Chemistry 132 NT

The most difficult thing to understand is the income tax.

Albert Einstein

Chem 132 NT

Solubility and Complex-ion Equilibria

Module 1

Solubility Equilibria

- **The Solubility Product Constant**
- **Solubility and the Common-Ion Effect**
- **Precipitation Calculations**
- **Effect of pH on Solubility**

Reaction of zinc metal with hydrochloric acid.

Solubility Equilibria

- Many natural processes depend on the precipitation or dissolving of a slightly soluble salt.
  - In the next section, we look at the **equilibria** of slightly soluble, or nearly insoluble, ionic compounds.
  - Their equilibrium constants can be used to answer questions regarding **solubility** and **precipitation**.

The Solubility Product Constant

- When an excess of a slightly soluble ionic compound is mixed with water, an equilibrium is established between the solid and the ions in the saturated solution.
  - For the salt calcium oxalate, CaC_2O_4, you have the following equilibrium.

$$CaC_2O_4(s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

The Solubility Product Constant

- When an excess of a slightly soluble ionic compound is mixed with water, an equilibrium is established between the solid and the ions in the saturated solution.
  - The equilibrium constant for this process is called the **solubility product constant**.

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

The Solubility Product Constant

- In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
  - It equals the **product of the equilibrium concentrations** of the ions in the compound.
  - Each concentration is **raised to a power** equal to the number of such ions in the formula of the compound.

The Solubility Product Constant

- In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
  - For example, lead iodide, PbI_2, is another slightly soluble salt. Its equilibrium is:

$$PbI_2(s) \overset{H_2O}{\rightleftharpoons} Pb^{2+}(aq) + 2I^-(aq)$$

The Solubility Product Constant

- In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
  - The expression for the solubility product constant is:

$$K_{sp} = [Pb^{2+}][I^-]^2$$

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4, contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
  - We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter.

$$M\ CaC_2O_4 = (0.0061 g\ CaC_2O_4/L) \times \frac{1 mol\ CaC_2O_4}{128 g\ CaC_2O_4}$$

$$= 4.8 \times 10^{-5}\ mol\ CaC_2O_4/L$$

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4, contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
  - When 4.8 x 10^{-5} mol of solid dissolve it forms 4.8 x 10^{-5} mol of each ion.

$$CaC_2O_4(s) \overset{H_2O}{=\!=} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

Starting	0	0
Change	+4.8 x 10^{-5}	+4.8 x 10^{-5}
Equilibrium	4.8 x 10^{-5}	4.8 x 10^{-5}

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4, contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
  - You can now substitute into the equilibrium-constant expression.

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

$$K_{sp} = (4.8 \times 10^{-5})(4.8 \times 10^{-5})$$

$$K_{sp} = 2.3 \times 10^{-9}$$

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - Note that in this example, you find that 1.2 x 10^{-3} mol of the solid dissolves to give 1.2 x 10^{-3} mol Pb^{2+} and (**2 x** (1.2 x 10^{-3})) mol of I^-.

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - The following table summarizes.

$$PbI_2(s) \overset{H_2O}{=\!=} Pb^{2+}(aq) + 2I^-(aq)$$

	Pb^{2+}	I^-
Starting	0	0
Change	+1.2 x 10^{-3}	+2 x (1.2 x 10^{-3})
Equilibrium	1.2 x 10^{-3}	2 x (1.2 x 10^{-3})

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - Substituting into the equilibrium-constant expression:

$$K_{sp} = [Pb^{2+}][I^-]^2$$

$$K_{sp} = (1.2 \times 10^{-3})(2 \times (1.2 \times 10^{-3}))^2$$

$$K_{sp} = 6.9 \times 10^{-9}$$

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - A table in your text lists the solubility product constants for various ionic compounds.
  - If the solubility product constant is known, the solubility of the compound can be calculated.

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - Let x be the molar solubility of CaF_2.

$$CaF_2(s) \xrightleftharpoons{H_2O} Ca^{2+}(aq) + 2F^-(aq)$$

Starting		**0**	**0**
Change		**+x**	**+2x**
Equilibrium		**x**	**2x**

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - You substitute into the equilibrium-constant equation

$$[Ca^{2+}][F^-]^2 = K_{sp}$$

$$(x)(2x)^2 = 3.4 \times 10^{-11}$$

$$4x^3 = 3.4 \times 10^{-11}$$

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - You now solve for x.

$$x = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}} = 2.0 \times 10^{-4}\ \text{mol } CaF_2/L$$

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - Convert to g/L (CaF_2 78.1 g/mol).

$$\textbf{solubility} = 2.0 \times 10^{-4}\,\text{mol/L} \times \frac{78.1\,\text{g CaF}_2}{1\,\text{mol CaF}_2}$$

$$= 1.6 \times 10^{-2}\,\text{g CaF}_2/\text{L}$$

Solubility and the Common-Ion Effect

- In this section we will look at calculating solubilities in the presence of other ions.
  - The importance of the K_{sp} becomes apparent when you consider the solubility of one salt in the solution of another **having the same cation**.

Solubility and the Common-Ion Effect

- In this section we will look at calculating solubilities in the presence of other ions.
  - For example, suppose you wish to know the solubility of calcium oxalate in a solution of calcium chloride.
  - Each salt contributes the same cation (Ca^{2+})
  - The effect is to make calcium oxalate **less soluble than it would be in pure water**.

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Note that before the calcium oxalate dissolves, there is already 0.15 M Ca^{2+} in the solution.

$$CaC_2O_4(s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

Starting	**0.15**	**0**
Change	**+x**	**+x**
Equilibrium	**0.15 + x**	**x**

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - You substitute into the equilibrium-constant equation

$$[Ca^{2+}][C_2O_4^{2-}] = K_{sp}$$

$$(0.15 + x)(x) = 2.3 \times 10^{-9}$$

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Now rearrange this equation to give

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} \approx \frac{2.3 \times 10^{-9}}{0.15}$$

  - We expect x to be negligible compared to 0.15.

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Now rearrange this equation to give

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} \cong \frac{2.3 \times 10^{-9}}{0.15}$$

$$x = 1.5 \times 10^{-8}$$

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Therefore, the molar solubility of calcium oxalate in 0.15 M $CaCl_2$ is 1.5×10^{-8} M.
  - In pure water, the molarity was 4.8×10^{-5} M, which is over **3000 times greater**.

Precipitation Calculations

- Precipitation is merely another way of looking at solubility equilibrium.
  - Rather than considering how much of a substance will dissolve, we ask: **Will precipitation occur for a given starting ion concentration?**

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - To predict the direction of reaction, you **compare Q_c with K_c** (Equilibrium Chapter).
  - The reaction quotient has the same form as the K_{sp} expression, but the concentrations of products are starting values.

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - Consider the following equilibrium.

$$\mathrm{PbCl_2(s)} \overset{H_2O}{\rightleftharpoons} \mathrm{Pb^{2+}(aq) + 2Cl^-(aq)}$$

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - The Q_c expression is

$$Q_c = [\mathrm{Pb^{2+}}]_i[\mathrm{Cl^-}]_i^2$$

where initial concentration is denoted by *i*.

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - If Q_c exceeds the K_{sp}, precipitation occurs.
  - If Q_c is less than K_{sp}, more solute can dissolve.
  - If Q_c equals the K_{sp}, the solution is saturated.

Predicting Whether Precipitation Will Occur

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0 x 10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3 x 10^{-9}.
  - The ion product quotient, Q_c, is:

$$Q_c = [Ca^{2+}]_i[C_2O_4^{2-}]_i$$

$$Q_c = (0.0025) \times (1.0 \times 10^{-7})$$

$$Q_c = 2.5 \times 10^{-10}$$

Predicting Whether Precipitation Will Occur

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0 x 10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3 x 10^{-9}.
  - This value is smaller than the K_{sp}, so **you do not expect precipitation to occur**.

$$Q_c = 2.5 \times 10^{-10} < K_{sp}$$

Fractional Precipitation

- Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
  - For example, when you slowly add potassium chromate, K_2CrO_4, to a solution containing Ba^{2+} and Sr^{2+}, **barium chromate precipitates first**.

Fractional Precipitation

- Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
  - After most of the Ba^{2+} ion has precipitated, strontium chromate begins to precipitate.
  - It is therefore possible to separate Ba^{2+} from Sr^{2+} by **fractional precipitation** using K_2CrO_4.

Effect of pH on Solubility

- Sometimes it is necessary to account for other reactions aqueous ions might undergo.
  - For example, if the anion is the **conjugate base of a weak acid**, it will react with H_3O^+.
  - You should expect the solubility to be affected by pH.

Effect of pH on Solubility

- Sometimes it is necessary to account for other reactions aqueous ions might undergo.
  - Consider the following equilibrium.

$$CaC_2O_4(s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

  - Because the oxalate ion is conjugate to a weak acid ($HC_2O_4^-$), it will react with H_3O^+.

$$C_2O_4^{2-}(aq) + H_3O^+(aq) \overset{H_2O}{\rightleftharpoons} HC_2O_4^-(aq) + H_2O(l)$$

Effect of pH on Solubility

- Sometimes it is necessary to account for other reactions aqueous ions might undergo.
  - According to Le Chatelier's principle, as $C_2O_4^{2-}$ ion is removed by the reaction with H_3O^+, more calcium oxalate dissolves.
  - Therefore, you expect calcium oxalate to be **more soluble in acidic solution (low pH) than in pure water**.

Separation of Metal Ions by Sulfide Precipitation

- Many metal sulfides are insoluble in water but dissolve in acidic solution.
  - **Qualitative analysis** uses this change in solubility of the metal sulfides with pH to separate a mixture of metal ions.
  - By adjusting the pH in an aqueous solution of H_2S, you adjust the sulfide concentration to precipitate the least soluble metal sulfide first.
  - **Qualitative analysis** is covered in your text.

Operational Skills

- Writing solubility product expressions
- Calculating K_{sp} from the solubility, or vice versa.
- Calculating the solubility of a slightly soluble salt in a solution of a common ion.
- Predicting whether precipitation will occur
- Determining the qualitative effect of pH on solubility

Time for a few review questions