Chapter 17 Solubility

■   **Solutions to Exercises**

17.1   a. $BaSO_4(s)$ ←→ $Ba^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

b. $Fe(OH)_3(s)$ ←→ $Fe^{3+}(aq) + 3OH^-(aq)$ $K_{sp} = [Fe^{3+}][OH^-]^3$

c. $Ca_3(PO_4)_2(s)$ ←→ $3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$; $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

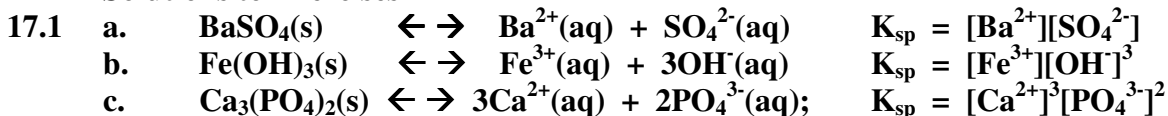**17.2   Calculate the molar solubility. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. (Because no concentrations can be given for solid AgCl, dashes are written; in later problems, similar spaces will be left blank.)**

$$\frac{1.9 \times 10^{-3} \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{143 \text{ g}} = 1.\underline{3}3 \times 10^{-5} \text{ M}$$ **Set up the table as usual.**

Conc. (M)	**AgCl(s)**	←→	**Ag^+**	+	**Cl^-**
Starting			0		0
Change			+1.33 x 10⁻⁵		+1.33 x 10⁻⁵
Equilibrium			1.33 x 10⁻⁵		1.33 x 10⁻⁵

$$K_{sp} = [Ag^+][Cl^-] = (1.33 \times 10^{-5})(1.33 \times 10^{-5}) = 1.\underline{7}68 \times 10^{-10} = 1.8 \times 10^{-10}$$

17.3   Calculate the molar solubility. Then, assemble the usual concentration table and substitute from it into the equilibrium-constant expression. (Because no concentrations can be given for solid $Pb_3(AsO_4)_2$, spaces are left blank.)

$$\frac{3.0 \times 10^{-5} \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{899 \text{ g}} = 3.\underline{3}4 \times 10^{-8} \text{ M}$$

Conc. (M)	$Pb_3(AsO_4)_2(s)$	←→	$3Pb^{2+}$	$+ 2AsO_4^{3-}$
Starting			0 0	
Change			+3(3.34 x 10⁻⁸) +2(3.34 x 10⁻⁸)	
Equilibrium			3(3.34 x 10⁻⁸) 2(3.34 x 10⁻⁸)	

$$K_{sp} = [Pb^{2+}]^3[AsO_4^{3-}]^2 = [3 \times (3.34 \times 10^{-8})]^3(2 \times 3.34 \times 10^{-8})^2$$

$$= 4.\underline{4}89 \times 10^{-36} = 4.5 \times 10^{-36}$$

17.4   Assemble the usual concentration table. Let x equal the molar solubility of $CaSO_4$. When x mol $CaSO_4$ dissolves in one L of solution, x mol Ca^{2+} and x mol SO_4^{2-} form.

Conc. (M)	**$CaSO_4(s)$**	←→	**Ca^{2+}**	+	**SO_4^{2-}**
Starting			0		0
Change			+x		+x
Equilibrium			x		x

Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x. Then, convert to g $CaSO_4$ per L.

$$[Ca^{2+}][SO_4^{2-}] = K_{sp}$$
$$(x)(x) = x^2 = 2.4 \times 10^{-5}$$
$$x = \sqrt{(2.4 \times 10^{-5})} = 4.\underline{8}9 \times 10^{-3} \text{ M}$$

$$\frac{4.89 \times 10^{-3} \text{ mol}}{\text{L}} \times \frac{136 \text{ g}}{1 \text{ mol}} = 0.6\underline{6}64 = 0.67 \text{ g/L}$$

17.5 a. Let x equal the molar solubility of BaF_2. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$BaF_2(s)$	⟵⟶	Ba^{2+}	+	$2F^-$
Starting			0		0
Change			+x		+2x
Equilibrium			x		2x

$$[Ba^{2+}][F^-]^2 = K_{sp}$$
$$(x)(2x)^2 = 4x^3 = 1.0 \times 10^{-6}$$
$$x = \sqrt[3]{\frac{1.0 \times 10^{-6}}{4}} = 6.\underline{2}99 \times 10^{-3} = 6.3 \times 10^{-3} \text{ M}$$

b. At the start, before any BaF_2 dissolves, the solution contains 0.15 M F^-. At equilibrium, x mol of solid BaF_2 dissolves to yield x mol Ba^{2+} and 2x mol F^-. Assemble the usual concentration table, and substitute the equilibrium concentrations into the equilibrium-constant expression. As an approximation, assume x is negligible compared to 0.15 M F^-.

Conc. (M)	$BaF_2(s)$	⟵⟶	Ba^{2+}	+	$2F^-$
Starting			0		0.15
Change			+x		+2x
Equilibrium			x		0.15 + 2x

$$[Ba^{2+}][F^-]^2 = K_{sp}$$
$$(x)(0.15 + 2x)^2 \cong (x)(0.15)^2 \cong 1.0 \times 10^{-6}$$
$$x \cong \frac{1.0 \times 10^{-6}}{(0.15)^2} = 4.\underline{4}44 \times 10^{-5} = 4.4 \times 10^{-5} \text{ M}$$

Note that adding 2x to 0.15 M will not change it (to two significant figures), so 2x is negligible compared to 0.15 M. The solubility of 4.4×10^{-5} M in 0.15 M NaF is lower than the solubility of 6.3×10^{-3} M in pure water.

17.6 Calculate the ion product, Q_c, after evaporation, assuming no precipitation has occurred. Compare it with the K_{sp}.

$$Q_c = [Ca^{2+}][SO_4^{2-}]$$
$$Q_c = (2 \times 0.0052)(2 \times 0.0041) = 8.528 \times 10^{-5}$$
Since $Q_c > K_{sp}$ (2.4×10^{-5}), precipitation occurs.

17.7 Calculate the concentrations of Pb^{2+} and SO_4^{2-}, assuming no precipitation. Use a total volume of 0.456 L + 0.255 L, or 0.711 L.

$$[Pb^{2+}] = \frac{\frac{0.00016 \text{ mol}}{L} \times 0.255 \text{ L}}{0.711 \text{ L}} = 5.\underline{7}4 \times 10^{-5} \text{ M}$$

$$[SO_4^{2-}] = \frac{\frac{0.00023 \text{ mol}}{L} \times 0.456 \text{ L}}{0.711 \text{ L}} = 1.\underline{4}8 \times 10^{-4} \text{ M}$$

Calculate the ion product, and compare it to K_{sp}.
$$Q_c = [Pb^{2+}][SO_4^{2-}] = (5.74 \times 10^{-5})(1.48 \times 10^{-4}) = 8.\underline{4}9 \times 10^{-9}$$
Because Q_c is less than the K_{sp} of 1.7×10^{-8}, no precipitation occurs, and the solution is unsaturated.

17.8 The <u>solubility of AgCN would increase as the pH decreases</u> because the increasing concentration of H_3O^+ would react with the CN^- to form the weakly ionized acid HCN. As CN^- is removed, more AgCN dissolves to replace the cyanide: In the case of AgCl, the chloride ion is the conjugate base of a strong acid and would, therefore, not be affected by any amount of hydrogen ion.

$$AgCN(s) \Longleftrightarrow Ag^+(aq) + CN^-(aq) \quad [+ H_3O^+ \rightarrow HCN + H_2O]$$
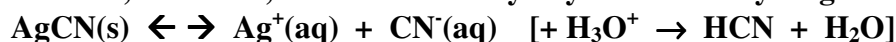
17.9   Because $K_f = 4.8 \times 10^{12}$ and because the starting concentration of NH_3 is much larger than that of the Cu^{2+} ion, you can make a rough assumption that most of the copper(II) is converted to $Cu(NH_3)_4^{2+}$ ion. This ion then dissociates slightly to give a small concentration of Cu^{2+} and additional NH_3. The amount of NH_3 remaining at the start after reacting with 0.015 M Cu^{2+} is

[0.100 M - (4 x 0.015 M)] = 0.040 M starting NH_3

Assemble the usual concentration table using this starting concentration for NH_3 and assuming the starting concentration of Cu^{2+} is zero.

Conc. (M)	$Cu(NH_3)_4^{2+}$	$\leftrightarrow$	Cu^{2+}	+	$4NH_3$
Starting	0.015		0		0.040
Change	-x		+x		+4x
Equilibrium	0.015 - x		x		0.040 + 4x

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 0.015 and 4x is negligible compared to 0.040.

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{(0.015 - x)}{(x)(0.040 + 4x)^4} \cong \frac{(0.015)}{(x)(0.040)^4} \cong 4.8 \times 10^{-12}$$

Rearrange and solve for x:

$$x = [Cu^{2+}] \cong (0.015) \div [(4.8 \times 10^{12})(0.040)^4] \cong 1.\underline{2}2 \times 10^{-9} = 1.2 \times 10^{-9} \text{ M}$$

17.10   Start by calculating the $[Ag^+]$ in equilibrium with the $Ag(CN)_2^-$ formed from Ag^+ and CN^-. Then, use the $[Ag^+]$ to decide whether or not AgI will precipitate by calculating the ion product and comparing it with the K_{sp} of 8.3×10^{-17} for AgI. Assume all the 0.0045 M Ag^+ reacts with CN^- to form 0.0045 M $Ag(CN)_2^-$, and calculate the remaining CN^-. Use these as starting concentrations for the usual concentration table.

[0.20 M KCN - (2 x 0.0045 M)] = 0.191 M starting CN^-

Conc. (M)	$Ag(CN)_2^-$	$\leftrightarrow$	Ag^+	+	$2CN^-$
Starting	0.0045		0		0.191
Change	-x		+x		+2x
Equilibrium	0.0045 - x		x		0.191 + 2x

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 0.0045 and 2x is negligible compared to 0.191.

$$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{(0.0045 - x)}{(x)(0.191 + 2x)^2} \cong \frac{(0.0045)}{(x)(0.191)^2} \cong 5.6 \times 10^{18}$$

Rearrange and solve for x:

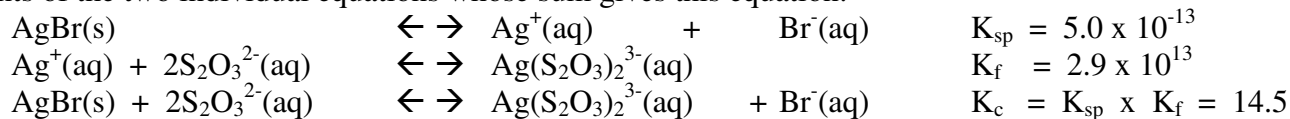$$x = [Ag^+] \cong (0.0045) \div [(5.6 \times 10^{18})(0.191)^2] \cong 2.\underline{2}02 \times 10^{-20} \text{ M}$$

Now, calculate the ion product for AgI:

$$Q_c = [Ag^+][I^-] = (2.20 \times 10^{-20})(0.15) = 3.\underline{3}0 \times 10^{-21} = 3.3 \times 10^{-21}$$

Because Q_c is less than the K_{sp} of 8.3×10^{-17}, no precipitate will form, and the solution is unsaturated.

17.11   Obtain the overall equilibrium constant for this reaction from the product of the individual equilibrium constants of the two individual equations whose sum gives this equation:

$AgBr(s)$	$\leftrightarrow$	$Ag^+(aq)$	+	$Br^-(aq)$	$K_{sp} = 5.0 \times 10^{-13}$
$Ag^+(aq) + 2S_2O_3^{2-}(aq)$	$\leftrightarrow$	$Ag(S_2O_3)_2^{3-}(aq)$			$K_f = 2.9 \times 10^{13}$
$AgBr(s) + 2S_2O_3^{2-}(aq)$	$\leftrightarrow$	$Ag(S_2O_3)_2^{3-}(aq)$	+	$Br^-(aq)$	$K_c = K_{sp} \times K_f = 14.5$

Assemble the usual table using 1.0 M as the starting concentration of $S_2O_3^{2-}$ and x as the unknown concentration of $Ag(S_2O_3)_2^{3-}$ formed.

Conc. (M)	AgBr(s)	+	$2S_2O_3^{2-}$	⟵⟶	$Ag(S_2O_3)_2^{3-}$	+	Br^-
Starting			1.0		0		0
Change			-2x		+x		+x
Equilibrium			1.0 - 2x		x		x

The equilibrium-constant expression can now be used. Simply substitute all exact equilibrium concentrations into the equilibrium-constant expression. The solution can be obtained without using the quadratic equation.

$$K_c = \frac{[Ag(S_2O_3)_2^{3-}][Br^-]}{[S_2O_3^{2-}]^2} = \frac{(x)^2}{(1.0 - 2x)^2} = 14.5$$

Take the square root of both sides of the two right-hand terms, and solve for x:

$$\frac{x}{(1.0 - 2x)} = 3.\underline{8}08$$

$$x = 3.808\,(1.0 - 2x)$$

$7.62x + x = 3.808$

$x = 0.4\underline{4}17 = 0.44$ M   (Molar solubility of AgBr in 1.0 M $Na_2S_2O_3$)

■   **Answers to Concept Checks**
17.1   Solubility and K_{sp} are related, although not directly. You can compare K_{sp}'s for a series of salts, however, if they have the same number of cations and anions in each of their formulas. (In that case, K_{sp} and solubility are related in the same way for each salt.) In this problem, each of the lead(II) compounds has one Pb^{2+} cation and one anion, so you can compare the K_{sp}'s directly.
Lead(II) sulfate has the largest K_{sp} and, therefore, is the most soluble of these lead(II) compounds.

**17.2**   Let's look at each compound in turn.
$NaNO_3$ has no ion in common with $PbSO_4$, so it should have little effect on its solubility.
Na_2SO_4 is a soluble compound and provides the common ion SO_4^{2-}, which would repress the solubility of $PbSO_4$.
PbS has an ion in common with $PbSO_4$ (Pb^{2+}), but the compound is so insoluble that very little of the Pb^{2+} ion is available.
Because of this, the solubility of $PbSO_4$ is little affected by the PbS. Therefore, the $NaNO_3$ solution will dissolve the most $PbSO_4$.

17.3   If NaCl were added to a saturated AgCl solution, the equilibrium would shift to consume the added chloride ion, and some AgCl would precipitate. After the addition of two Cl^- ions, there would be five Cl^- ions, three Ag^+ ions, and two AgCl molecules. The solution would look like the following (Na^+ not shown for clarity).
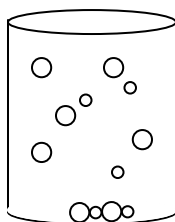
AgCl
Cl^-
Ag^+

17.4   If you compare K_{sp}'s for magnesium oxalate (8.5×10^{-5}) and calcium oxalate (2.3×10^{-9}), you can see magnesium oxalate is much more soluble in water solution than the calcium salt (the K_{sp} is larger). This means it provides a greater concentration of oxalate ion. In water solution, some of the magnesium oxalate dissolves, giving an oxalate ion concentration that tends to repress the dissolution of calcium oxalate (common-ion effect). The addition of acid tends to remove oxalate ion, but this is replenished by the dissolution of more magnesium oxalate. Therefore, you would expect the magnesium oxalate to be more likely to dissolve.