CHAPTER 17 (MOORE)
EQUILIBRIA FOR SLIGHTLY SOLUBLE SALTS

This chapter deals with slightly soluble salts and their equilibria. By convention, we will treat the salts as the reactants and their ions as the products in these equilibria. Many ionic compounds (salts) are only slightly soluble in water. As a class, they are in between salts that are 100% ionized and those that are essentially insoluble. In this chapter, we examine the equilibria that describe the behavior of these salts and govern their solubilities in water.

Recall that, in Chapter 5 (Section 5.1), you looked at exchange reactions that form precipitates. See Moore, pp. 164-171 to review what you should already know about precipitation reactions and solubility rules as you begin this chapter.

The Molar Solubility Product Constant, $K_{sp}$
Consider a slightly soluble salt like BaSO$_4$. When it dissolves in water, how do we represent the process?

$$\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$

Now write the equilibrium expression for this equilibrium: $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$

The equilibrium constant for the process in which a slightly soluble solid dissolves is called the molar solubility product constant, $K_{sp}$. The solution is saturated with BaSO$_4$. Question: What does saturated mean?

Writing $K_{sp}$ Expressions
Note that this is the equilibrium that exists between the slightly soluble salt and its ions in a saturated aqueous solution of the salt.

Example 17.1
(a) Write a solubility product constant expression for equilibrium in a saturated aqueous solution of the slightly soluble salt, iron(III) phosphate, FePO$_4$. (write the equilibrium equation with the solid salt on the left of the double arrows)

$$\text{FePO}_4(\text{s}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$$

Then, $K_{sp} = [\text{Fe}^{3+}][\text{PO}_4^{3-}]$

(b) Write a solubility product constant expression for equilibrium in a saturated aqueous solution of the slightly soluble salt, chromium(III) hydroxide, Cr(OH)$_3$. Again, begin by writing the solid salt on the left of the double arrows …then the ions on the right …

$$\text{Cr(OH)}_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq})$$

$K_{sp} = [\text{Cr}^{3+}][\text{OH}^-]^3$

Solubility Product Constants. See Table 16.1 (Hill, p. 678)

Molar Solubility and the Molar Solubility Product
The molar solubility $(S)$ of a slightly soluble salt is the number of moles of that compound that will dissolve in exactly 1.00 liter of solution. The molar solubility product constant of a slightly soluble salt is its $K_{sp}$.
The solubility of a slightly soluble salt depends upon both the value of its $K_{sp}$ and the form of its equilibrium constant expression. Unlike $K_C$ values, a larger $K_{sp}$ doesn’t necessarily mean a more soluble salt.

**Calculating $K_{sp}$ from Solubility Data**

**Example 17.2**

At 20 °C, a saturated aqueous solution of silver carbonate contains 32 mg of Ag$_2$CO$_3$ per liter of solution. Calculate $K_{sp}$ for Ag$_2$CO$_3$ at 20 °C.

First, the balanced equation is Ag$_2$CO$_3$(s) $\rightleftharpoons$ 2 Ag$^+$ (aq) + CO$_3^{2-}$(aq) $\quad K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$

Convert 32 mg Ag$_2$CO$_3$/L to mol Ag$_2$CO$_3$/L … why?

$$\text{mol Ag}_2\text{CO}_3/\text{L} = (0.032 \text{ g/L})(1 \text{ mol/275.75 g}) = 1.16 \times 10^{-4} \text{ M}$$

**Calculating Molar Solubility from $K_{sp}$ Values**

The problem - to calculate the molar solubility (S) of a slightly soluble salt, in mol/L, from its $K_{sp}$ value. Strategy: write the equilibrium equation and the $K_{sp}$ expression. Let $S$ = molar solubility of the salt and solve for S.

**Example 17.3** From the $K_{sp}$ value for silver sulfate, calculate its molar solubility at 25 °C, where $K_{sp} = 1.4 \times 10^{-5}$

Ag$_2$SO$_4$(s) $\rightleftharpoons$ 2 Ag$^+$ (aq) + SO$_4^{2-}$(aq) $\quad K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$

$$2S \quad S \quad 2S \quad S \quad K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = 1.4 \times 10^{-5} \quad \text{or} \quad (2S)^2(S) = 4S^3 = 1.4 \times 10^{-5}$$

$$S = 1.5 \times 10^{-2} \quad = \quad \text{molar solubility}$$

If we want equilibrium concentrations,

$[\text{Ag}^+] = 2S = 2(1.5 \times 10^{-2}) = 3.0 \times 10^{-2} \text{ M}$

$[\text{SO}_4^{2-}] = S = 1.5 \times 10^{-2} \text{ M}$

**An easy problem …**

AgCl (s) $\rightleftharpoons$ Ag$^+$ (aq) + Cl$^{-}$ (aq) $\quad K_{sp} = 1.8 \times 10^{-10}$

What is the molar solubility of AgCl?

$$S \quad S \quad S \quad K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \quad \text{or} \quad (S)(S) = 1.8 \times 10^{-10} \quad S^2 = 1.8 \times 10^{-10}$$

$$S = 1.3 \times 10^{-5} \text{ M}$$

**The Common Ion Effect in Solubility Equilibria**

Solubilities of slightly soluble ionic compounds are lowered when a second solute that furnishes a “common ion” is added to their solutions.
Ag₂SO₄ (s) ⇌ 2 Ag⁺ (aq) + SO₄²⁻ (aq)  (equilibrium)

Now add Na₂SO₄ (aq) to the system …the equilibrium shifts to left! Ag₂SO₄ precipitates and the added sulfate ion reduces the solubility of Ag₂SO₄ as measured by the equilibrium concentration of Ag⁺.

**Common Ion Effect Illustrated**
What happens when Na₂SO₄(aq) is added to a sat. solution of Ag₂SO₄? [Ag⁺] has new, lower equilibrium concentration (some Ag⁺ reacts with SO₄²⁻ to make more Ag₂SO₄(s)).

**Example 17.5** Calculate the molar solubility of Ag₂SO₄ in 1.00 M Na₂SO₄(aq).

**Will Precipitation Occur? Is It Complete?**

Q_{ip} is the ion product reaction quotient and is based on initial conditions of the reaction.

Q_{ip} can then be compared to K_{sp}.
Precipitation should occur if Q_{ip} > K_{sp}.
Precipitation cannot occur if Q_{ip} < K_{sp}.
A solution is just saturated if Q_{ip} = K_{sp}.

**Example 17.6**
If 1.00 mg of Na₂CrO₄ is added to 225 mL of 0.00015 M AgNO₃, will a precipitate form?

Ag₂CrO₄ (s) ⇌ 2 Ag⁺ (aq) + CrO₄²⁻ (aq)  K_{sp} = 1.1 x 10⁻¹²

**Example 17.7** A Conceptual Example
Pictured here is the result of adding a few drops of concentrated KI(aq) to a dilute solution of Pb(NO₃)₂. What is the solid that first appears? Explain why it then disappears.

**Example 17.8**
If 0.100 L of 0.0015 M MgCl₂ and 0.200 L of 0.025 M NaF are mixed, should a precipitate of MgF₂ form? MgF₂ (s) ⇌ Mg²⁺ (aq) + 2 F⁻ (aq)  K_{sp} = 3.7 x 10⁻₈

**To Determine Whether Precipitation Is Complete**
We generally consider precipitation to be “complete” if about 99.9% of the “target ion” is precipitated (i.e. 0.1% or less left in solution).

Three conditions generally favor completeness of precipitation:
1. Very small values of K_{sp}
2. high initial concentrations of the target ion
3. concentrations of common ion that greatly exceeds that of the target ion
Example 17.9
To a solution with \([\text{Ca}^{2+}] = 0.0050\) M, we add sufficient solid ammonium oxalate, \((\text{NH}_4)_2\text{C}_2\text{O}_4\), to make the initial \([\text{C}_2\text{O}_4^{2-}] = 0.0051\) M. Will precipitation of \(\text{Ca}^{2+}\) as \(\text{CaC}_2\text{O}_4(s)\) be complete?

\[
\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \quad K_{sp} = 2.7 \times 10^{-9}
\]

Example 17.11
What is the molar solubility of \(\text{Mg(OH)}_2(s)\) in a buffer solution having \([\text{OH}^-] = 1.0 \times 10^{-5}\) M, that is, \(\text{pH} = 9.00\)?

Cation Group 1
If aqueous HCl is added to an unknown solution of cations, and a precipitate forms, then the unknown contains one or more of these cations: \(\text{Pb}^{2+}, \text{Hg}_2^{2+}\), or \(\text{Ag}^+\). These are the only metal cations that should form insoluble chlorides.

Any precipitate (\(\text{PbCl}_2, \text{Hg}_2\text{Cl}_2\) or \(\text{AgCl}\)) is then separated from the mixture and further tests are performed to determine which of the three Group 1 cations is/are present.

The supernatant liquid is also saved for further analysis (it contains any other cation present). If there is no precipitate when HCl is added, then Group 1 ions are not present in the mixture.