

### EXAMPLE 12-1

The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as  $\text{CaC}_2\text{O}_4$ . 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

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

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

### 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  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  by the addition of  $\text{NH}_3$ . After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure  $\text{Fe}_2\text{O}_3$  (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the %  $\text{Fe}_3\text{O}_4$  (231.54 g/mol) in the sample.

#### Solution

For both parts of this problem, we need to calculate the number of moles of  $\text{Fe}_2\text{O}_3$ . Thus,

$$\begin{aligned} \text{amount Fe}_2\text{O}_3 &= 0.5394 \text{ g Fe}_2\text{O}_3 \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.69 \text{ g Fe}_2\text{O}_3} \\ &= 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3 \end{aligned}$$

(a) The number of moles of Fe is twice the number of moles of  $\text{Fe}_2\text{O}_3$ , and

$$\begin{aligned} \text{mass Fe} &= 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}}{\text{mol Fe}_2\text{O}_3} \times \frac{55.847 \text{ g Fe}}{\text{mol Fe}} \\ &= 0.37728 \text{ g Fe} \\ \% \text{ Fe} &= \frac{0.37728 \text{ g Fe}}{1.1324 \text{ g sample}} \times 100\% = 33.32\% \end{aligned}$$

(b) As shown by the following balanced equation, 3 mol of  $\text{Fe}_2\text{O}_3$  is chemically equivalent to 2 mol of  $\text{Fe}_3\text{O}_4$ , that is,



$$\begin{aligned} \text{mass Fe}_3\text{O}_4 &= 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}_3\text{O}_4}{3 \text{ mol Fe}_2\text{O}_3} \times \frac{231.54 \text{ g Fe}_3\text{O}_4}{\text{mol Fe}_3\text{O}_4} \\ &= 0.52140 \text{ g Fe}_3\text{O}_4 \\ \% \text{ Fe}_3\text{O}_4 &= \frac{0.52140 \text{ g Fe}_3\text{O}_4}{1.1324 \text{ g sample}} \times 100\% = 46.04\% \end{aligned}$$

### EXAMPLE 12-3

A 0.2356-g sample containing *only* NaCl (58.44 g/mol) and BaCl<sub>2</sub> (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<sub>2</sub> 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,

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

The mass of AgCl from this source is

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

Proceeding in the same way, we can write that the number of moles of AgCl from the BaCl<sub>2</sub> is given by

$$\begin{aligned}\text{amount AgCl from BaCl}_2 &= y \text{ g BaCl}_2 \times \frac{1 \text{ mol BaCl}_2}{208.23 \text{ g BaCl}_2} \times \frac{2 \text{ mol AgCl}}{\text{mol BaCl}_2} \\ &= 9.605 \times 10^{-3} y \text{ mol AgCl}\end{aligned}$$

$$\begin{aligned}\text{mass AgCl from BaCl}_2 &= 9.605 \times 10^{-3} y \text{ mol AgCl} \times 143.32 \frac{\text{g AgCl}}{\text{mol AgCl}} \\ &= 1.3766y \text{ g AgCl}\end{aligned}$$

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

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

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  $1.0758x = 0.13942$

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

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

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

### Properties of precipitating reagent

- 1- The analyte should selectively react with the Precipitating agent
- 2- Which should preferably have high molecular mass because this will increase the sensitivity of the method
- 3- Lower the conc. Limit of the analyte that can be determined
- 4- The resulting precipitate should have minimum solubility so as de

### **Properties of good precipitate:**

- 1- Easily filtrate and washed free of contamination**
- 2- Low solubility that no significant loss of the analyte accrues during filtration and washing**
- 3- Un reactive with constituents of the atmosphere**
- 4- Of known chemical composition after it is dried or if necessary , ignited.**

### **Factors that determine the particle size of ppts:**

#### **1- Colloidal suspension:**

Colloidal ppts are very diffecalt to filter and are susceptible to peptization aprocess through which filtered ppt will return to the colloidal state whene washed with water whose tiny particals are invisible to the naked ege( $10^{-7}$  -  $10^{-4}$ )cm in diameter.

#### **2- Crystalline suspension:**

A crystalline suspension is composed of particles having large diameters about a tenth of a millimeter or greater. The effect of gravity on these large particles is considerably higher than that of colloidal particles. Hence, the particles of the crystalline suspensions tend to settle down spontaneously and are easily filtered. These precipitates are easily purified. The particle size of a precipitate is influenced by precipitate solubility, temperature, reactant concentration and the rate in which the reactants are mixed.

## **Formation of nuclei versus groughth of crystals**

### **Precipitation**

This required addition of a precipitation agent solution to the sample solution upon addition of the first drops of the precipitating agent, supersaturating occurs, then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleus. At this point addition of extra precipitating agent will either form new nuclei or will build upon existing nuclei to give a precipitate.

This can be predicated by VonWeimarn ratio where , according to this relation the particles size is inversely proportional to a quantity called the relative supersaturation where:

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

Q= is the conc. Of reactants before pptn

S= is the solubility of precipitate in the medium from which it is being precipitated

Therefore, in order to get particle growth instead of further nucleation we need to make the relative supersaturation ratio as small as possible.

The optimum conditions for ppt. which make the supersaturation low are:

- a- Pptn using dilute solutions to decrease Q
- b- Slow addition of ppting agent to keep Q as low as possible.
- c- Stirring the solution during addition of ppting agent to avoid conc. Sites and keep Q low
- d- Increase solubility by pptn from hot solution
- e- Adjust the pH in order to increase S but not too much increase as we do not want to lose ppt by dissolution
- f- Usually add a little excess of the ppting agent for quantitative pptn and check for completeness of the pptn

-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.

### **Colloidal precipitation**

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.