Lecture 4 - Gravimetric Analysis

1. Precipitation Methods – dissolved analyte converted to sparingly soluble precipitate.

   a. readily filtered
   b. low solubility
   c. converted to product of known composition (heat)

Ex. Excess of oxalic acid ($H_2C_2O_4^{2-}$) added carefully to measured volume of Ca^{2+}.

(1) In basic sol'n:

$$Ca^{2+}{}_{(aq)} + C_2O_4{}_{(aq)} \rightarrow CaC_2O_4{}_{(s)}$$

(2) $CaC_2O_4(s)$ is collected in a filtering crucible then dried

(3) CaC_2O_4 ignited to produce calcium oxide:

$$CaC_2O_4{}_{(s)} \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2{}_{(g)}$$

(4) CaO(s) cooled, weighed

(5) Original concentration of Ca^{2+} computed

2. Volatilization Methods

a. Analyte is volatilized at suitable temperature
b. Volatile product is collected and weighed

3. Precipitates – Particle Size & Filterability

a. Colloids – (d = 10^{-7} to 10^{-4} cm)
-invisible to naked eye
-not easily filtered, don't settle out of solution

b. Particles – (0.10 mm or greater)
-spontaneously settle out of solution
-readily filtered and washed free of impurities
-more desirable

*Size of particles influenced by relative supersaturation of the solutions in which is formed:

$$\text{Relative Supersaturation} = \frac{Q - S}{S}$$

Where Q = concentration of solute, S = solute's equilibrium constant

-Precipitate solubility
-Temperature
-Reactant concentration
-Rate of reactant mixing

If $\frac{Q-S}{S}$ is large = small particles (colloids)

If $\frac{Q-S}{S}$ is small = crystalline solid likely

c. Crystalline Formation

(1) Raising temperature (increases S)
(2) Using dilute solutions (minimizes Q)
(3) Slow addition of precipitating agent w/stirring (minimizes Q)

4. Mechanism of Precipitate Formation

a. Nucleation – formation of a stable solid due to # of atoms, ions or molecules join together, e.g. formation on surface of suspended contaminants (dust particles).
b. Particle Growth – growth on existing nuclei

$\frac{Q-S}{S}$ high – rate of nucleation increases

$\frac{Q-S}{S}$ low – particle growth dominates, excluding nucleation

*Nucleation dominates – results in a large # of very fine particles

*Particle growth dominates – small # of larger particles

5. <u>Gravimetric Calculations</u>

$$\% \text{ Analyte} = \frac{W_{analyte}}{W_{sample}} \text{x } 100$$

$$CaCl_2 + 2AgNO_3 \rightarrow 2AgCl_{2(s)} + Ca(NO_3)_2$$

$$\text{wt } CaCl_2 = \text{wt AgCl x } \left(\frac{\text{FW } CaCl_2}{\text{FW AgCl}} \text{ x } \frac{1 \text{ mol } CaCl_2}{2 \text{ mol AgCl}}\right)$$

Gravimetric Factor (F)

F – Relates mass of product to mass of analyte, stoichiometry

$$F = \frac{a(\text{FW of substance A})}{b(\text{FW of substance B})}$$

where a and b are the coefficients of A and B, respectively

Ex. <u>Calculate the % Phosphorus in a 0.3516 g detergent sample. Final yield is 0.2161 g $Mg_2P_2O_4$</u>

$$\%\text{Analyte} = \frac{\text{Mass Analyte}}{\text{Mass Sample}} \text{x } 100$$

a. Mass P =

$$0.2161\text{ g } Mg_2P_2O_4 \text{ x } \frac{1\text{ mol } Mg_2P_2O_4}{222.57\text{ g } Mg_2P_2O_4} \text{x} \frac{2\text{ mol P}}{1\text{ mol } Mg_2P_2O_4} \text{x} \frac{30.97\text{g P}}{1\text{ mol P}}$$

Mass product Gravimetric Factor

$$= 0.0614 \text{ g P}$$

$$\%\text{ P} = \frac{0.0614\text{g P}}{0.3516\text{g sample}} = 17.10\ \%$$

or…

$$F = \frac{a}{b} \text{ x } \frac{\text{FW analyte}}{\text{FW sample}}$$

$$F = \frac{2}{1} \text{ x } \frac{30.97\text{g}}{222.57\text{g}} = 0.27833$$

$$\%P = \frac{(0.2161\text{g } Mg_2P_2O_7)(0.27833)}{0.3516\text{g}} \text{x}100 = 17.10\%$$

<u>Ex:</u> A 10.00 mL solution containing Cl^- was treated with excess $AgNO^3$ to precipitate 0.4368 g of AgCl. What was the molarity of Cl- in the unknown?

Formula mass of AgCl = 143.321. A precipitate weighing 0.4368 g contains:

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

*Note: 1 mol of AgCl contains 1 mol of Cl^-

$$[Cl\text{-}] = \frac{3.048 \text{ x } 10\text{-}3 \text{ mol AgCl}}{0.0100L} = 0.3048 \text{ M}$$

*** IN CLASS PROBLEMS TO FOLLOW!**

Ex1:Phosphate is precipitated from its solution with ammonium molybdate, as $(NH_4)_3[PMo_{12}O_{40}\bullet xH_20]$. Since the precipitate does not have a constant composition with regard to water content, it is dissolved in ammonia and the molybdate is precipitated with $Pb(NO_3)_2$, as $PbMoO_4$.

a) What is the value of the gravimetric factor for the calculation of %P?

b) If the final precipitate weighs 0.100 g, what is the weight of P in the initial sample?

Ex2: A 0.2025 g sample consisting of only $BaCl_2$ and KCl required 20.25 mL of 0.1200 M $AgNO_3$ solution for the quantitative precipitation of chloride. Calculate the %Ba and %K in the sample.

Ex3: A 0.4994 g sample of a hydrate of $CuSO_4 \bullet xH_2O$, is heated to a constant weight of 0.3184 g (total loss of water). Calculate the value of x.

Ex4: In the gravimetric determination of sulfate in a 0.2841 g sample of pure Na_2SO_4, a $BaSO_4$ precipitate weighing 0.4604 g was obtained. The weight of the precipitate was smaller than the theoretical one, since some $BaSO_4$ was converted to BaS during the heating process.

a) Calculate the per cent of BaS in the precipitate (**Hint**: best to solve algebraically).

b) The per cent error of the analysis (**Hint**: compare calculated with weight stated in problem).