Selective Precipitation and Qualitative Analysis

- Our understanding of equilibrium allows us to predict the amount of a substance that can be dissolved into solution to form a saturated solution.
- This equilibrium can be obtained from either side of the reaction.
- Either by:
  1) adding the salt itself to solution to dissolve it.
  2) Or, by adding soluble salts of each ion to solution in order to precipitate out the solid.

For Example:

\[ AB_{(s)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)} \]

If AB is added to water, it will dissolve until equilibrium is reached.

If AX and YB are both soluble compounds and they are added to solution, AB will be precipitated until equilibrium is reached. Addition of a common ion can further drive the ppt.

Predicting Precipitation

- Recognizing that equilibrium can be obtained from either side of the reaction and knowing what we know about the relationship between solubility and the solubility product constant of a partially soluble salt (salts formed from cations of weak bases and anions of weak acids), we can predict whether a precipitate will form when two solutions are mixed.

Selective Precipitation

- Ions can be separated from each other based on the solubility of their salts called selective precipitation.
- Examine the solution containing silver nitrate and copper nitrate.
- What if we wanted to separate the metal ions from one another?

1. Will SrSO₄ precipitate from a solution containing 2.5 x 10⁻⁴ M strontium ion, if enough of the soluble salt of Na₂SO₄ is added to make the solution 2.5 x 10⁻⁴ M SO₄²⁻?

\[ K_{sp} \text{ for SrSO}_4 \text{ is } 3.4 \times 10^{-7} \]

Remember:
- If Q > Ksp, precipitation occurs until Q = Ksp
- If Q = Ksp, saturated solution (eq exists)
- If Q < Ksp, solid dissolves until Q = Ksp
**Selective Precipitation**

Answer: Add HCl

In the solution, Cl\(^-\) has very little affinity for Cu\(^{2+}\) or H\(^+\), however the Ag\(^+\) and Cl\(^-\) ions form an insoluble salt, AgCl, which exists in equilibrium having a 

\[ K_{sp} = 1.8 \times 10^{-10}. \]

At that low solubility high concentrations of Ag\(^+\) and Cl\(^-\) will precipitate out to reach the condition \(Q=K\).

**Selective Precipitation**

The question now becomes, how do we separate two metal ions when both ions form a precipitate with an added reagent?

**Solution**

**Analysis** We are asked to determine the concentration of Cl\(^-\) necessary to begin the precipitation from a solution containing Ag\(^+\) and Pb\(^{2+}\) ions, and to predict which metal chloride will begin to precipitate first.

**Plan** We are given \(K_{sp}\) values for the two precipitates. Using these and the metal ion concentrations, we can calculate what Cl\(^-\) ion concentration is necessary to precipitate each salt. The salt requiring the lower Cl\(^-\) concentration precipitates first.

**Solve**

For AgCl we have 

\[ K_{sp} = [Ag^{+}][Cl^{-}] = 1.8 \times 10^{-10}. \]

Because \([Ag^{+}] = 1.0 \times 10^{-2} M\), the greatest concentration of Cl\(^-\) that can be present without causing precipitation of AgCl can be calculated from the \(K_{sp}\) expression:

\[ [Cl^{-}] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8} M. \]

Any Cl\(^-\) in excess of this very small concentration will cause AgCl to precipitate from solution. Proceeding similarly for PbCl\(_2\), we have

\[ [Cl^{-}] = \frac{4.8 \times 10^{-20}}{2.0 \times 10^{-11}} = 2.4 \times 10^{-9} M. \]

Thus, a concentration of Cl\(^-\) in excess of causes PbCl\(_2\) to precipitate.

Comparing the concentration required to precipitate each salt, we see that as Cl\(^-\) is added, AgCl precipitates first because it requires a much smaller concentration of Cl\(^-\). Thus, Ag\(^+\) can be separated from Pb\(^{2+}\) slowly adding Cl\(^-\) so that the chloride ion concentration remains between 1.8 \(\times\) 10\(^{-10}\) M and 2.4 \(\times\) 10\(^{-9}\) M.

Comment Precipitation of AgCl will keep the Cl\(^-\) concentration low until the number of moles of Cl\(^-\) added exceeds the number of moles of Ag\(^+\) in the solution. Once past this point, [Cl\(^-\)] rises sharply and PbCl\(_2\) will soon begin to precipitate.

**2. A solution consists of both 0.050 M Mg\(^{2+}\) and Cu\(^{2+}\). Which ion precipitates first as OH\(^-\) is added?**

\[ K_{sp} = 1.8 \times 10^{-11} \text{ for Mg(OH)\(_2\)} \]

\[ K_{sp} = 4.8 \times 10^{-20} \text{ for Cu(OH)\(_2\)} \]

**3. What concentration of OH\(^-\) is necessary to begin the precipitation of each cation?**
This can be done by adding a ligand

\[ \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ \]

With the addition of a common ligand of silver, high \( K_f \), the rxn is driven to the right with the formation of the complex ion.

Knowledge of how the equilibrium of a saturated solution can be effected by...

- Temperature (affects \( K_{sp} \))
- Common-ion Effect
- pH
- Formation of Complex Ions
- Amphoterism

...Allows for the separation of metal ions in a mixture known as Qualitative Analysis

The Cation Qualitative Analysis Scheme

A Qualitative Analysis Scheme uses selective precipitation to separate and identify ions in solution.

Ion analysis typically occurs in three stages:
1. Separation of ions into groups
2. Selective precipitation of each ion in the group
3. Identification of individual ions by specific tests

The Cation Qualitative Analysis Scheme

1. Insoluble chlorides
   
   Dilute HCl will precipitate silver, mercury(I) \([\text{Hg}_2^{2+}\]) and lead(II) ions.

2. Acid-Insoluble Sulfides
   
   The addition of \( \text{H}_2\text{S} \) will precipitate the most soluble metal sulfides- those of copper(II), bismuth, cadmium, lead(II), mercury(II), Arsenic, antimony, tin(IV).

3. Base-Insoluble Sulfides and Hydroxides
   
   The addition of \((\text{NH}_4)_2\text{S}\) generates a basic solution resulting in the precipitation of more soluble \( S^{2-} \) compounds, including zinc, nickel, cobalt, and manganese. Aluminum, chromium(III) and iron(III) are precipitated out as hydroxides.

   Remember \( \text{Al}(\text{H}_2\text{O})_{6}^{3+} \)? Iron?
4. Insoluble Phosphates

The addition of ammonium hydrogen phosphate further precipitates magnesium, calcium, strontium, and barium as phosphates.

5. Soluble Ions

The remaining ions are always soluble—sodium, potassium, Magnesium(I), and ammonium.

The ions in each qualitative group is next selectively precipitated, then the precipitate is redissolved and tested against a test reagent.

A schematic of the group separation, selective precipitation and test of individual ions is the Qualitative Analysis Scheme.

Example:
- Separation of Group I: Ag⁺, Hg₂²⁺ and Pb²⁺
  All precipitated by HCl.
- Selective precipitation of Ag⁺
  AgCl can be dissolved with the addition of a ligand:
  \[ \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ \]
  Once the solution is filtered, the filtrate contains Ag⁺.
- Test for selected ion
  The silver ion again precipitated by adding nitric acid to make acidic and remove ammonia releasing the Ag⁺, reforming AgCl.

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