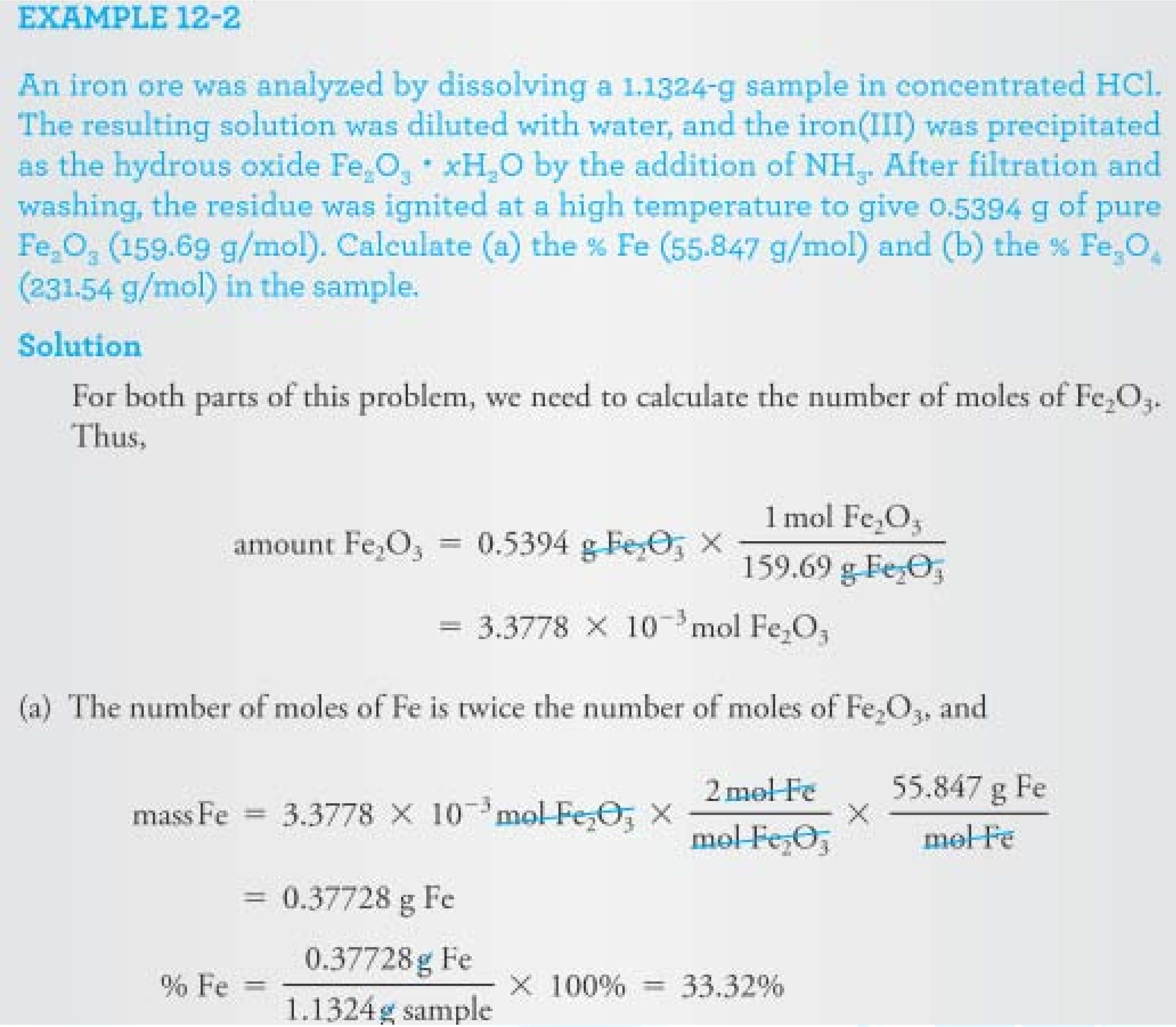
The mass of CaO is

$$26.7134\,\text{g} - 26.6002 = 0.1132\,\text{g}$$

The number of moles of Ca in the sample is equal to the number of moles of CaO, or

$$\begin{aligned}\text{amount of Ca} &= 0.1132\,\cancel{\text{g CaO}} \times \frac{1\,\cancel{\text{mol CaO}}}{56.077\,\cancel{\text{g CaO}}} \times \frac{1\,\text{mol Ca}}{\cancel{\text{mol CaO}}}\\ &= 2.0186 \times 10^{-3}\,\text{mol Ca}\end{aligned}$$

$$\begin{aligned}\text{conc. Ca} &= \frac{2.0186 \times 10^{-3}\,\cancel{\text{mol Ca}} \times 40.078\text{ g Ca}/\cancel{\text{mol Ca}}}{200\text{ mL sample}} \times \frac{100}{100}\\ &= 0.04045\text{ g}/100\text{ mL sample}\end{aligned}$$



EXAMPLE 12-2

An iron ore was analyzed by dissolving a 1.1324-g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

Solution

For both parts of this problem, we need to calculate the number of moles of Fe_2O_3. Thus,

$$\text{amount } Fe_2O_3 = 0.5394\ \cancel{\text{g } Fe_2O_3} \times \frac{1\text{ mol } Fe_2O_3}{159.69\ \cancel{\text{g } Fe_2O_3}}$$

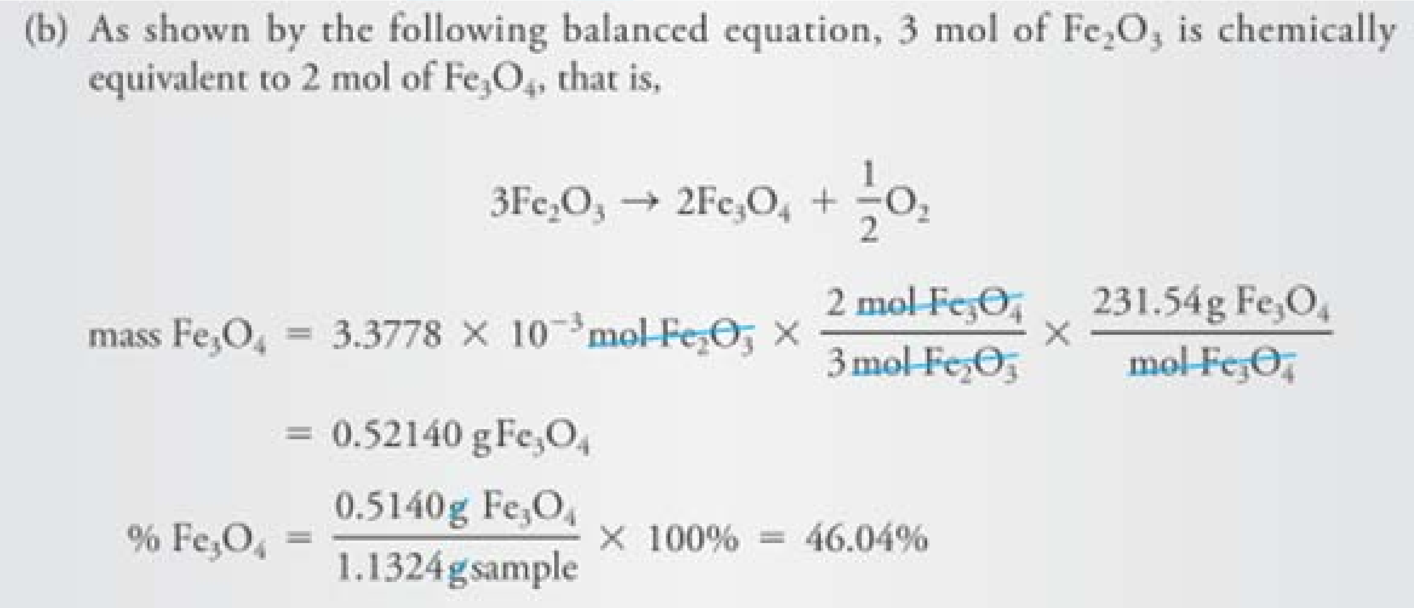
$$= 3.3778 \times 10^{-3}\text{ mol } Fe_2O_3$$

(a) The number of moles of Fe is twice the number of moles of Fe_2O_3, and

$$\text{mass Fe} = 3.3778 \times 10^{-3}\ \cancel{\text{mol } Fe_2O_3} \times \frac{2\ \cancel{\text{mol Fe}}}{\cancel{\text{mol } Fe_2O_3}} \times \frac{55.847\text{ g Fe}}{\cancel{\text{mol Fe}}}$$

$$= 0.37728\text{ g Fe}$$

$$\%\ \text{Fe} = \frac{0.37728\ \cancel{\text{g}}\text{ Fe}}{1.1324\ \cancel{\text{g}}\text{ sample}} \times 100\% = 33.32\%$$



(b) As shown by the following balanced equation, 3 mol of Fe_2O_3 is chemically equivalent to 2 mol of Fe_3O_4, that is,

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$$

$$\text{mass } Fe_3O_4 = 3.3778 \times 10^{-3}\,\cancel{\text{mol } Fe_2O_3} \times \frac{2\,\cancel{\text{mol } Fe_3O_4}}{3\,\cancel{\text{mol } Fe_2O_3}} \times \frac{231.54\,\text{g } Fe_3O_4}{\cancel{\text{mol } Fe_3O_4}}$$

$$= 0.52140\ \text{g}Fe_3O_4$$

$$\%\ Fe_3O_4 = \frac{0.5140\,\text{g } Fe_3O_4}{1.1324\,\text{g}\,\text{sample}} \times 100\% = 46.04\%$$

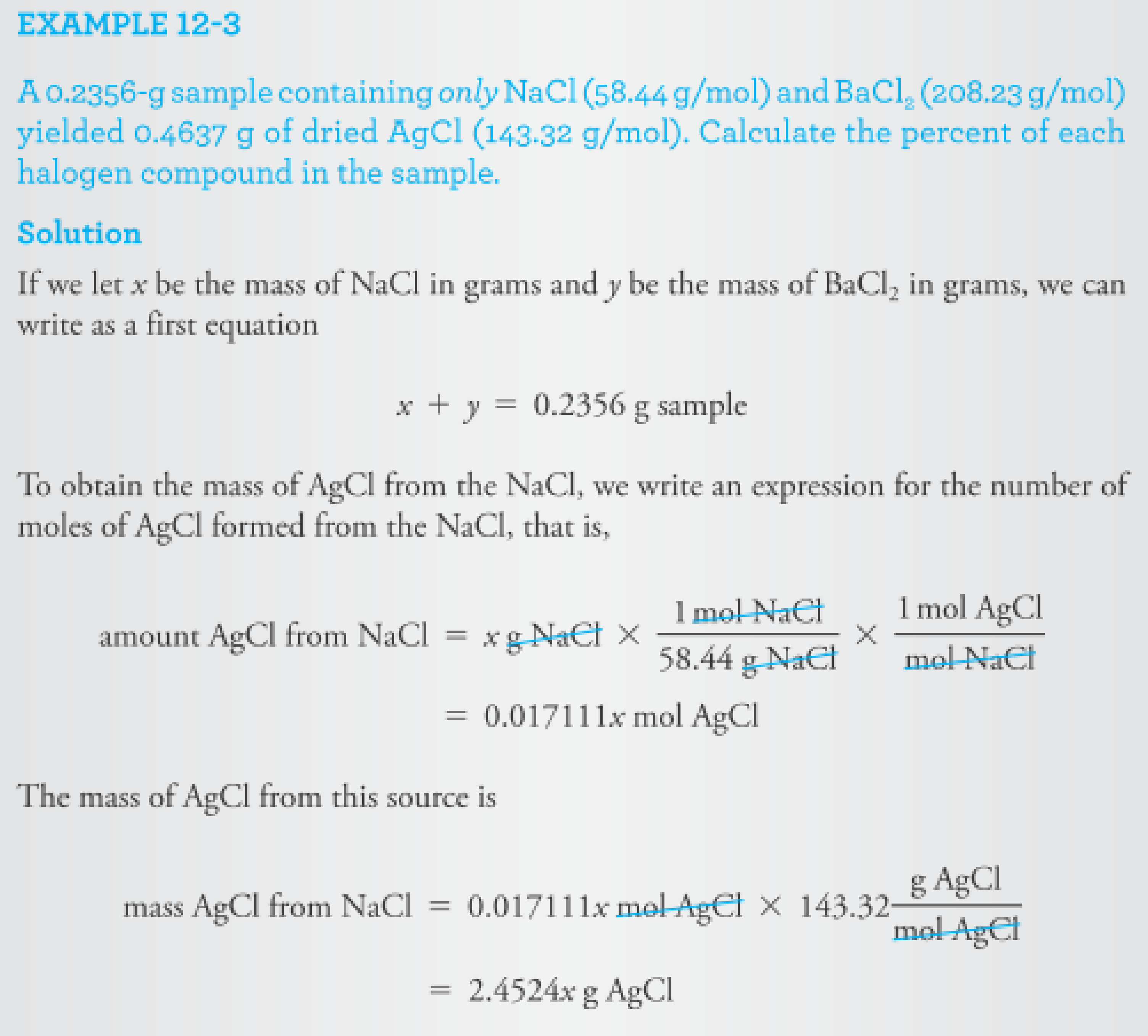
- ***Gravimetric factor:*** A gravimetric factor is an algebraic expression that converts grams of a compound into grams of a single element. It is the ratio of the formula weight (FW) of the substance being sought to that of the substance weighed.

Example 1. **Fe** is sought, Fe_2O_3 is weighed:

$$\text{gravimetric factor} = \frac{1\,\cancel{\text{mol } Fe_2O_3}}{159.69\text{ g } Fe_2O_3} \times \frac{2\,\cancel{\text{mol Fe}}}{\cancel{\text{mol } Fe_2O_3}} \times \frac{55.847\text{ g Fe}}{\cancel{\text{mol Fe}}} = 0.69944\,\frac{\text{g Fe}}{\text{g } Fe_2O_3}$$

Example 2. $\mathbf{Fe_3O_4}$ is sought, Fe_2O_3 is weighed:

$$\text{gravimetric factor} = \frac{1\,\cancel{\text{mol } Fe_2O_3}}{159.69\text{ g } Fe_2O_3} \times \frac{2\,\cancel{\text{mol } Fe_3O_4}}{3\,\cancel{\text{mol } Fe_2O_3}} \times \frac{231.54\text{ g } Fe_3O_4}{\cancel{\text{mol } Fe_3O_4}} = 0.96662\,\frac{\text{g } Fe_3O_4}{\text{g } Fe_2O_3}$$



EXAMPLE 12-3

A 0.2356-g sample containing *only* NaCl (58.44 g/mol) and $BaCl_2$ (208.23 g/mol) yielded 0.4637 g of dried AgCl (143.32 g/mol). Calculate the percent of each halogen compound in the sample.

Solution

If we let x be the mass of NaCl in grams and y be the mass of $BaCl_2$ in grams, we can write as a first equation

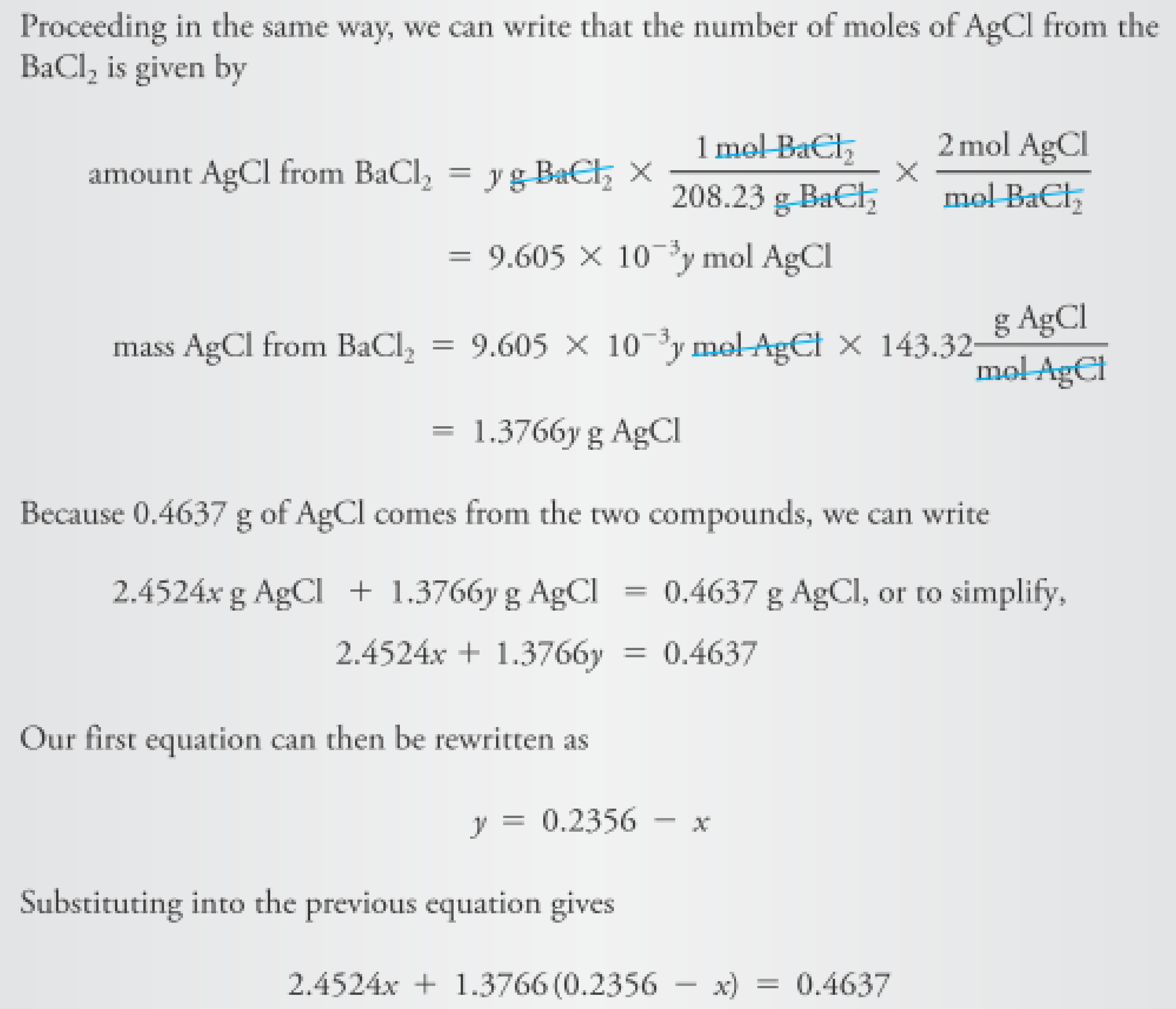
$$x + y = 0.2356 \text{ g sample}$$

To obtain the mass of AgCl from the NaCl, we write an expression for the number of moles of AgCl formed from the NaCl, that is,

$$\begin{aligned}\text{amount AgCl from NaCl} &= x\,\cancel{\text{g NaCl}} \times \frac{1\,\cancel{\text{mol NaCl}}}{58.44\,\cancel{\text{g NaCl}}} \times \frac{1 \text{ mol AgCl}}{\cancel{\text{mol NaCl}}}\\ &= 0.017111x \text{ mol AgCl}\end{aligned}$$

The mass of AgCl from this source is

$$\begin{aligned}\text{mass AgCl from NaCl} &= 0.017111x\,\cancel{\text{mol AgCl}} \times 143.32\frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}}\\ &= 2.4524x \text{ g AgCl}\end{aligned}$$



Proceeding in the same way, we can write that the number of moles of AgCl from the $BaCl_2$ is given by

$$\text{amount AgCl from BaCl}_2 = y\ \cancel{\text{g BaCl}_2} \times \frac{1\ \cancel{\text{mol BaCl}_2}}{208.23\ \cancel{\text{g BaCl}_2}} \times \frac{2\ \text{mol AgCl}}{\cancel{\text{mol BaCl}_2}}$$

$$= 9.605 \times 10^{-3} y \text{ mol AgCl}$$

$$\text{mass AgCl from BaCl}_2 = 9.605 \times 10^{-3} y\ \cancel{\text{mol AgCl}} \times 143.32 \frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}}$$

$$= 1.3766 y \text{ g AgCl}$$

Because 0.4637 g of AgCl comes from the two compounds, we can write

$$2.4524x \text{ g AgCl} + 1.3766y \text{ g AgCl} = 0.4637 \text{ g AgCl, or to simplify,}$$

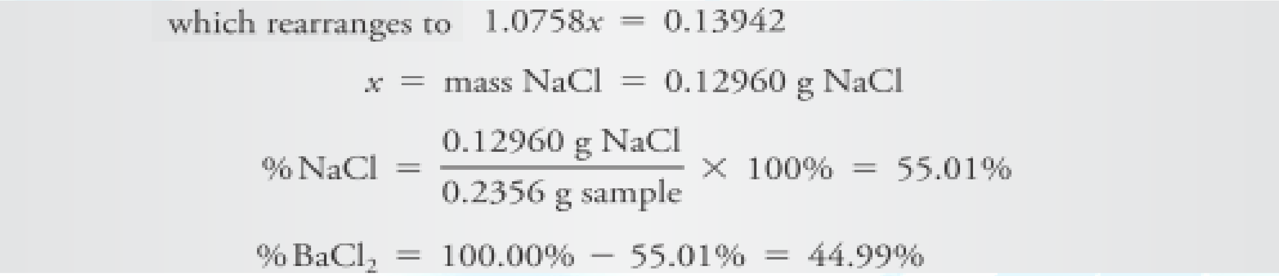
$$2.4524x + 1.3766y = 0.4637$$

Our first equation can then be rewritten as

$$y = 0.2356 - x$$

Substituting into the previous equation gives

$$2.4524x + 1.3766(0.2356 - x) = 0.4637$$



which rearranges to $1.0758x = 0.13942$

$$x = \text{mass NaCl} = 0.12960 \text{ g NaCl}$$

$$\%\text{NaCl} = \frac{0.12960 \text{ g NaCl}}{0.2356 \text{ g sample}} \times 100\% = 55.01\%$$

$$\%\text{BaCl}_2 = 100.00\% - 55.01\% = 44.99\%$$

12C Applications of gravimetric methods

12C -1 Inorganic Precipitating Agents

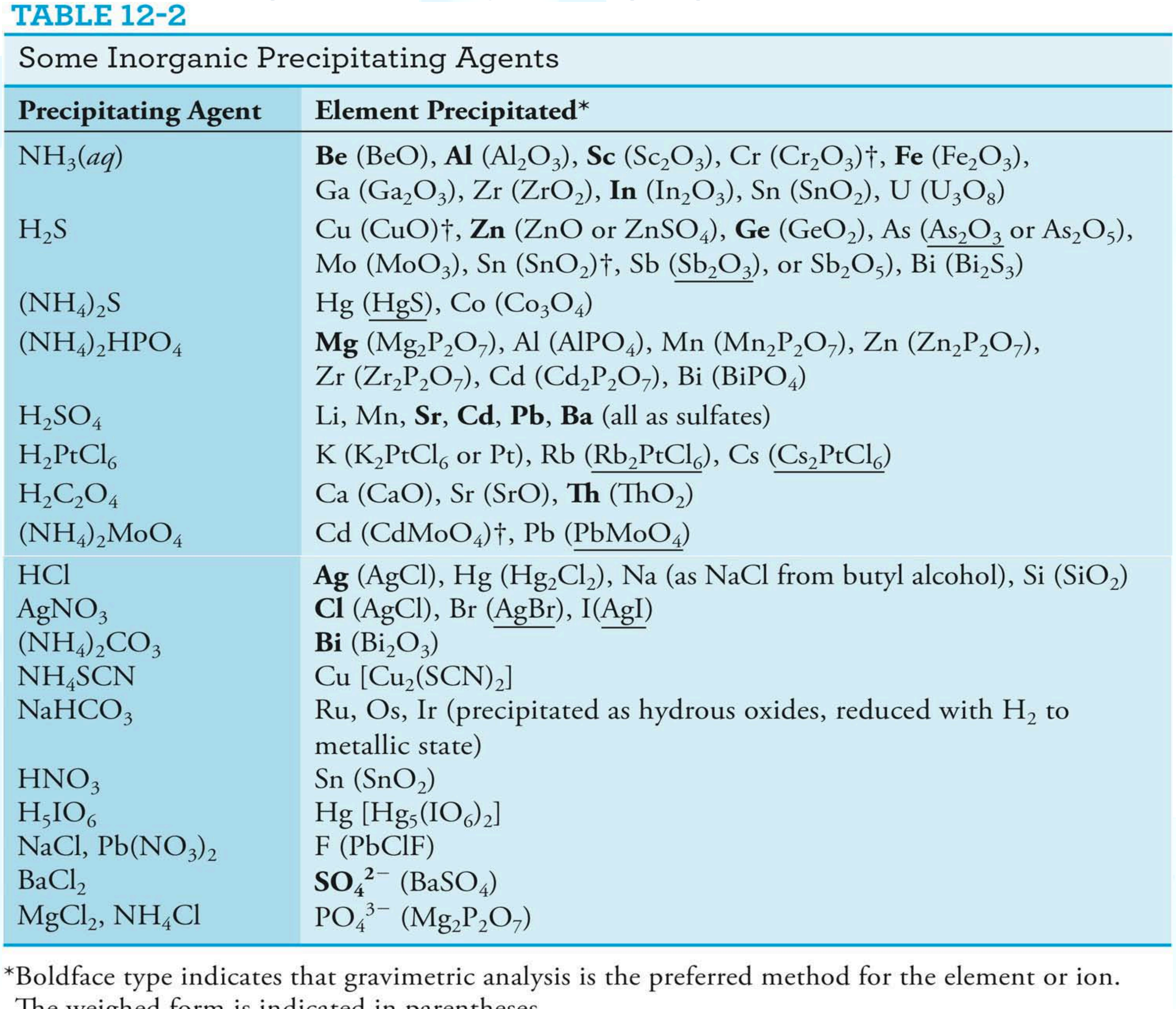


TABLE 12-2

Some Inorganic Precipitating Agents

Precipitating Agent	**Element Precipitated***
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), Cr (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO or $ZnSO_4$), **Ge** (GeO_2), As ($\underline{As_2O_3}$ or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb ($\underline{Sb_2O_3}$), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg ($\underline{HgS}$), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr**, **Cd**, **Pb**, **Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 or Pt), Rb ($\underline{Rb_2PtCl_6}$), Cs ($\underline{Cs_2PtCl_6}$)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($\underline{PbMoO_4}$)
HCl	**Ag** ($AgCl$), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** ($AgCl$), Br ($\underline{AgBr}$), I($\underline{AgI}$)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
$NaCl$, $Pb(NO_3)_2$	F ($PbClF$)
$BaCl_2$	$\mathbf{SO_4^{2-}}$ ($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-} ($Mg_2P_2O_7$)

*Boldface type indicates that gravimetric analysis is the preferred method for the element or ion. The weighed form is indicated in parentheses.

* These reagents typically form slightly soluble salts or hydrous oxides with the analyte. As you can see from the many entries for each reagent, few inorganic reagents are selective.

12C-2 Reducing Agents

(convert an analyte to its elemental form form for weighing)

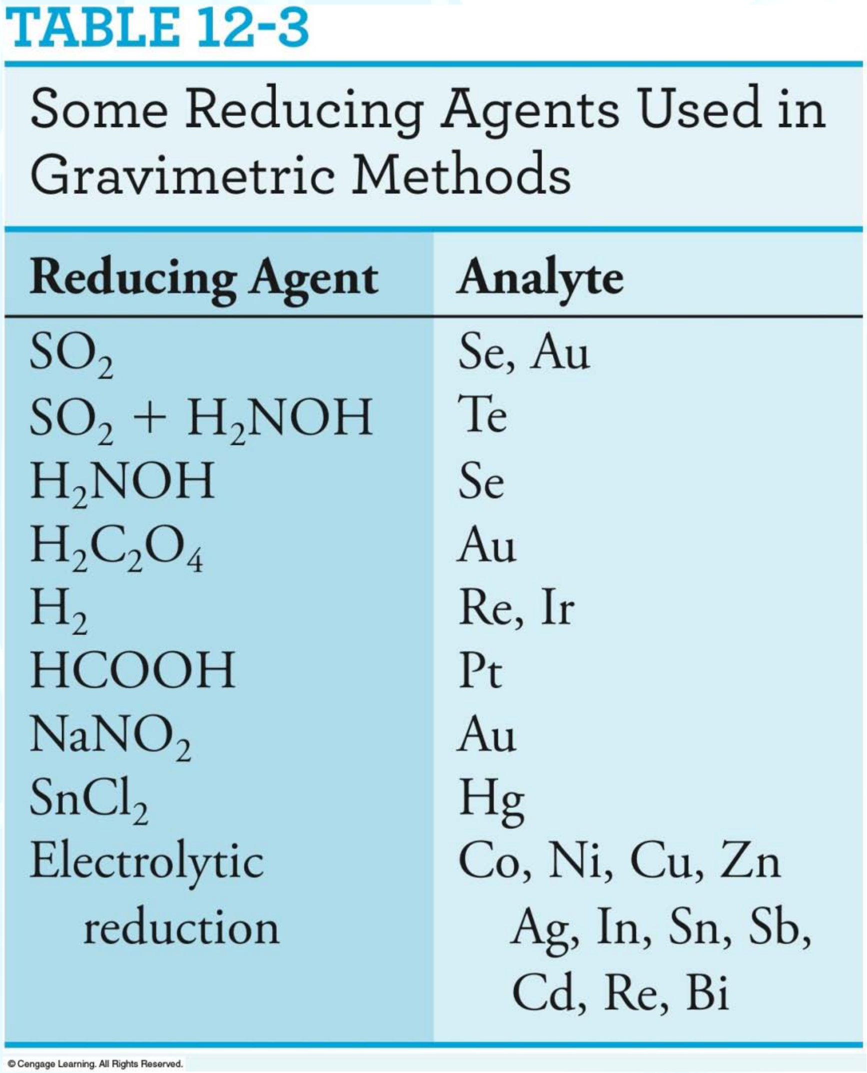


TABLE 12-3

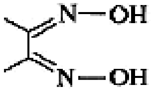
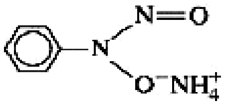
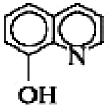
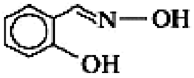
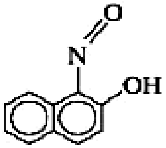
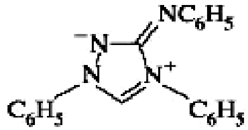
Some Reducing Agents Used in Gravimetric Methods

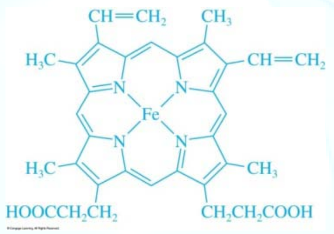
Reducing Agent	Analyte
SO_2	Se, Au
$SO_2 + H_2NOH$	Te
H_2NOH	Se
$H_2C_2O_4$	Au
H_2	Re, Ir
HCOOH	Pt
$NaNO_2$	Au
$SnCl_2$	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

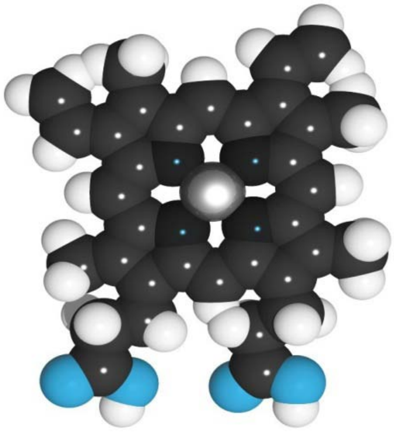
12C-3 Organic Precipitating Agents

- ✓Some organic reagents react with metal ions then produce insoluble coordination cmpds.
- ✓ Reagents that form coordination compounds of this type are called **chelating agents**, and their products are called **chelates**.
- ✓ Those metal chelates are relatively nonpolar and have **low solubilities in water**.
- ✓ Usually, these compounds possess low densities and are often intensely colored. Because they are not wetted by water, coordination compounds are easily freed of moisture at low temperatures.

Common organic precipitating agents

Name	**Structure**	**Ions precipitated**
Dimethylglyoxime		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine)		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
Salicylaldoxime		Cu^{2+}, Pb^{2+}, Bi^{3+}, Zn^{2+}, Ni^{2+}, Pd^{2+}
1-Nitroso-2-naphthol		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ions
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-





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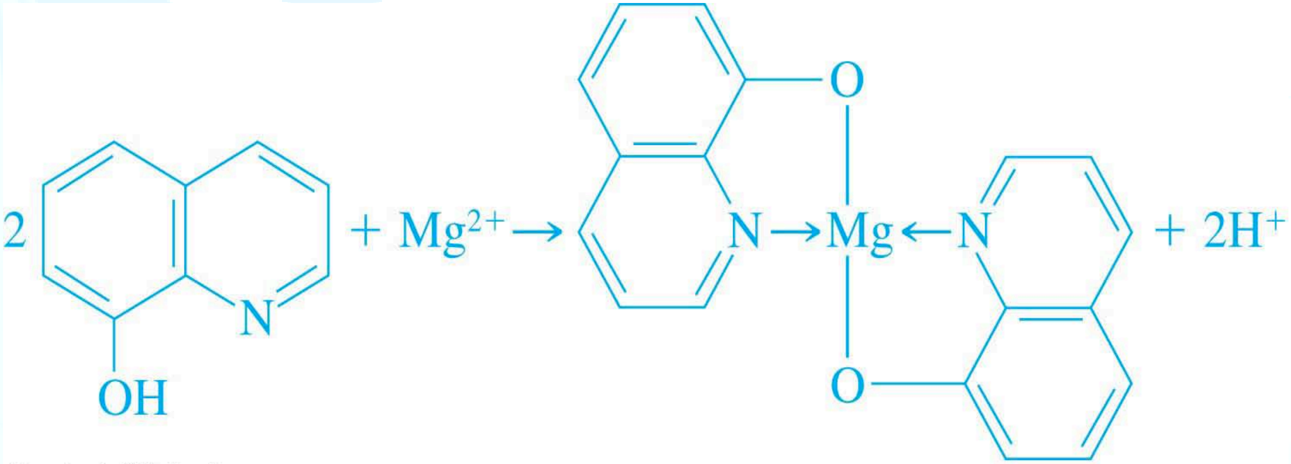
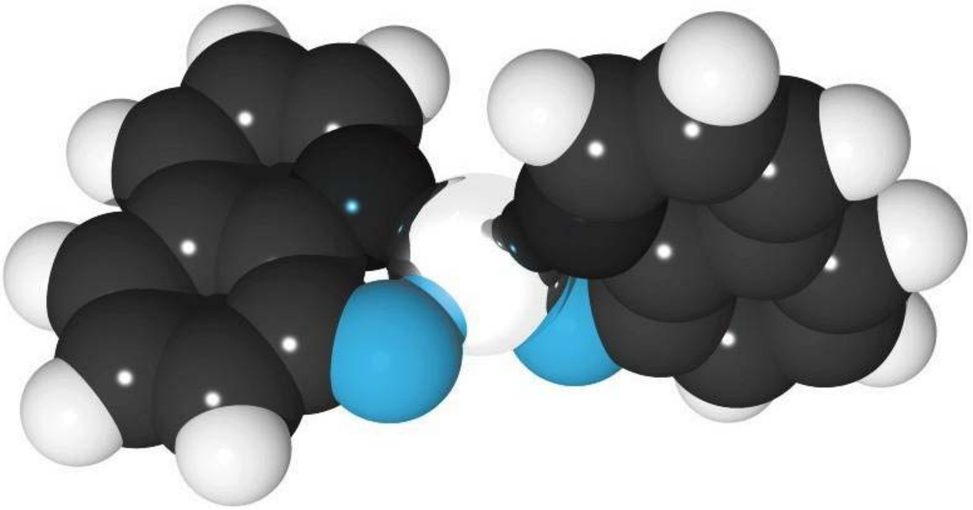
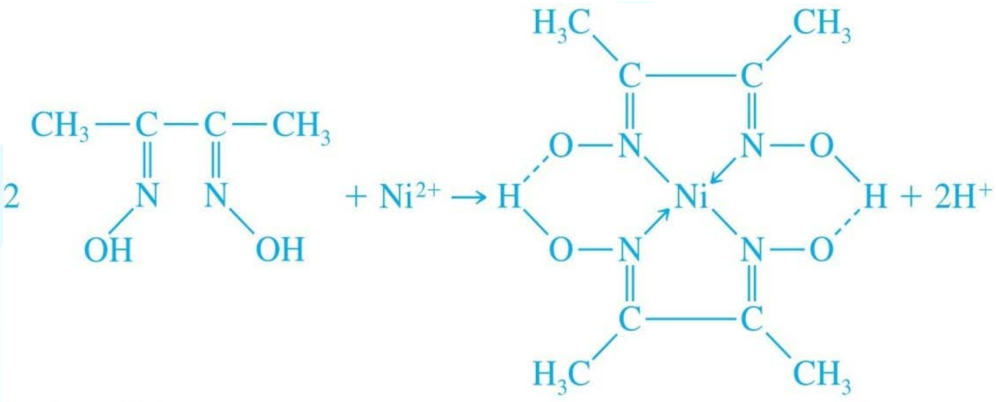
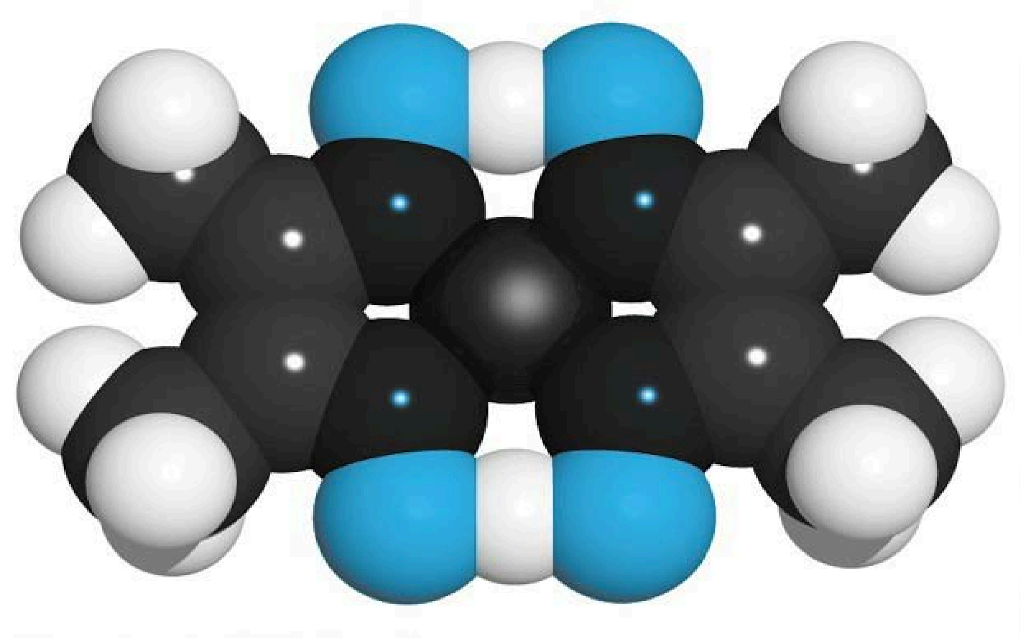
Magnesium complex with 8-hydroxyquinoline.

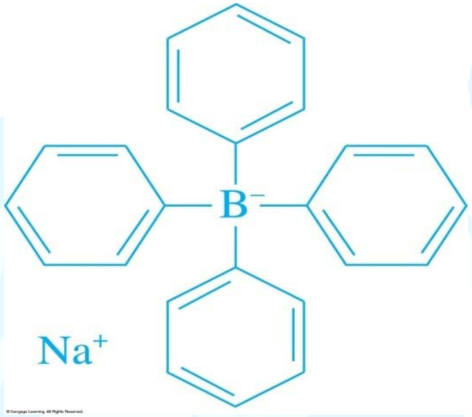




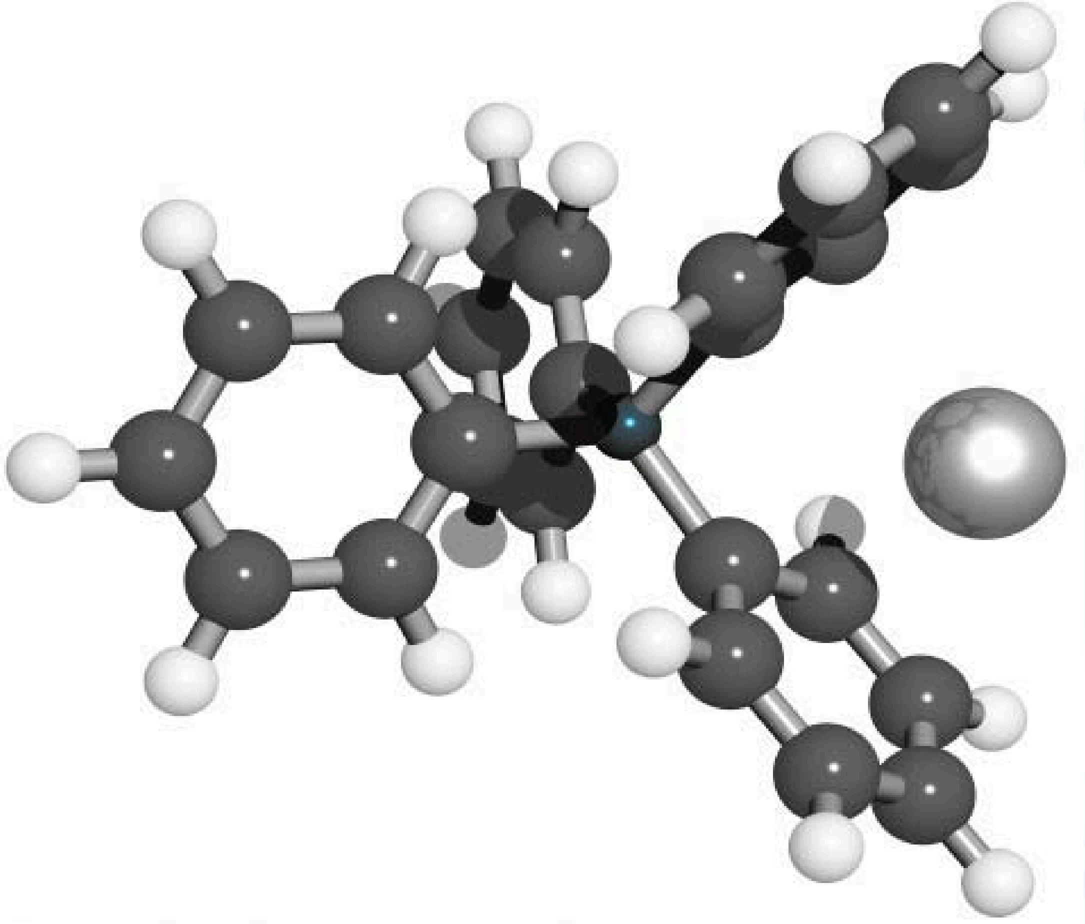


Nickel dimethylglyoxime is spectacular in appearance. As shown in color plate 7, it has a beautiful vivid red color.





sodium tetraphenylborate.



12C-4 Organic Functional Group Analysis

- Several reagents react selectively with certain organic functional groups and thus can be used for the determination of most compounds containing these groups.
- Many of the reactions shown can also be used for volumetric and spectrophotometric

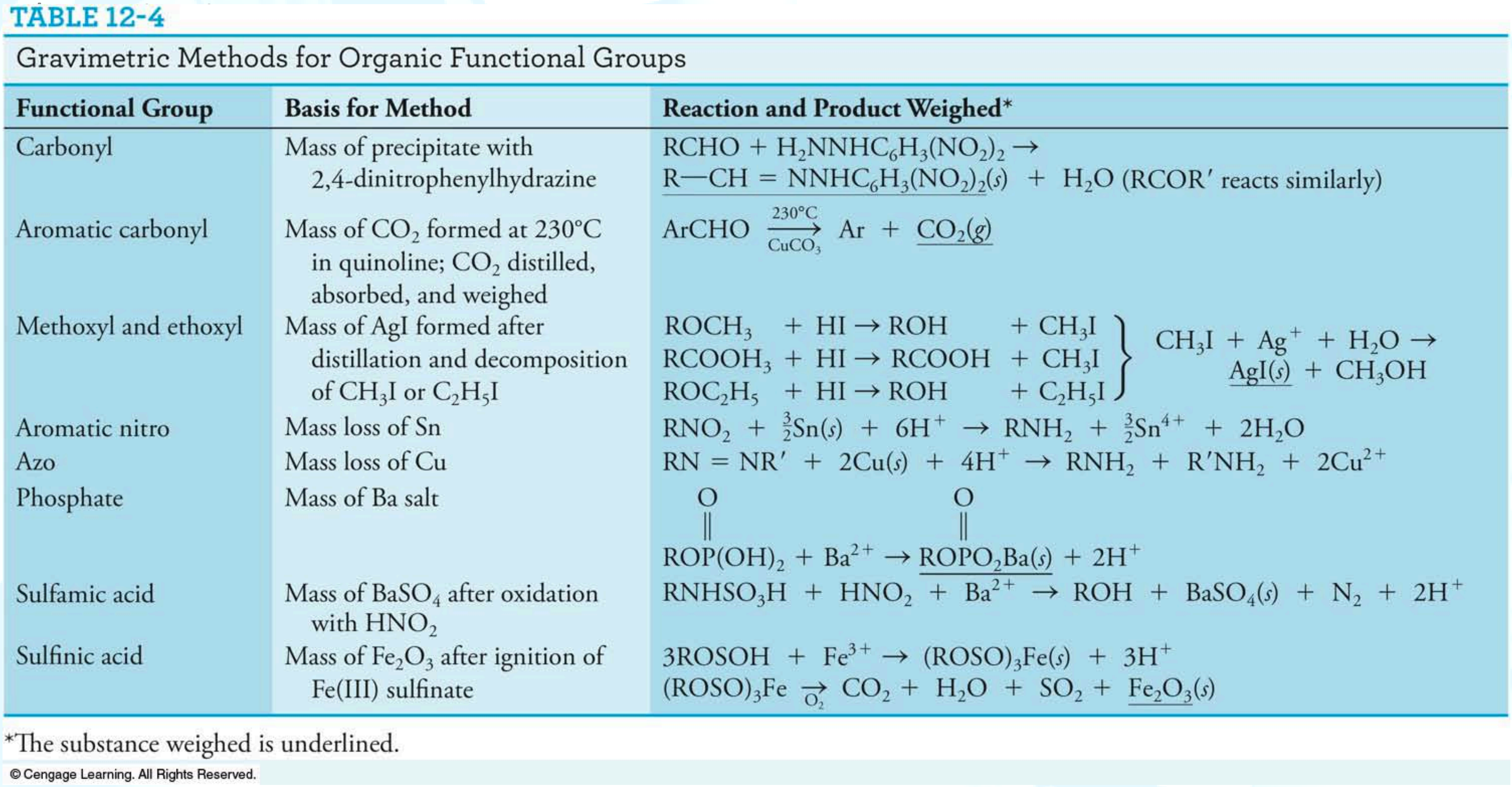


TABLE 12-4

Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow$ $\underline{R{-}CH = NNHC_6H_3(NO_2)_2(s)} + H_2O$ (RCOR′ reacts similarly)
Aromatic carbonyl	Mass of CO_2 formed at 230°C in quinoline; CO_2 distilled, absorbed, and weighed	$ArCHO \xrightarrow[CuCO_3]{230°C} Ar + \underline{CO_2(g)}$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH_3I or C_2H_5I	$\left.\begin{array}{l} ROCH_3 + HI \rightarrow ROH + CH_3I \\ RCOOH_3 + HI \rightarrow RCOOH + CH_3I \\ ROC_2H_5 + HI \rightarrow ROH + C_2H_5I \end{array}\right\} \begin{array}{l} CH_3I + Ag^+ + H_2O \rightarrow \\ \underline{AgI(s)} + CH_3OH \end{array}$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \frac{3}{2}Sn(s) + 6H^+ \rightarrow RNH_2 + \frac{3}{2}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN = NR' + 2Cu(s) + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$RO\overset{O}{\overset{\Vert}{P}}(OH)_2 + Ba^{2+} \rightarrow \underline{RO\overset{O}{\overset{\Vert}{P}}O_2Ba(s)} + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with HNO_2	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow ROH + \underline{BaSO_4(s)} + N_2 + 2H^+$
Sulfinic acid	Mass of Fe_2O_3 after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$ $(ROSO)_3Fe \xrightarrow[O_2]{} CO_2 + H_2O + SO_2 + \underline{Fe_2O_3(s)}$

*The substance weighed is underlined.

12C-5 Volatilization Gravimetry

- ✓ The two most common: determining water and carbon dioxide.

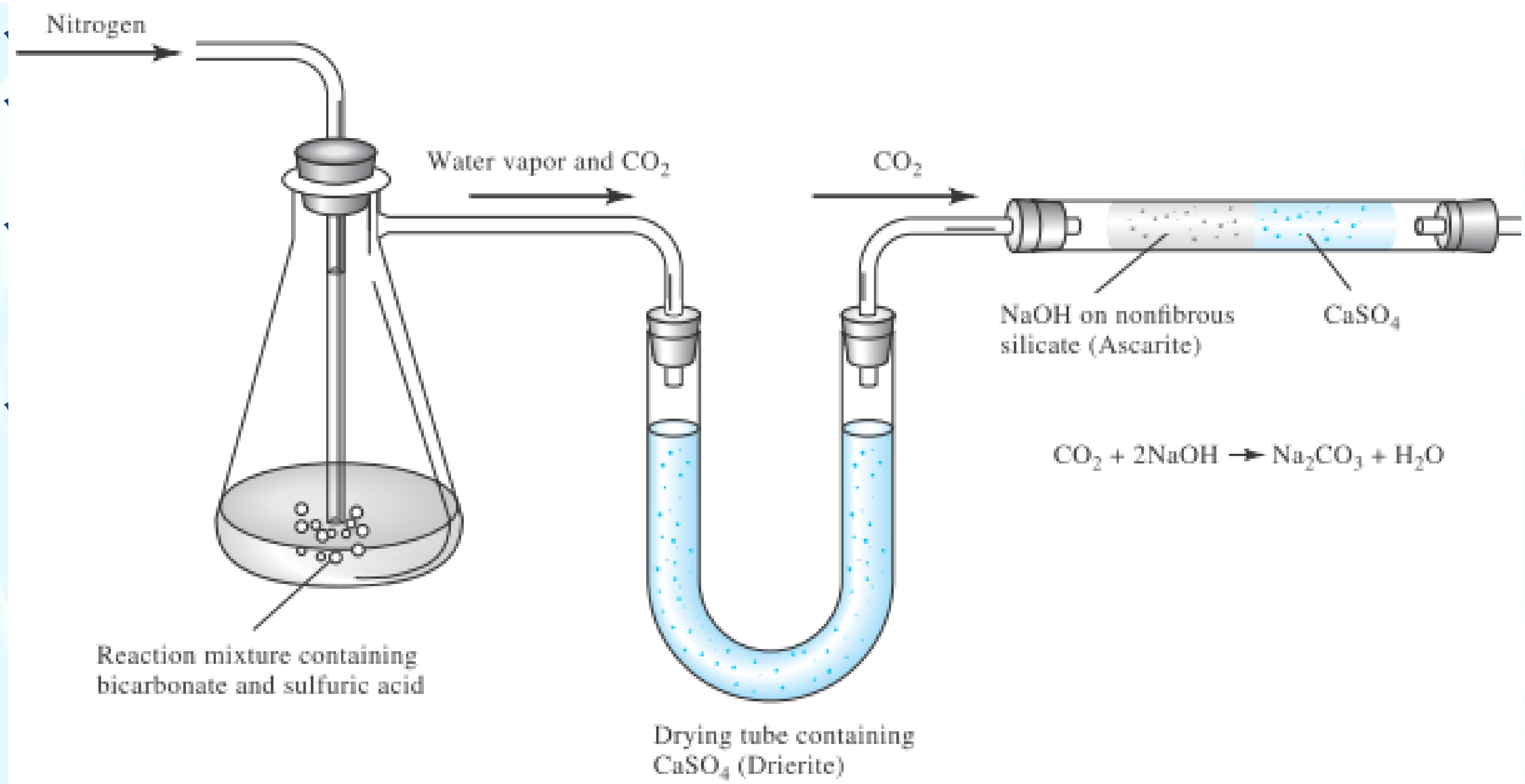


Figure 12-8 Apparatus for determining the sodium hydrogen carbonate content of antacid tablets by a gravimetric volatilization procedure.

$$NaHCO_3(aq) + H_2SO_4(aq) \rightarrow CO_2(g) + H_2O(l) + NaHSO_4(aq$$

12C-5 Volatilization Gravimetry

- Sulfides and sulfites can also be determined by volatilization. Hydrogen sulfide or sulfur dioxide evolved from the sample after treatment with acid is collected in a suitable absorbent.
- Finally, the classical method for the determination of carbon and hydrogen in organic compounds is a gravimetric volatilization procedure in which the combustion products (H_2O and CO_2) are collected selectively on weighed absorbents.
- The increase in mass serves as the analytical variable.

Homework (Due 06/03/2018)

Chapter 12, Questions and Problems

12-1, 12-2, 12-4, 12-5, 12-7, 12-9-(a,c,e), 12-10, 12-12, 12-18, 12-20

12-22, 12-25, 12-29, 12-30, 12-33

End of Chapter 12