PHARMACEUTICAL ANALYTICAL CHEMISTRY

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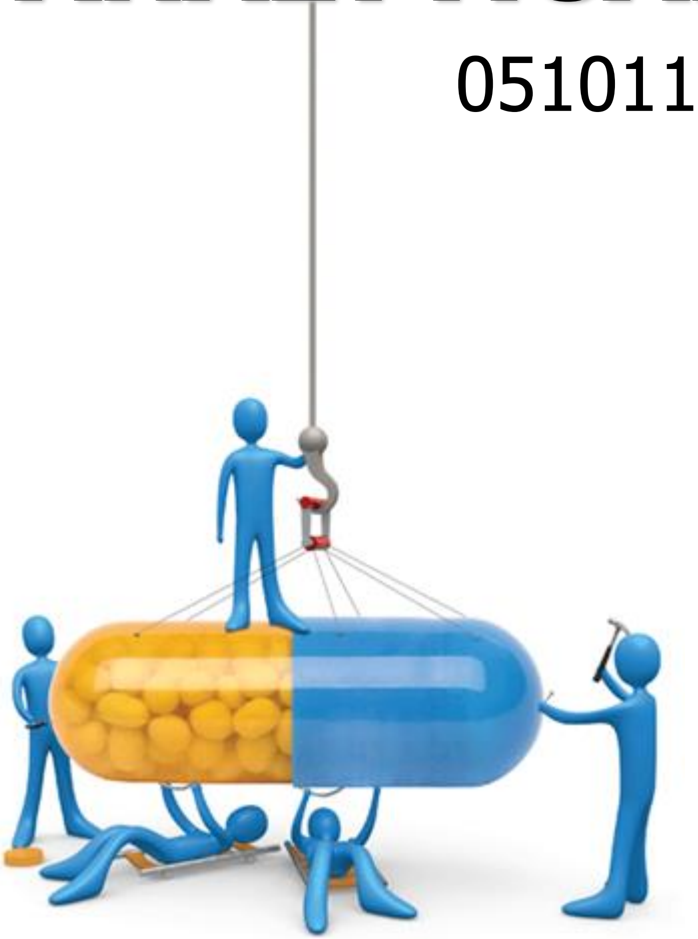
Gravimetric Analysis and Precipitation Equilibria



Dr. Ahmad Najjar
Philadelphia University
Faculty of Pharmacy
Department of Pharmaceutical Sciences
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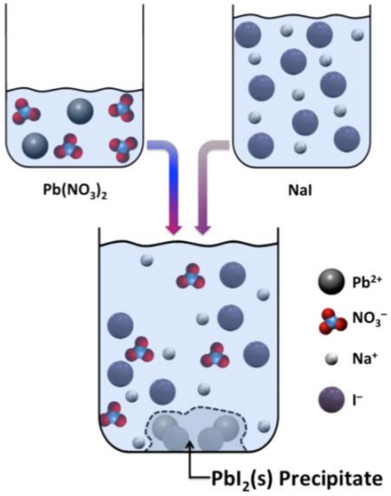
Gravimetric Analysis and Precipitation Equilibria

Chapter 10



Learning Objectives

- *To describe the steps of a gravimetric analysis*
- *To conduct gravimetric calculations*
- *To perform calculations involving the solubility product and the common ion effect*
- *To outline the optimum conditions for precipitation that will obtain a pure and filterable precipitate*

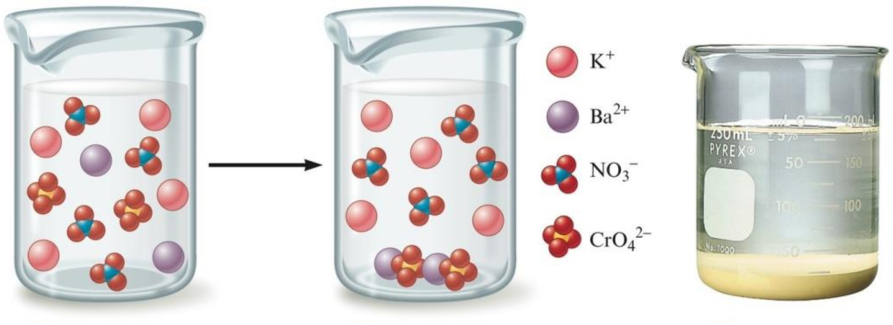
Gravimetric Analysis

Key Concepts

- Gravimetric analysis is the quantitative isolation of a substance by precipitation and weighing of the precipitate.
- A precipitating reagent is the reactant used to precipitate the analyte.

$$\underset{\text{Analyte}}{Ba^{+2}} + \underset{\text{Reagent}}{CrO_4^{-2}} \rightarrow \underset{\text{Solid Product}}{BaCrO_4(s)}$$

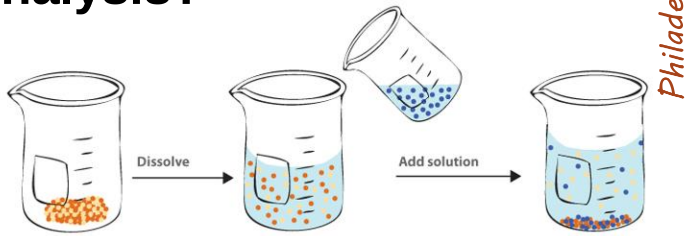
- Usually, the precipitation reagent should be selective for the analyte.
- The precipitate should be pure, filterable and suitable for weighing.

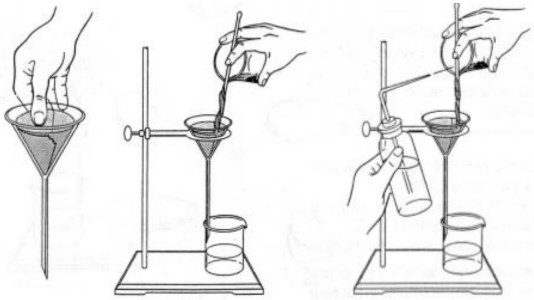


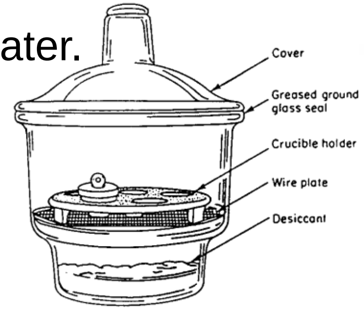
Gravimetric Analysis

How to perform a successful Gravimetric Analysis?

- Weigh the sample to be analyzed.
- Dissolve the sample in a suitable solvent, eg, water.
- Add an excess of the precipitating reagent to precipitate the analyte.
- Digest the precipitate to make larger and more pure crystals.
- Filter the mixture to separate the precipitate from the solution.
- Wash the precipitate to remove any impurities.
- Dry the precipitate by heating to remove water.
- Cool the precipitate in a desiccator to prevent the precipitate absorbing moisture from the air.
- Weigh the cooled precipitate.
- Repeat the drying and weighing process until a constant mass for the precipitate is achieved.
- Calculate the percent by mass of analyte in the sample.







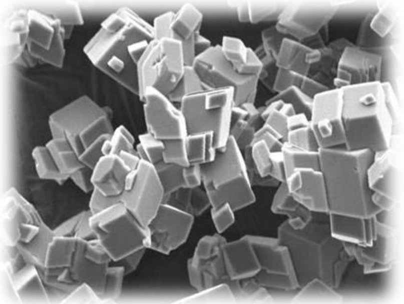
Gravimetric Analysis

Important notes:

- Suitable solvent is not only the solvent that dissolve the analyte, but it could be used to eliminate interfering materials and to maintain low solubility of the precipitate. Solution conditions (polarity, pH, ionic strength) could be adjusted to achieve these goals.
- During the precipitation process, supersaturation occurs, followed by nucleation and precipitation. Supersaturation should be minimized to *prevent the formation of large numbers of nuclei and as a result producing more total crystals of smaller size*.
- The initial nucleus will grow to form a crystal by depositing other precipitate particles. Again, the greater the supersaturation, the more rapid the crystal growth rate which increases the chances of imperfections in the crystal and trapping of impurities.

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

where Q is the concentration of the mixed reagents before precipitation occurs, S is the solubility of the precipitate at equilibrium.



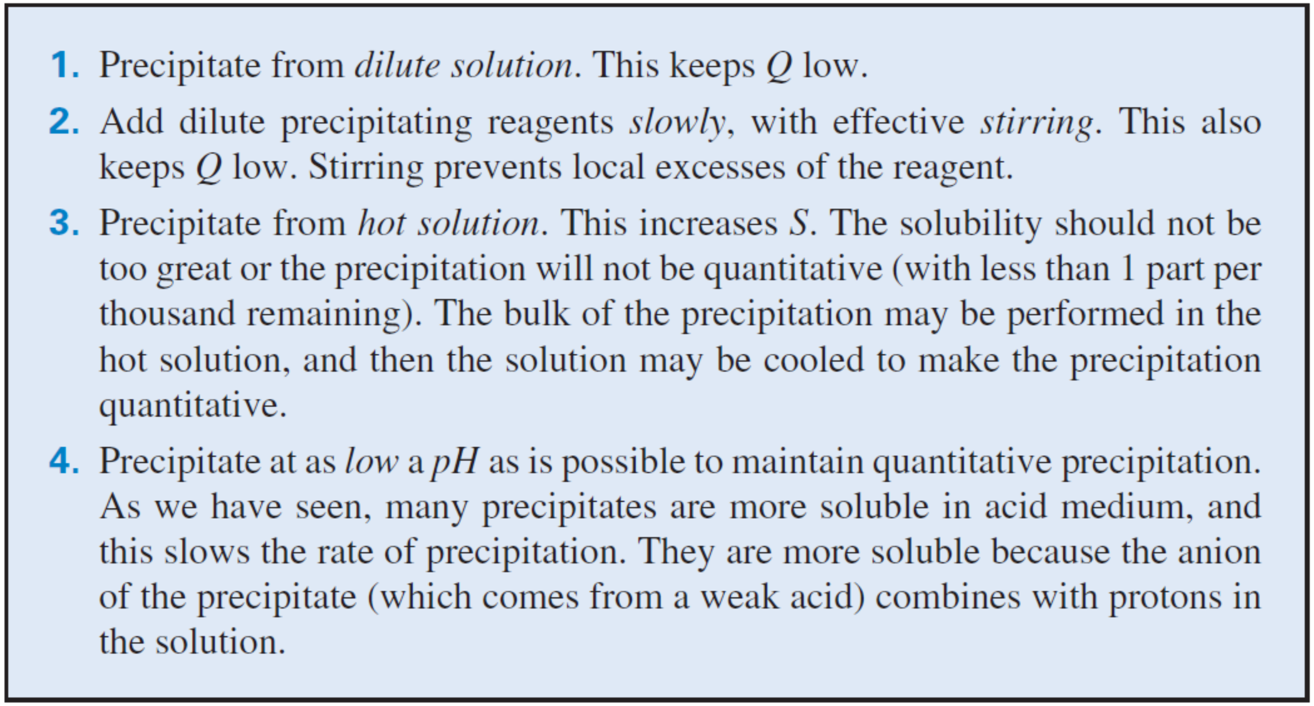
High relative supersaturation → many small crystals (high surface area)

Low relative supersaturation → fewer, larger crystals (low surface area)

Gravimetric Analysis

Important notes:

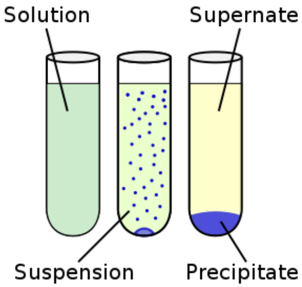
- Several steps are commonly taken to maintain favorable conditions for precipitation:



1. Precipitate from *dilute solution*. This keeps *Q* low.
2. Add dilute precipitating reagents *slowly*, with effective *stirring*. This also keeps *Q* low. Stirring prevents local excesses of the reagent.
3. Precipitate from *hot solution*. This increases *S*. The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.
4. Precipitate at as *low* a *pH* as is possible to maintain quantitative precipitation. As we have seen, many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate (which comes from a weak acid) combines with protons in the solution.

- Very insoluble precipitates are not the best candidates for gravimetric analysis! They supersaturate too easily**.**
- Don’t add too much excess precipitating agent. This will increase adsorption.

Gravimetric Analysis



Important notes:

- Digestion is a process to improves the purity and crystallinity of the precipitate. In this process, the small particles were dissolved and re-precipitate on larger crystals, this is usually done by heating the solution gently with contentious stirring.

- When coagulated particles are filtered, they retain the adsorbed primary and secondary ion layers along with solvent. Washing the particles with water increases the extent of solvent (water) molecules between the layers, causing the secondary layer to be loosely bound, and the particles revert to the colloidal state. This process is called peptization. Adding an **electrolyte** will result in a closer secondary layer and will promote coagulation.

- The **electrolyte** must be one that is volatile at the temperature to be used for drying or ignition, like HNO_3 or NH_4NO_3.

- Drying removes the solvent and wash electrolytes. The drying can usually be done by heating at 110 to 120°C for 1 to 2 h.

- There are a number of ways in which a foreign material may be coprecipitated: Occlusion and Inclusion, Surface Adsorption, Isomorphous Replacement, and Postprecipitation.

Gravimetric Analysis

General calculation of the percent by mass of analyte in a sample:

- Weight the balanced chemical equation for the precipitation reaction
- Calculate the moles of precipitate:

  moles = mass ÷ molecular mass

- Calculate moles of analyte from the balanced chemical equation using the mole ratio of (analyte : precipitate)
- Calculate mass of analyte:

  mass = moles x molecular mass

- Calculate percent by mass of analyte in sample:

  = (mass analyte ÷ mass sample) x 100

Gravimetric Analysis

Example

A 2.00g sample of limestone was dissolved in hydrochloric acid and all the calcium present in the sample was converted to Ca^{2+}. Excess ammonium oxalate solution, $(NH_4)_2C_2O_4$ was added to the solution to precipitate the calcium ions as calcium oxalate, CaC_2O_4. The precipitate was filtered, dried and weighed to a constant mass of 2.43g.

Determine the percentage by mass of calcium in the limestone sample.

kidney stone

a. Write the balanced chemical equation for the precipitation reaction:

$$Ca^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \text{ -----> } CaC_2O_{4(s)}$$

b. Calculate the moles of calcium oxalate precipitated.

$n(CaC_2O_{4(s)}) = \text{mass} \div MM = 2.43 \div (40.08 + 2 \times 12.01 + 4 \times 16.00)$

$n(CaC_2O_{4(s)}) = 2.43 \div 128.10 = 0.019 \text{ mol}$

c. Find the moles of $Ca^{2+}_{(aq)}$.

From the balanced chemical equation, the mole ratio of $Ca^{2+} : CaC_2O_{4(s)}$ is 1 : 1. So, $n(Ca^{2+}_{(aq)}) = n(CaC_2O_{4(s)}) = 0.019\text{mol}$

d. Calculate the mass of calcium in grams

$\text{mass (Ca)} = n \times MM = 0.019 \times 40.08 = 0.76\text{g}$

e. Calculate the percentage by mass of calcium in the original sample:

$\%Ca = (\text{mass Ca} \div \text{mass sample}) \times 100 = (0.76 \div 2.00) \times 100 = 38\%$

Gravimetric Analysis

Example

What is the %KCl in a solid if 5.1367 g of this solid gives 0.8246g AgCl when reacted with $AgNO_3$?

$$Cl^- + Ag^+ \rightarrow AgCl_{(s)}$$

Moles of precipitate (AgCl) = 0.8246/143.3 = 0.00575 mole

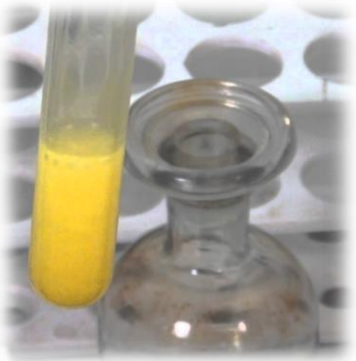
Moles of analyte (Cl or KCl) = 0.00575 x (1 mole Cl / 1 mole AgCl) = 0.00575 mole

Mass of analyte (KCl) = 0.00575 x 74.55 = 0.429 g

Percentage by mass of analyte = (0.429/5.1367)x100 = 8.35%

Example

Orthophosphate (PO_4^{3-}) is determined by weighing as $(NH_4)_3PO_4 \cdot 12MoO_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682 g precipitate were obtained from a 0.2711 g sample (molar mass for P is 30.97 g/mol, for P_2O_5 is 141.95 g/mol and for $(NH_4)_3PO_4 \cdot 12MoO_3$ is 1876.5 g/mol)



Solution $\% P = 7.111\%$ $\% P_2O_5 = 16.30\%$

Precipitation Equilibria: The Solubility Product

"Insoluble" substances still have **slight** solubility

For example $\underline{AgCl} \rightleftharpoons (AgCl)_{aq} \rightleftharpoons Ag^+ + Cl^-$

the **solubility product** K_{sp} of AgCl is $K_{sp} = [Ag^+][Cl^-]$

"Note: the solid does not appear in Ksp expression"

another example is Ag_2CrO_4

$$Ag_2CrO_4 \rightleftharpoons 2\,Ag^+ + CrO_4{}^{2-}$$

$$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$$

The K_{sp} of AgCl at 25°C is 1.0×10^{-10}. Calculate the concentrations of Ag^+ and Cl^- in a saturated solution of AgCl, and the molar solubility of AgCl.

Solution $[Ag^+] = [Cl^-] = s = 1.0 \times 10^{-5}\ M$

The solubility of AgCl is $1.0 \times 10^{-5}\ M$.

Precipitation Equilibria: The Solubility Product

Ten milliliters of 0.20 M $AgNO_3$ is added to 10 mL of 0.10 M NaCl. Calculate the concentration of Cl^- remaining in solution at equilibrium.

Solution $[Cl^-] = 2.0 \times 10^{-9} M$ and again equals the solubility of the AgCl

What is the solubility of PbI_2, in g/L, if the solubility product is 7.1×10^{-9}?

Solution

The equilibrium is $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$, and $K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9}$. Let s represent the molar solubility of PbI_2. Then

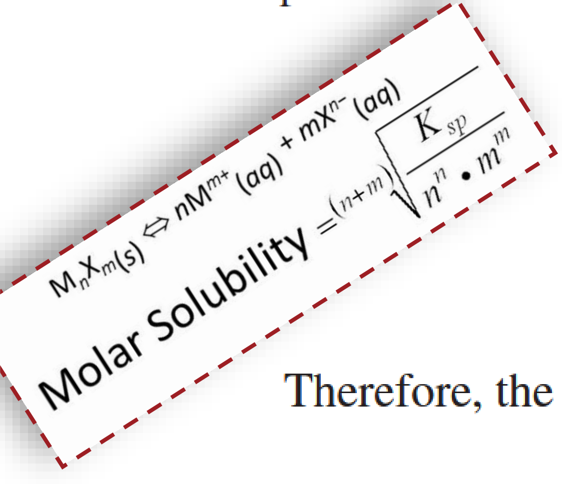
$$[Pb^{2+}] = s \quad \text{and} \quad [I^-] = 2s$$

$$(s)(2s)^2 = 7.1 \times 10^{-9}$$

$$s = \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3}\ M$$

Therefore, the solubility, in g/L, is

$$1.2 \times 10^{-3}\ \text{mol/L} \times 461.0\ \text{g/mol} = 0.55\ \text{g/L}$$



$M_nX_m(s) \Leftrightarrow nM^{m+}(aq) + mX^{n-}(aq)$

Molar Solubility $= \sqrt[(n+m)]{\frac{K_{sp}}{n^n \cdot m^m}}$

Precipitation Equilibria: The Solubility Product

What pH is required to just precipitate iron(III) hydroxide from a 0.10 *M* $FeCl_3$ solution? (K_{sp} for $Fe(OH)_3$ is $4x10^{-38}$)

Solution

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$[Fe^{3+}][OH^-]^3 = 4 \times 10^{-38}$$

$$(0.1)[OH^-]^3 = 4 \times 10^{-38}$$

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}\ M$$

$$pOH = -\log\ 7 \times 10^{-13} = 12.2$$

$$pH = 14.0 - 12.2 = 1.8$$

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Thank You!