<u>Solubility Equilibria</u>

Solubility Product Constant (K_{sp})

- Example $CaF_2(s) \Leftrightarrow Ca^{2+}(aq) + 2F^{-}(aq)$ $K_{sp} = [Ca^{2+}][F^{-}]^2$
- Solubility is an equilibrium position; the solubility product and the solubility of a substance are not the same thing.
- The solid is not included in the equilibrium expression the amount of excess solid in a solution does not affect the position of the equilibrium and thus does not affect the solubility of that solid.
- Molar solubility can be obtained from K_{sp} and vice versa.

Examples will be worked in class.

Common Ion Effect

- The solubility of a slightly soluble ionic compound is lowered when a common ion is present.
- This is commonly used in analytical chemistry.

Precipitation

Ion product (Q_{ip}) - (reaction quotient) uses the initial concentrations.

To determine if a reaction will occur:

- 1. Determine initial concentrations of ions.
- 2. Calculate Q_{ip}.
- 3. Compare Q_{ip}^{T} and K_{sp} to determine if a reaction will occur.

 $Q_{ip} > K_{sp}$ Precipitation should occur and continue until the concentrations satisfy K_{sp} .

 $Q_{ip} < K_{sp}$ No precipitation occurs

Complete precipitation is favored when

- 1. K_{sp} is very small
- 2. The target ion has a high initial concentration.
- 3. There is a common ion whose concentration greatly exceeds that of the target ion.

Selective Precipitation

• Separation of ions by precipitation.

Effects of pH

- The solubility of an ionic solute can be greatly affected by changes in pH.
- Changes in pH can also be used to selectively precipitate out ions.

Complex Ions

Complex ion - a charged species consisting of a metal ion surrounded by ligands.

Ligand - a Lewis base; a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond.

Common ligands - H₂O, NH₃, Cl⁻, CN⁻, OH⁻, SCN⁻

Coordination number - the number of ligands attached to a metal ion. The most common coordination numbers are 6, 4, and 2. Example: $\text{Co(OH}_2)_6^{2+}$, $\text{Ni(NH}_3)_6^{2+}$, CoCl_4^{2-} , $\text{Cu(NH}_3)_4^{2+}$, $\text{Ag(NH}_3)^{2+}$

(Note: a handout will be given in class to show naming and reactions for complex ions)

Metal ions add ligands one at a time.

Formation constants (stability constants) - the equilibrium constant, K_f , associated with each step of the complex ion formation.

Example: The reaction taking place when solutions containing Ag^+ and NH_3 are mixed.

$$\begin{split} Ag^{+}(aq) + NH_{3}(aq) & \Leftrightarrow Ag(NH_{3})^{+}(aq) & K_{f} = 2.1 \text{ x } 10^{3} \\ Ag(NH_{3})^{+}(aq) + NH_{3}(aq) & \Leftrightarrow Ag(NH_{3})_{2}^{+}(aq) & K_{f} = 8.2 \text{ x } 10^{3} \end{split}$$

• Note, all the species, NH_3 , Ag^+ , $Ag(NH_3)^+$, and $Ag(NH_3)_2^+$ exist at equilibrium.

Qualitative Analysis

- identifies the components of unknown materials.
- can be done by selective precipitation.