"Every electrolyte (in aqueous solution), consists partly of active (in electrical and chemical relation), and partly of inactive molecules..."

Svante Arrhenius

# Solubility Equilibria

As you saw in acid-base chemistry and the pH scale, pure water is actually a solution that contains tiny amounts of hydrogen ions and hydroxide ions in addition to water molecules. Although 0.0000001 mole per liter of these ions  $(1 \times 10^{-7} \text{ M})$  may seem insignificant, slight variations in their concentrations can result in major changes in many important properties of the solution. For example, the hydrogen ion concentration in your blood is normally 0.000000035 mole per liter ( $3.5 \times 10^{-7} \text{ M}$ ), but if it changes to 0.000000010 mole per liter ( $1.0 \times 10^{-8} \text{ M}$ ), death may occur in only a few seconds. This points to the great importance of buffering blood. A well-founded understanding of tiny concentrations is not limited to water, but it is an important aspect of solution chemistry at large.

Consider solutions of so-called insoluble salts. Even though these salts are generally referred to as being "insoluble", there are actually tiny amounts of the ions that make up the salts in their solutions. For example, you may recall that the solubility rules said that all chlorides are soluble with the exception of certain heavy metal chlorides such as silver chloride. Thus, you classified silver chloride as insoluble. In fact, a concentration of 0.00009 mole per liter of silver and chloride ions exist in such a solution. These small concentrations of dissolved ions can be very important to environmental, industrial, and analytical chemists, as well as in medicine, toxicology, ecology and geology.

## **The Solubility Product Constant**

If undissolved silver chloride is present in a water solution, some will dissolve. When the process reaches equilibrium, the macroscopic concentrations of silver and chloride ions will remain constant, and the process can be represented by the equation:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

Recalling that solids are not included in an equilibrium constant expression, the K expression for this reaction is

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

where the subscript "sp" on the K refers to the term "solubility product." K<sub>sp</sub> is called the *solubility product constant*.

 $K_{sp}$  expressions are written in the same manner as any other equilibrium expression. Just keep in mind that solids are not included in those expressions. If we have a solution with lead(II) chloride, the dissolving equation and solubility product constant expression are:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2 Cl^{-}(aq) \qquad K_{sp} = [Pb^{2+}] [Cl^{-}]^2$$

Recall that ion concentrations are raised to the power of their stoichiometric coefficient in equilibrium constant expressions.

As with all equilibrium constant expressions, the solubility product constant is temperature dependent. We will restrict our interest to reactions occurring at 25°C, the standard thermodynamic temperature, in this lesson.

## **Determination of Solubility Product Constant Values**

If we know the solubility of a salt in water, we can calculate its K<sub>sp</sub> value. We follow a four-step procedure:

- 1. Write the balanced equation representing the dissolving process.
- 2. Write the K<sub>sp</sub> expression, based on the equation from Step 1.
- 3. Calculate the mole per liter (M) concentration of each of the ions represented in the K<sub>sp</sub> expression.
- 4. Substitute the ion concentrations into the K<sub>SD</sub> expression and calculate its value.

### EXAMPLE 1

It is experimentally determined that  $1.3 \times 10^{-5}$  g of silver bromide will dissolve in 100.0 mL of water at 25°C. What is the solubility product constant for silver bromide?

#### SOLUTION

The first step is to write the balanced equation for dissolving silver bromide:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

Now we write the solubility product constant expression:

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

The third step requires changing concentration in g/100 mL to mol/L:

$$\frac{1.3 \times 10^{-5} \text{ g AgBr}}{100 \text{ mL}} \times \frac{1 \text{ mol AgBr}}{187.8 \text{ g AgBr}} \times \frac{1 \text{ mol Ag}^+}{1 \text{ mol AgBr}} \times \frac{1000 \text{ mL}}{\text{L}} = \frac{6.9 \times 10^{-7} \text{ mol Ag}^+}{\text{L}} = 6.9 \times 10^{-7} \text{ M Ag}^+$$

Since one bromide ion is formed for each silver ion formed,  $[Br^-] = [Ag^+] = 6.9 \times 10^{-7} M.$ 

Now we can substitute the mole per liter concentrations into the K<sub>sp</sub> expression and solve:

$$K_{sp} = [Ag^+][Br^-] = (6.9 \times 10^{-7})(6.9 \times 10^{-7}) = 4.8 \times 10^{-13}$$

## **Determining Solubility**

Solubility product constant values are known for a large number of compounds, so in the majority of cases, they can be obtained from reference sources. Therefore, a more common calculation is to find solubility from known  $K_{SD}$  values. The procedure for determining solubility from  $K_{SD}$  is:

- 1. Write the balanced equation representing the dissolving process.
- 2. Write the K<sub>sp</sub> expression, based on the equation from Step 1.
- 3. Assign the algebraic variable x to one of the ions on the right side of the equilibrium equation that has the same stoichiometric coefficient as the solid on the left side of the equation.
- 4. Assign algebraic variables for the other ions on the right side of the equilibrium equation in terms of their relationship to the ion from Step 3.
- 5. Substitute the algebraic variables into the  $K_{sp}$  expression, solve for x, and determine the solubility in the units requested in the problem statement.

### EXAMPLE 2

Determine the g/100 cm<sup>3</sup> solubility of lead(II) bromide, given that one reference source gives its K<sub>sp</sub> as 9  $\times 10^{-6}$ .

#### SOLUTION

The first two steps are to write the equation and K<sub>sp</sub> expression:

$$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2 Br^{-}(aq) \qquad K_{sp} = [Pb^{2+}] [Br^{-}]^2$$

We want to know the solubility of PbBr<sub>2</sub>(s). There is a 1:1 stoichiometric relationship between PbBr<sub>2</sub>(s) and Pb<sup>2+</sup>(aq), so if we find the [Pb<sup>2+</sup>], we have the solubility of PbBr<sub>2</sub>(s). Thus we let  $x = [Pb^{2+}]$ . Since the coefficient on Br<sup>-</sup>(aq) is twice that on Pb<sup>2+</sup>(aq), [Br<sup>-</sup>] = 2x. This completes Steps 3 and 4. Now we substitute and solve:

$$K_{sp} = [Pb^{2+}] [Br^{-}]^2 = 9 \times 10^{-6} = (x) (2x)^2$$
  
9 \times 10^{-6} = 4x^3  
x = 0.013 mol/L = [Pb^{2+}] = solubility of PbBr\_2(s)

To complete the problem, we need to convert moles per liter to grams per 100 cm<sup>3</sup>:

$$\frac{0.013 \text{ mol PbBr}_2}{\text{L}} \times \frac{367.0 \text{ g PbBr}_2}{\text{mol PbBr}_2} \times \frac{0.1 \text{ L}}{[100 \text{ cm}^3]} = 0.5 \text{ g PbBr}_2/100 \text{ cm}^3$$

## **The Ion Product**

The **ion product**, **IP**, for a slightly soluble salt has the same form as the expression for the solubility product constant, but it is free from the restriction of only applying to an equilibrium situation. The ion product is valid whether or not an equilibrium situation exists, whereas  $K_{sp}$ , an equilibrium constant, only refers to an equilibrium situation. Returning to our silver chloride example, we have

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
  $K_{sp} = [Ag^+][Cl^-]$   $IP = [Ag^+][Cl^-]$ 

The ion product is particularly useful in predicting whether or not precipitation will occur when solutions containing ions that, when combined, will form a slightly soluble salt.

If we allow a saturated solution of silver chloride to come to equilibrium, IP will be equal to  $K_{Sp}$ :

$$IP = [Ag^+] [Cl^-] = K_{sp}$$

In other words, the ion product and the equilibrium constant are the same for an equilibrium situation. On the other hand, if we were to begin with a non-equilibrium condition, and then give the system time to come to equilibrium, that equilibrium will occur at concentrations such that  $IP = K_{sp}$ .

What about when the system is not at equilibrium? First, let's consider the case when IP is less than  $K_{sp}$ , IP <  $K_{sp}$ . In this case, the solution is unsaturated because there is not a great enough concentration of ions for crystallization to exceed dissolving. No precipitate will form.

The other potential nonequilibrium situation occurs when the ion product is greater than the equilibrium constant,  $IP > K_{sp}$ . In this case, the concentration of the aqueous ions in solution is greater than the equilibrium concentration. Therefore, for the system to come to equilibrium, the solution ion concentrations must decrease. Solid will precipitate until  $IP = K_{sp}$ . Thus if solutions are combined such that  $IP > K_{sp}$ , precipitation will occur.

In summary, if solutions are combined such that the IP is greater than  $K_{sp}$ , the slightly soluble salt will precipitate. If the ion product does not exceed  $K_{sp}$ , no precipitation will occur.

#### EXAMPLE 3

In Example 1, we determined that the K<sub>sp</sub> of silver bromide is  $4.8 \times 10^{-13}$ . If 50.0 mL 0.010 M silver nitrate and 100.0 mL 0.0020 M potassium bromide are combined, will a precipitate form?

#### SOLUTION

As with all problems involving slightly soluble salts, we start with the equilibrium equation and the  $K_{sp}$  expression. This time, however, the reaction for the potential precipitation of the slightly soluble salt is not immediately obvious. Let's consider what ions we have in solution:  $Ag^+(aq)$  and  $NO3^-(aq)$  from the silver nitrate solution and  $K^+(aq)$  and  $Br^-(aq)$  from the potassium bromide solution. A double replacement reaction is possible, forming AgBr and KNO3. From the solubility rules, we know that potassium and nitrate salts are soluble, and that bromide salts are generally soluble, but AgBr is an exception. Thus the precipitation is:

$$Ag^{+}(aq) + Br^{-}(aq) \rightleftharpoons AgBr(s)$$
  $K_{sp} = [Ag^{+}][Br^{-}] = 4.8 \times 10^{-13}$ 

The ion product expression follows from the K<sub>sp</sub> expression:

 $IP = [Ag^+] [Br^-]$ 

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Next, we need the concentrations of the silver and bromide ions. When the two solutions are combined, each original solution is diluted, and thus we use the formula for calculating a dilution,  $M_cV_c = M_dV_d$ , where the subscript c stands for concentrated and the subscript d stands for dilute, M is molarity, and V is volume.

For silver ion, 
$$M_d = \frac{M_c \propto V_c}{V_d} = \frac{0.010 \text{ M Ag}^+ \propto 50.0 \text{ mL}}{150.0 \text{ mL}} = 0.033 \text{ M Ag}^+$$

For bromide ion,  $M_d = \frac{M_c \propto V_c}{V_d} = \frac{0.0020 \text{ M Br} \sim 100.0 \text{ mL}}{150.0 \text{ mL}} = 0.0013 \text{ M Br}$ 

Note that the total volume of solution after the two solutions are combined,  $V_d$ , is the sum of the solution volumes: 50.0 Ml + 100.0 mL = 150.0 mL.

Now we can calculate the ion product and compare it to the K<sub>sp</sub> value:

IP = 
$$[Ag^+]$$
 [Br<sup>-</sup>] = (0.033) (0.0013) = 4.3 × 10<sup>-5</sup> > 4.8 × 10<sup>-13</sup> = K<sub>sp</sub>

 $IP > K_{sp}$ , therefore, we predict that a precipitate of AgBr will form when the solutions are combined.