

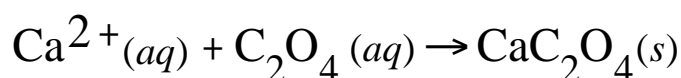
## Lecture 4 - Gravimetric Analysis

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

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

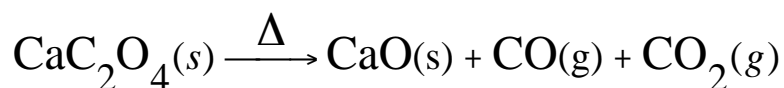
Ex. Excess of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4^{2-}$ ) added carefully to measured volume of  $\text{Ca}^{2+}$ .

(1) In basic sol'n:



(2)  $\text{CaC}_2\text{O}_4(\text{s})$  is collected in a filtering crucible then dried

(3)  $\text{CaC}_2\text{O}_4$  ignited to produce calcium oxide:



(4)  $\text{CaO}(\text{s})$  cooled, weighed

(5) Original concentration of  $\text{Ca}^{2+}$  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

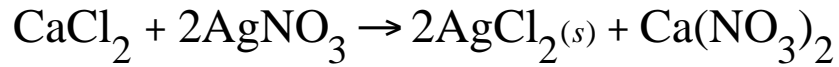
$\frac{Q-S}{S}$  low – particle growth dominates, excluding nucleation

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

\*Particle growth dominates – small # of larger particles

## 5. Gravimetric Calculations

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



$$\text{wt CaCl}_2 = \text{wt AgCl} \times \left( \frac{\text{FW CaCl}_2}{\text{FW AgCl}} \times \frac{1 \text{ mol CaCl}_2}{2 \text{ mol AgCl}} \right)$$

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. Calculate the % Phosphorus in a 0.3516 g detergent sample.  
Final yield is 0.2161 g Mg<sub>2</sub>P<sub>2</sub>O<sub>4</sub>

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

a. Mass P =

$$0.2161 \text{ g Mg}_2\text{P}_2\text{O}_4 \times \frac{1 \text{ mol Mg}_2\text{P}_2\text{O}_4}{222.57 \text{ g Mg}_2\text{P}_2\text{O}_4} \times \frac{2 \text{ mol P}}{1 \text{ mol Mg}_2\text{P}_2\text{O}_4} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}}$$

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...

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

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

$$\% \text{P} = \frac{(0.2161 \text{ g Mg}_2\text{P}_2\text{O}_7)(0.27833)}{0.3516 \text{ g}} \times 100 = 17.10\%$$

Ex: A 10.00 mL solution containing  $\text{Cl}^-$  was treated with excess  $\text{AgNO}_3$  to precipitate 0.4368 g of  $\text{AgCl}$ . What was the molarity of  $\text{Cl}^-$  in the unknown?

Formula mass of  $\text{AgCl} = 143.321$ . A precipitate weighing 0.4368 g contains:

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

\*Note: 1 mol of  $\text{AgCl}$  contains 1 mol of  $\text{Cl}^-$

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

**\* IN CLASS PROBLEMS TO FOLLOW!**

Ex1: Phosphate is precipitated from its solution with ammonium molybdate, as  $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}]$ . 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  $\text{Pb}(\text{NO}_3)_2$ , as  $\text{PbMoO}_4$ .

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  $\text{BaCl}_2$  and  $\text{KCl}$  required 20.25 mL of 0.1200 M  $\text{AgNO}_3$  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  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ , 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  $\text{Na}_2\text{SO}_4$ , a  $\text{BaSO}_4$  precipitate weighing 0.4604 g was obtained. The weight of the precipitate was smaller than the theoretical one, since some  $\text{BaSO}_4$  was converted to  $\text{BaS}$  during the heating process.

a) Calculate the per cent of  $\text{BaS}$  in the precipitate (**Hint**: best to solve algebraically).

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