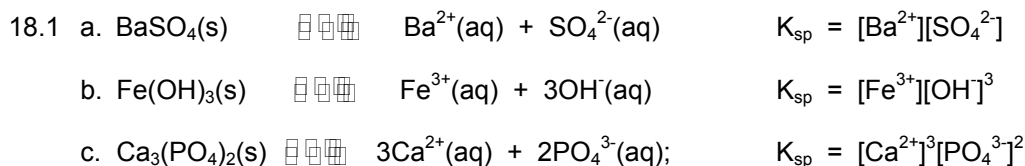# 18. SOLUBILITY AND COMPLEX-ION EQUILIBRIA

■ Solutions to Exercises

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

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

18.2   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			$+1.33 \times 10^{-5}$		$+1.33 \times 10^{-5}$
Equilibrium			1.33×10^{-5}		1.33×10^{-5}

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

18.3   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			$+3(3.34 \times 10^{-8})$		$+2(3.34 \times 10^{-8})$
Equilibrium			$3(3.34 \times 10^{-8})$		$2(3.34 \times 10^{-8})$

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

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

18.4   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.

(continued)

$$[Ca^{2+}][SO_4^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 2.4 \times 10^{-5}$$

$$x = \sqrt{(2.4 \times 10^{-5})} = 4.\underline{8}9 \times 10^{-3} \text{ M}$$

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

18.5 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.

18.6   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.

18.7   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.

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

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

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.

18.8   The solubility of AgCN would increase as the pH decreases 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:

$$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq) \quad [+ H_3O^+ \rightarrow HCN + H_2O]$$
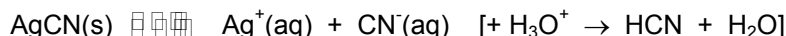
In the case of AgCl, the chloride ion is the conjugate base of a strong acid and would, therefore, not be affected by any amount of hydrogen ion.

18.9   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

$$[0.100 \text{ M} - (4 \times 0.015 \text{ M})] = 0.040 \text{ M starting } NH_3$$

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

Conc. (M)	$Cu(NH_3)_4^{2+}$ $\rightleftharpoons$	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:

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

18.10   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)	$Ag(CN)_2^-$	🔲🔲🔳	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.

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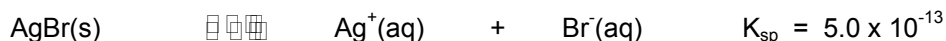
Rearrange and solve for x:

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

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.

18.11 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:

$AgBr(s)$ $\rightleftharpoons$ $Ag^+(aq)$ + $Br^-(aq)$ $\qquad K_{sp} = 5.0 \times 10^{-13}$

$Ag^+(aq) + 2S_2O_3^{2-}(aq)$ $\rightleftharpoons$ $Ag(S_2O_3)_2^{3-}(aq)$ $\qquad K_f = 2.9 \times 10^{13}$

$AgBr(s) + 2S_2O_3^{2-}(aq)$ $\rightleftharpoons$ $Ag(S_2O_3)_2^{3-}(aq)$ + $Br^-(aq)$

$$K_c = K_{sp} \times K_f = 14.5$$

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)	+ $2S_2O_3^{2-}$	$\rightleftharpoons$	$Ag(S_2O_3)_2^{3-}$ +	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:

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

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

$$7.62x + x = 3.808$$

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

■ Answers to Concept Checks

18.1   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.

18.2   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 $PbSO_4$.

18.3   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).
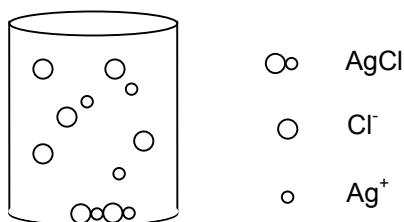
18.4   If you compare K_{sp}'s for magnesium oxalate (8.5×10^{-5}) and calcium oxalate (2.3×10^{-9}), you can see magnesium oxalate is much more soluble in water solution than the calcium salt (the K_{sp} is larger). This means it provides a greater concentration of oxalate ion. In water solution, some 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.

■ Answers to Review Questions

18.1 The solubility equation is $Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$. If the molar solubility of $Ni(OH)_2$ = x molar, the concentrations of the ions in the solution must be x M Ni^{2+} and 2x M OH^-. Substituting into the equilibrium-constant expression gives

$$K_{sp} = [Ni^{2+}][OH^-]^2 = (x)(2x)^2 = 4x^3$$

18.2 Calcium sulfate is less soluble in a solution containing sodium sulfate because the increase in sulfate from the sodium sulfate causes the equilibrium composition in the equation below to shift to the left:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

The result is a decrease in both the calcium ion and the calcium sulfate concentrations.

18.3 Substitute the 0.10 M concentration of chloride into the solubility product expression and solve for $[A^+]$:

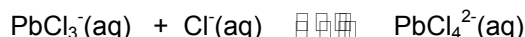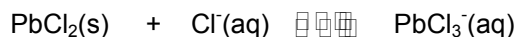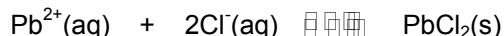$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.10} = 1.\underline{8}0 \times 10^{-9} = 1.8 \times 10^{-9} \text{ M}$$

18.4 In order to predict whether or not PbI_2 will precipitate when lead nitrate and potassium iodide are mixed, the concentrations of Pb^{2+} and I^- after mixing would have to be calculated first (if the concentrations are not known or are not given). Then, the value of Q_c, the ion product, would have to be calculated for PbI_2. Finally, Q_c would have to be compared with the value of K_{sp}. If $Q_c > K_{sp}$, then a precipitate will form at equilibrium. If Q_c is ≤ than K_{sp}, no precipitate will form.

18.5 Barium fluoride, normally insoluble in water, dissolves in dilute hydrochloric acid because the fluoride ion, once it forms, reacts with the hydronium ion to form weakly ionized HF:

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq) \ [+ 2H_3O^+ \rightarrow 2HF + 2H_2O]$$
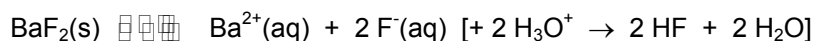
18.6 Metal ions such as Pb^{2+} and Zn^{2+} are separated by controlling the $[S^{2-}]$ in a solution of saturated H_2S by means of adjusting the pH correctly. Because the K_{sp} of 2.5×10^{-27} for PbS is smaller than the K_{sp} of 1.1×10^{-21} for ZnS, the pH can be adjusted to make the $[S^{2-}]$ just high enough to precipitate PbS without precipitating ZnS.

18.7 When NaCl is first added to a solution of $Pb(NO_3)_2$, a precipitate of $PbCl_2$ forms. As more NaCl is added, the excess chloride reacts further with the insoluble $PbCl_2$, forming soluble complex ions of $PbCl_3^-$ and $PbCl_4^{2-}$:

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

$$PbCl_2(s) \quad + \quad Cl^-(aq) \quad \rightleftharpoons \quad PbCl_3^-(aq)$$

$$PbCl_3^-(aq) \quad + \quad Cl^-(aq) \quad \rightleftharpoons \quad PbCl_4^{2-}(aq)$$

18.8 When a small amount of NaOH is added to a solution of $Al_2(SO_4)_3$, a precipitate of $Al(OH)_3$ forms at first. As more NaOH is added, the excess hydroxide ion reacts further with the insoluble $Al(OH)_3$, forming a soluble complex ion of $Al(OH)_4^-$.

18.9 The Ag^+, Cu^{2+}, and Ni^{2+} ions can be separated in two steps: (1) Add HCl to precipitate just the Ag^+ as AgCl, leaving the others in solution. (2) After pouring the solution away from the precipitate, add 0.3 M HCl and H_2S to precipitate only the CuS away from the Ni^{2+} ion, whose sulfide is soluble under these conditions.

18.10 By controlling the pH through the appropriate buffer, one can control the $[CO_3^{2-}]$ using the equilibrium reaction:

$$H_3O^+(aq) \quad + \quad CO_3^{2-}(aq) \quad \rightleftharpoons \quad HCO_3^-(aq) \quad + \quad H_2O(l)$$

Calcium carbonate is much more insoluble than magnesium carbonate and thus will precipitate in weakly basic solution, whereas magnesium carbonate will not. Magnesium carbonate will precipitate only in highly basic solution. (There is the possibility that $Mg(OH)_2$ might precipitate, but the $[OH^-]$ is too low for this to occur.)

■ Answers to Conceptual Problems

18.11 a. Since both compounds contain the same number of ions, the salt with the larger K_{sp} value will be more soluble. The K_{sp} for AgCl is 1.8×10^{-10} and for AgI is 8.3×10^{-17}. Therefore, silver chloride (AgCl) is more soluble.

b. Since both compounds contain the same number of ions, the salt with the larger K_{sp} value will be more soluble. The K_{sp} for $Mg(OH)_2$ is 1.8×10^{-11} and for $Cu(OH)_2$ is 2.6×10^{-19}. Therefore, magnesium hydroxide ($Mg(OH)_2$) is more soluble.

18.12 Dissolve a sample of each mineral in water in a separate container. NaCl is soluble in water, and CaF_2 is insoluble in water ($K_{sp} = 3.4 \times 10^{-11}$), so the sample that dissolves is NaCl, and the sample that doesn't dissolve is CaF_2.

18.13 0.1 M NaCl will be most effective in causing a precipitate from a saturated solution of $PbCl_2$, since it is completely soluble and contains the common ion Cl^-. Therefore, the answer is a.

18.14   The beaker on the left depicts all the AgCl as individual formula units in solution. This implies AgCl is a soluble nonelectrolye, which is not the case since AgCl as a slightly soluble ionic compound. The center beaker depicts AgCl as a soluble ionic compound that completely dissolves in solution, leaving no AgCl(s). Once again, this cannot be correct since AgCl is slightly soluble. The beaker on the right indicates there are ions of Ag^+ and Cl^- present in the solution along with solid AgCl. This is consistent with AgCl being a slightly soluble ionic compound.

18.15   The beaker on the left depicts all the NaCl as individual formula units in solution. This implies NaCl is a soluble nonelectrolye, which is not the case since NaCl is a very soluble ionic compound that produces ions in solution. The center beaker depicts NaCl as a soluble ionic compound that completely dissolves in solution, producing as only $Na^+(aq)$ and $Cl^-(aq)$. This must be correct since NaCl is a very soluble ionic compound. The beaker on the right indicates there are ions of Na^+ and Cl^- present in the solution along with solid NaCl. The presence of solid is not consistent with NaCl being a very soluble ionic compound.

18.16   When first added to a solution of copper(II) nitrate, the ammonia causes a pale blue precipitate of $Cu(OH)_2$ to form (K_{sp} = 2.6 x 10^{-19}). After enough ammonia has been added, however, the complex ion $Cu(NH_3)_4^{2+}$ forms (K_f = 4.8 x 10^{12}), and the precipitate dissolves.

18.17   Add just enough Na_2SO_4 to precipitate all the Ba^{2+}; filter off the $BaSO_4$; add more Na_2SO_4 to precipitate all the Ca^{2+}; filter off the $CaSO_4$; Mg^{2+} remains in the solution.

18.18   When a precipitate fails to form when HCl is added to the solution, this indicates no silver ion is present. When a precipitate fails to form when the solution is acidified and H_2S is added, this indicates no copper(II) ion is present in the solution.

■ Solutions to Practice Problems

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

18.19 a. NaBr is soluble (Group IA salts are soluble).

   b. PbI_2 is insoluble (PbI_2 is an insoluble iodide).

   c. $BaCO_3$ is insoluble (Carbonates are generally insoluble).

   d. $(NH_4)_2SO_4$ is soluble (All ammonium salts are soluble).

18.20 a. $Ca(NO_3)_2$ is soluble (Nitrate salts are soluble).

b. AgBr is insoluble (AgBr is an insoluble bromide salt).

c. MgI_2 is soluble (Iodide salts are generally soluble).

d. $PbSO_4$ is insoluble ($PbSO_4$ is an insoluble sulfate salt).

18.21 a. $K_{sp} = [Mg^{2+}][OH^-]^2$ b. $K_{sp} = [Sr^{2+}][CO_3^{2-}]$

c. $K_{sp} = [Ca^{2+}]^3[AsO_4^{3-}]^2$ d. $K_{sp} = [Fe^{3+}][OH^-]^3$

18.22 a. $K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2$ b. $K_{sp} = [Fe^{3+}][PO_4^{3-}]$

c. $K_{sp} = [Pb^{2+}][I^-]^2$ d. $K_{sp} = [Ag^+]^2[S^{2-}]$

18.23   Calculate molar solubility, assemble the usual table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. (Dashes are given for $AgBrO_3(s)$; in later problems, the dashes are omitted.)

$$\frac{7.2 \times 10^{-3} \text{ g}}{L} \times \frac{1 \text{ mol}}{236 \text{ g}} = 3.0\underline{5} \times 10^{-5} \text{ M}$$

Conc. (M)	$AgBrO_3(s)$ ⇌	Ag^+	+	BrO_3^-
Starting	—	0		0
Change	—	$+3.05 \times 10^{-5}$		$+3.05 \times 10^{-5}$
Equilibrium	—	3.05×10^{-5}		3.05×10^{-5}

$K_{sp} = [Ag^+][BrO_3^-] = (3.05 \times 10^{-5})(3.05 \times 10^{-5}) = 9.\underline{3}02 \times 10^{-10} = 9.3 \times 10^{-10}$

18.24   Assemble the usual concentration table, and substitute from it the equilibrium concentrations into the equilibrium-constant expression.

Conc. (M)	$MgC_2O_4(s)$ ⇌	Mg^{2+}	+	$C_2O_4^{2-}$
Starting		0		0
Change		$+9.3 \times 10^{-3}$		$+9.3 \times 10^{-3}$
Equilibrium		9.3×10^{-3}		9.3×10^{-3}

$K_{sp} = [Mg^{2+}][C_2O_4^{2-}] = (9.3 \times 10^{-3})(9.3 \times 10^{-3}) = 8.\underline{6}49 \times 10^{-5} = 8.6 \times 10^{-5}$

18.25 Calculate the molar solubility. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$$\frac{0.13 \text{ g}}{0.100 \text{ L}} \times \frac{1 \text{ mol}}{413 \text{ g}} = 3.\underline{1}47 \times 10^{-3} \text{ M}$$

Conc. (M)	$Cu(IO_3)_2(s)$	⇌	Cu^{2+}	+	$2IO_3^-$
Starting			0		0
Change			$+3.147 \times 10^{-3}$		$+2 \times 3.147 \times 10^{-3}$
Equilibrium			3.147×10^{-3}		$2 \times 3.147 \times 10^{-3}$

$K_{sp} = [Cu^{2+}][IO_3^-]^2 = (3.147 \times 10^{-3})[2(3.147 \times 10^{-3})]^2 = 1.\underline{2}47 \times 10^{-7} = 1.2 \times 10^{-7}$

18.26 Calculate the molar solubility. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$$\frac{0.022 \text{ g}}{\text{L}} \times \frac{1 \text{ mol}}{332 \text{ g}} = 6.\underline{6}2 \times 10^{-5} \text{ M}$$

Conc. (M)	$Ag_2CrO_4(s)$	⇌	$2Ag^+$	+	CrO_4^{2-}
Starting			0		0
Change			$+2(6.62 \times 10^{-5})$		6.62×10^{-5}
Equilibrium			$2(6.62 \times 10^{-5})$		6.62×10^{-5}

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = [2(6.62 \times 10^{-5})]^2(6.62 \times 10^{-5}) = 1.\underline{1}6 \times 10^{-12} = 1.2 \times 10^{-12}$

18.27 Calculate the pOH from the pH, and then convert pOH to [OH⁻]. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$pOH = 14.00 - 10.52 = 3.48$

$[OH^-] = \text{antilog} (-pOH) = \text{antilog} (-3.48) = 3.\underline{3}11 \times 10^{-4} \text{ M}$

$[Mg^{2+}] = [OH^-] \div 2 = (3.311 \times 10^{-4}) \div 2 = 1.655 \times 10^{-4} \text{ M}$

Conc. (M)	$Mg(OH)_2(s)$	⇌	Mg^{2+}	+	$2OH^-$
Starting			0		0
Change			$+1.655 \times 10^{-4}$		$+3.311 \times 10^{-4}$
Equilibrium			1.655×10^{-4}		3.311×10^{-4}

$K_{sp} = [Mg^{2+}][OH^-]^2 = (1.655 \times 10^{-4})(3.311 \times 10^{-4})^2 = 1.\underline{8}1 \times 10^{-11} = 1.8 \times 10^{-11}$

18.28   Calculate the pOH from the pH, and then convert pOH to [OH⁻].

$$pOH = 14.00 - 12.35 = 1.65$$

$$[OH^-] = \text{antilog }(-pOH) = \text{antilog }(-1.65) = 2.\underline{2}38 \times 10^{-2} \text{ M}$$

$$[Ca^{2+}] = [OH^-] \div 2 = (2.238 \times 10^{-2}) \div 2 = 1.119 \times 10^{-2} \text{ M}$$

Assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

Conc. (M)	Ca(OH)$_2$(s)	⇌	Ca^{2+}	+	2OH⁻
Starting			0		0
Change			+1.119 × 10⁻²		+2.238 × 10⁻²
Equilibrium			1.119 × 10⁻²		2.238 × 10⁻²

$$K_{sp} = [Ca^{2+}][OH^-]^2 = (1.119 \times 10^{-2})(2.238 \times 10^{-2})^2 = 5.\underline{6}0 \times 10^{-6} = 5.6 \times 10^{-6}$$

18.29   Assemble the usual concentration table. Let x equal the molar solubility of SrCO$_3$. When x mol SrCO$_3$ dissolves in one L of solution, x mol Sr^{2+} and x mol CO$_3^{2-}$ form.

Conc. (M)	SrCO$_3$(s)	⇌	Sr^{2+}	+	CO$_3^{2-}$
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 grams SrCO$_3$ per liter.

$$[Sr^{2+}][CO_3^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 9.3 \times 10^{-10}$$

$$x = \sqrt{(9.3 \times 10^{-10})} = 3.\underline{0}4 \times 10^{-5} \text{ M}$$

$$\frac{3.04 \times 10^{-5} \text{ mol}}{L} \times \frac{147.63 \text{ g}}{1 \text{mol SrCO}_3} = 4.\underline{5}0 \times 10^{-3} = 0.0045 \text{ g/L}$$

18.30 Assemble the usual concentration table. Let x equal the molar solubility of $MgCO_3$.
When x mol $MgCO_3$ dissolves in one L of solution, x mol Mg^{2+} and x mol CO_3^{2-} form.

Conc. (M)	$MgCO_3(s)$	⇌	Mg^{2+}	+	CO_3^{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 grams $MgCO_3$ per liter.

$$[Mg^{2+}][CO_3^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 1.0 \times 10^{-5}$$

$$x = \sqrt{(1.0 \times 10^{-5})} = 3.\underline{1}62 \times 10^{-3} \text{ M}$$

$$\frac{3.162 \times 10^{-3} \text{ mol}}{L} \times \frac{84.32 \text{ g}}{1 \text{ mol } MgCO_3} = 0.2\underline{6}66 = 0.27 \text{ g/L}$$

18.31 Let x equal the molar solubility of PbF_2. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$PbF_2(s)$	⇌	Pb^{2+}	+	$2F^-$
Starting			0		0
Change			+x		+2x
Equilibrium			x		2x

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

$$(x)(2x)^2 = 4x^3 = 2.7 \times 10^{-8}$$

$$x = \sqrt[3]{\frac{2.7 \times 10^{-8}}{4}} = 1.\underline{8}8 \times 10^{-3} = 1.9 \times 10^{-3} \text{ M}$$

18.32 Let x equal the molar solubility of MgF_2. Assemble the usual concentration table.

Conc. (M)	$MgF_2(s)$	⇌	Mg^{2+}	+	$2F^-$
Starting			0		0
Change			+x		+2x
Equilibrium			x		2x

Substitute from the table into the equilibrium-constant expression

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

$$(x)(2x)^2 = 4x^3 = 7.4 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{7.4 \times 10^{-11}}{4}} = 2.\underline{6}44 \times 10^{-4} = 2.6 \times 10^{-4} \text{ M}$$

18.33 At the start, before any $SrSO_4$ dissolves, the solution contains 0.23 M SO_4^{2-}. At equilibrium, x mol of solid $SrSO_4$ dissolves to yield x mol Sr^{2+} and x mol SO_4^{2-}. Assemble the usual concentration table, and substitute the equilibrium concentrations into the equilibrium-constant expression. As an approximation, assume x is negligible compared to 0.23 M SO_4^{2-}.

Conc. (M)	$SrSO_4(s)$	⇌	Sr^{2+}	+	SO_4^{2-}
Starting			0		0.23
Change			+x		+x
Equilibrium			x		0.23 + x

$$[Sr^{2+}][SO_4^{2-}] = K_{sp}$$

$$(x)(0.23 + x) \cong (x)(0.23) \cong 2.5 \times 10^{-7}$$

$$x \cong \frac{2.5 \times 10^{-7}}{0.23} = 1.\underline{0}86 \times 10^{-6} \text{ M}$$

$$\frac{1.086 \times 10^{-6} \text{ mol}}{L} \times \frac{183.69 \text{ g}}{1 \text{ mol } SrSO_4} = 1.\underline{9}9 \times 10^{-4} = 2.0 \times 10^{-4} \text{ g/L}$$

Note that adding x to 0.23 M will not change it (to two significant figures), so x is negligible compared to 0.23 M.

18.34 Let x = the molar solubility of $PbCrO_4$. At the start, before any $PbCrO_4$ dissolves, the solution contains 0.13 M CrO_4^{2-}. At equilibrium, x mol of solid $PbCrO_4$ dissolves to yield x mol Pb^{2+} and x mol CrO_4^{2-}. Assemble the usual concentration table, and substitute the equilibrium concentrations into the equilibrium-constant expression. As an approximation, assume x is negligible compared to 0.13 M CrO_4^{2-}.

Conc. (M)	$PbCrO_4(s)$	⇌	Pb^{2+}	+	CrO_4^{2-}
Starting			0		0.13
Change			+x		+x
Equilibrium			x		0.13 + x

$[Pb^{2+}][CrO_4^{2-}] = K_{sp}$

$(x)(0.13 + x) \cong (x)(0.13) \cong 1.8 \times 10^{-14}$

$$x \cong \frac{1.8 \times 10^{-14}}{0.13} = 1.\underline{3}8 \times 10^{-13} \text{ M}$$

$$\frac{1.38 \times 10^{-13} \text{ mol}}{L} \times \frac{323.2 \text{ g}}{1 \text{ mol } PbCrO_4} = 4.\underline{4}7 \times 10^{-11} = 4.5 \times 10^{-11} \text{ g/L}$$

Note that adding x to 0.13 M will not change it (to two significant figures), so x is negligible compared to 0.13 M.

18.35 Calculate the value of K_{sp} from the solubility using the concentration table. Then, using the common-ion calculation, assemble another concentration table. Use 0.020 M NaF as the starting concentration of F^- ion. Substitute the equilibrium concentrations from the table into the equilibrium-constant expression. As an approximation, assume 2x is negligible compared to 0.020 M F^- ion.

$$\frac{0.016 \text{ g}}{L} \times \frac{1 \text{ mol } MgF_2}{62.31 \text{ g}} = 2.\underline{5}67 \times 10^{-4} \text{ M}$$

Conc. (M)	$MgF_2(s)$	⇌	Mg^{2+}	+	$2F^-$
Starting			0		0
Change			+2.\underline{5}67 × 10⁻⁴		+2 × 2.\underline{5}67 × 10⁻⁴
Equilibrium			2.\underline{5}67 × 10⁻⁴		2 × 2.\underline{5}67 × 10⁻⁴

(continued)

$$K_{sp} = [Mg^{2+}][F^-]^2 = (2.\underline{5}67 \times 10^{-4})[2(2.\underline{5}67 \times 10^{-4})]^2 = 6.\underline{7}72 \times 10^{-11}$$

Now, use K_{sp} to calculate the molar solubility of MgF_2.

Conc. (M)	$MgF_2(s)$	⇌	Mg^{2+}	+	$2F^-$
Starting			0		0.020
Change			+x		+2x
Equilibrium			x		0.020 + 2x

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

$$(x)(0.020 + 2x)^2 \cong (x)(0.020)^2 = 6.\underline{7}72 \times 10^{-11}$$

$$x \cong \frac{6.772 \times 10^{-11}}{(0.020)^2} = 1.\underline{6}93 \times 10^{-7} \text{ M}$$

$$\frac{1.693 \times 10^{-7} \text{ mol}}{L} \times \frac{62.31 \text{ g}}{1 \text{ mol } MgF_2} = 1.\underline{0}54 \times 10^{-5} = 1.1 \times 10^{-5} \text{ g/L}$$

18.36   Calculate the value of K_{sp} from the solubility using the concentration table. Then, using the common-ion calculation, assemble another concentration table. Use 0.45 M Na_2SO_4 as the starting concentration of SO_4^{2-} ion. Substitute the equilibrium concentrations from the table into the equilibrium-constant expression. As an approximation, assume x is negligible compared to 0.45 M SO_4^{2-} ion.

$$\frac{8.0 \text{ g}}{L} \times \frac{1 \text{ mol } Ag_2SO_4}{311.81 \text{ g}} = 0.02\underline{5}65 \text{ M}$$

Conc. (M)	$Ag_2SO_4(s)$	⇌	$2Ag^+$	+	SO_4^{2-}
Starting			0		0
Change			+2 x 0.02565		+0.02565
Equilibrium			2 x 0.02565		0.02565

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2 \times 0.02565)^2(0.02565) = 6.\underline{7}55 \times 10^{-5}$$

Now, use K_{sp} to calculate the molar solubility of Ag_2SO_4.

(continued)

Conc. (M)	$Ag_2SO_4(s)$	⇌	$2Ag^+$	+	SO_4^{2-}
Starting			0		0.45
Change			+2x		+x
Equilibrium			2x		0.45 + x

$$[Ag^+]^2[SO_4^{2-}] = K_{sp}$$

$$(2x)^2(0.45 + x) \cong (2x)^2(0.45) = 6.755 \times 10^{-5}$$

$$x \cong \sqrt{\frac{(6.755 \times 10^{-5})}{4 \times 0.45}} = 6.\underline{1}25 \times 10^{-3} \text{ M}$$

$$\frac{6.125 \times 10^{-3} \text{ mol}}{L} \times \frac{311.81 \text{ g}}{1 \text{ mol } Ag_2SO_4} = 1.\underline{9}10 = 1.9 \text{ g/L}$$

18.37 The concentration table follows.

Conc. (M)	$MgC_2O_4(s)$	⇌	Mg^{2+}	+	$C_2O_4^{2-}$
Starting			0		0.020
Change			+x		+x
Equilibrium			x		0.020 + x

The equilibrium-constant equation is

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

$$8.5 \times 10^{-5} = x(0.020 + x)$$

$$x^2 + 0.020x - (8.5 \times 10^{-5}) = 0$$

Solving the quadratic equation gives

$$x = \frac{-0.020 \pm \sqrt{(0.020)^2 + 4(8.5 \times 10^{-5})}}{2} = 0.00\underline{3}6 \text{ M}$$

The solubility in grams per liter is

$$\frac{0.0036 \text{ mol}}{L} \times \frac{112 \text{ g}}{1 \text{ mol}} = 0.4\underline{0}3 = 0.4 \text{ g/L}$$

18.38   The concentration table follows.

Conc. (M)	SrSO$_4$(s)	⇌	Sr^{2+}	+	SO$_4^{2-}$
Starting			0		0.0015
Change			+x		+x
Equilibrium			x		0.0015 + x

K_{sp} = 2.5 x 10^{-7} = x(0.0015 + x)

x^2 + 0.0015x - (2.5 x 10^{-7}) = 0

Solving the quadratic equation gives

$$x = \frac{-0.0015 \pm \sqrt{(0.0015)^2 + 4(2.5 \times 10^{-7})}}{2} = 1.\underline{5}1 \times 10^{-4} \text{ M}$$

The solubility in grams per liter is

$$\frac{1.51 \times 10^{-4} \text{ mol}}{L} \times \frac{183.69 \text{ g}}{1 \text{ mol SrSO}_4} = 0.02\underline{7}7 = 0.03 \text{ g/L}$$

18.39 a. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then, compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then, use parentheses for the concentrations.

Q_c = [Ba^{2+}][F$^-$]^2

Q_c = (0.020)(0.015)^2 = 4.$\underline{5}$0 x 10^{-6}

Since Q_c > K_{sp} (1.0 x 10^{-6}), precipitation will occur.

b. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then, compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then, use parentheses for the concentrations.

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

Q_c = (0.0035)(0.15)^2 = 7.$\underline{8}$7 x 10^{-5}

Since Q_c > K_{sp} (1.6 x 10^{-5}), precipitation will occur.

18.40 a. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then, compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then, use parentheses for the concentrations.

$$Q_c = [Sr^{2+}][CrO_4^{2-}]$$

$$Q_c = (0.012)(0.0015) = 1.\underline{8}0 \times 10^{-5}$$

Since $Q_c < K_{sp}$ (3.5×10^{-5}), no precipitation will occur.

b. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then, compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then, use parentheses for the concentrations.

$$Q_c = [Mg^{2+}][CO_3^{2-}]$$

$$Q_c = (0.0012)(0.041) = 8.\underline{6}1 \times 10^{-5}$$

Since $Q_c > K_{sp}$ (1.0×10^{-5}), precipitation will occur.

18.41 Calculate the ion product, Q_c, after preparation of the solution, assuming no precipitation has occurred. Compare it with the K_{sp}.

$$Q_c = [Pb^{2+}][CrO_4^{2-}]$$

$$Q_c = (5.0 \times 10^{-4})(5.0 \times 10^{-5}) = 2.\underline{5}0 \times 10^{-8} \, M^2 \ (> K_{sp} \text{ of } 1.8 \times 10^{-14})$$

The solution is supersaturated before equilibrium is reached. At equilibrium, precipitation occurs, and the solution is saturated.

18.42 Calculate the ion product, Q_c, after preparation of the solution and assuming no precipitation has occurred. Compare it with the K_{sp}.

$$Q_c = [Pb^{2+}][SO_4^{2-}]$$

$$Q_c = (5.0 \times 10^{-4})(1.0 \times 10^{-5}) = 5.\underline{0}0 \times 10^{-9} \, M^2 \ (< K_{sp} \text{ of } 1.7 \times 10^{-8})$$

At equilibrium, no precipitation occurs, and the solution is unsaturated.

18.43 Calculate the concentrations of Mg^{2+} and OH^-, assuming no precipitation. Use a total volume of 1.0 L + 1.0 L, or 2.0 L. (Note the concentrations are halved when the volume is doubled.)

$$[Mg^{2+}] = \frac{\frac{0.0020 \text{ mol}}{L} \times 1.0 \text{ L}}{2.0 \text{ L}} = 1.\underline{0}0 \times 10^{-3} \text{ M}$$

$$[OH^-] = \frac{\frac{0.00010 \text{ mol}}{L} \times 1.0 \text{ L}}{2.0 \text{ L}} = 5.\underline{0}0 \times 10^{-5} \text{ M}$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = (Mg^{2+})(OH^-)^2 = (1.00 \times 10^{-3})(5.00 \times 10^{-5})^2 = 2.\underline{5}0 \times 10^{-12}$$

Because Q_c is less than the K_{sp} of 1.8×10^{-11}, no precipitation occurs, and the solution is unsaturated.

18.44 Calculate the concentrations of Ca^{2+} and SO_4^{2-}, assuming no precipitation. Use a total volume of 0.045 L + 0.055 L, or 0.100 L.

$$[Ca^{2+}] = \frac{\frac{0.015 \text{ mol}}{L} \times 0.045 \text{ L}}{0.100 \text{ L}} = 0.006\underline{7}5 \text{ M}$$

$$[SO_4^{2-}] = \frac{\frac{0.010 \text{ mol}}{L} \times 0.055 \text{ L}}{0.100 \text{ L}} = 0.005\underline{5}0 \text{ M}$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = [Ca^{2+}][SO_4^{2-}] = (0.00675)(0.00550) = 3.\underline{7}1 \times 10^{-5}$$

Because Q_c is greater than the K_{sp} of 2.4×10^{-5}, the solution is supersaturated before equilibrium is reached. At equilibrium, precipitation occurs, and the solution is saturated.

18.45 Calculate the concentrations of Ba^{2+} and F^-, assuming no precipitation. Use a total volume of 0.045 L + 0.075 L, or 0.120 L.

$$[Ba^{2+}] = \frac{\dfrac{0.0015 \text{ mol}}{L} \times 0.045 \text{ L}}{0.120 \text{ L}} = 5.\underline{6}25 \times 10^{-4} \text{ M}$$

$$[F^-] = \frac{\dfrac{0.0025 \text{ mol}}{L} \times 0.075 \text{ L}}{0.120 \text{ L}} = 1.\underline{5}6 \times 10^{-3} \text{ M}$$

Calculate the ion product and compare it to K_{sp}.

$$Q_c = [Ba^{2+}][F^-]^2 = (5.625 \times 10^{-4})(1.56 \times 10^{-3})^2 = 1.\underline{3}6 \times 10^{-9}$$

Because Q_c is less than the K_{sp} of 1.0×10^{-6}, no precipitation occurs, and the solution is unsaturated.

18.46 Calculate the concentrations of Pb^{2+} and Cl^-, assuming no precipitation. Use a total volume of 0.040 L + 0.065 L, or 0.105 L.

$$[Pb^{2+}] = \frac{\dfrac{0.010 \text{ mol}}{L} \times 0.065 \text{ L}}{0.105 \text{ L}} = 6.\underline{1}9 \times 10^{-3} \text{ M}$$

$$[Cl^-] = \frac{\dfrac{0.035 \text{ mol}}{L} \times 0.040 \text{ L}}{0.105 \text{ L}} = 1.\underline{3}3 \times 10^{-2} \text{ M}$$

Calculate the ion product and compare it to K_{sp}.

$$Q_c = [Pb^{2+}][Cl^-]^2 = (6.19 \times 10^{-3})(1.33 \times 10^{-2})^2 = 1.\underline{0}9 \times 10^{-6}$$

Because Q_c is less than the K_{sp} of 1.6×10^{-5}, no precipitation occurs, and the solution is unsaturated.

18.47 A mixture of $CaCl_2$ and K_2SO_4 can only precipitate $CaSO_4$ because KCl is soluble. Use the K_{sp} expression to calculate the $[Ca^{2+}]$ needed to just begin precipitating the 0.020 M SO_4^{2-} (in essentially a saturated solution). Then, convert to moles.

$$[Ca^{2+}][SO_4^{2-}] = K_{sp} = 2.4 \times 10^{-5}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{2.4 \times 10^{-5}}{2.0 \times 10^{-2}} = 1.\underline{2}0 \times 10^{-3} \text{ M}$$

The number of moles in 1.5 L of this calcium-containing solution is (mol $CaCl_2$ = mol Ca^{2+}):

$$1.5 \text{ L} \times (1.20 \times 10^{-3}) \text{ mol/L} = 1.\underline{8}0 \times 10^{-3} = 0.0018 \text{ mol } CaCl_2$$

18.48 A mixture of $MgSO_4$ and NaOH can only precipitate $Mg(OH)_2$ because Na_2SO_4 is soluble. Use the K_{sp} expression to calculate the $[Mg^{2+}]$ needed to just begin precipitating the 0.040 M OH^- (in essentially a saturated solution). Then, convert to moles and finally to grams.

$$[Mg^{2+}][OH^-]^2 = K_{sp} = 1.8 \times 10^{-11}$$

$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(0.040)^2} = 1.\underline{1}25 \times 10^{-8} \text{ M}$$

The number of moles, and grams, in 0.456 L (456 mL) of this magnesium-containing solution is (mol $MgSO_4$ = mol Mg^{2+}).

$$0.456 \text{ L} \times (1.125 \times 10^{-8} \text{ mol/L}) = 5.\underline{1}3 \times 10^{-9} \text{ mol } MgSO_4$$

$$(5.13 \times 10^{-9} \text{ mol } MgSO_4) \times (120 \text{ g } MgSO_4/1 \text{ mol } MgSO_4)$$

$$= 6.\underline{1}56 \times 10^{-7} = 6.2 \times 10^{-7} \text{ g } MgSO_4$$

18.49 Because the $AgNO_3$ solution is relatively concentrated, ignore the dilution of the solution of Cl^- and I^- from the addition of $AgNO_3$. The $[Ag^+]$ just as the AgCl begins to precipitate can be calculated from the K_{sp} expression for AgCl using $[Cl^-] = 0.015$ M. Therefore, for AgCl

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

$[Ag^+][0.015] = 1.8 \times 10^{-10}$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.015} = 1.\underline{2}0 \times 10^{-8} \text{ M}$$

The [I⁻] at this point can be obtained by substituting the [Ag⁺] into the K_{sp} expression for AgI. Therefore, for AgI

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

$[1.20 \times 10^{-8}][I^-] = 8.3 \times 10^{-17}$

$$[I^-] = \frac{8.3 \times 10^{-17}}{1.2 \times 10^{-8}} = 6.\underline{9}1 \times 10^{-9} = 6.9 \times 10^{-9} \text{ M}$$

18.50 Because the problem asks you to find [Cl⁻] at the point when Ag_2CrO_4 just begins to precipitate, we start with the K_{sp} expression for Ag_2CrO_4, and ignore temporarily what may have happened to the Cl⁻ ion. Also, because the $AgNO_3$ solution is relatively concentrated, ignore the dilution of the solution of Cl⁻ and CrO_4^{2-} from the addition of $AgNO_3$. The [Ag⁺] just as the Ag_2CrO_4 begins to precipitate can be calculated from the K_{sp} expression for Ag_2CrO_4 using $[CrO_4^{2-}] = 0.015$ M. Thus, for Ag_2CrO_4

$[Ag^+]^2[CrO_4^{2-}] = K_{sp}$

$[Ag^+]^2[0.015] = 1.1 \times 10^{-12}$

$$[Ag^+] = \sqrt{\frac{1.1 \times 10^{-12}}{0.015}} = 8.\underline{5}6 \times 10^{-6} \text{ M}$$

The [Cl⁻] at this point can be obtained by substituting the [Ag⁺] into the K_{sp} expression for AgCl. Therefore, for AgCl

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

$[8.56 \times 10^{-6}][Cl^-] = 1.8 \times 10^{-10}$

$$[Cl^-] = \frac{1.8 \times 10^{-10}}{8.56 \times 10^{-6}} = 2.\underline{1}02 \times 10^{-5} = 2.1 \times 10^{-5} \text{ M}$$

Because this Cl⁻ concentration is extremely small compared to the initial 0.015 M concentration, you can also deduce that essentially all the chloride ion precipitates before the Ag_2CrO_4 begins to precipitate.

18.51   The net ionic equation is

$$BaF_2(s) + 2\,H_3O^+(aq) \rightleftharpoons Ba^{2+}(aq) + 2\,HF(aq) + 2\,H_2O(l)$$

18.52   The net ionic equation is

$$PbCO_3(s) + 2\,H_3O^+(aq) \rightleftharpoons Pb^{2+}(aq) + CO_2(g) + 2\,H_2O(l)$$

18.53   Calculate the value of K for the reaction of H_3O^+ with both the SO_4^{2-} and F^- anions as they form by the slight dissolving of the insoluble salts. These constants are the reciprocals of the K_a values of the conjugate acids of these anions.

$$F^-(aq) + H_3O^+(aq) \rightleftharpoons HF(aq) + H_2O(l)$$

$$K = \frac{1}{K_a} = \frac{1}{6.8 \times 10^{-4}} = 1.\underline{4}7 \times 10^3$$

$$SO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HSO_4^-(aq) + H_2O(l)$$

$$K = \frac{1}{K_{a2}} = \frac{1}{1.1 \times 10^{-2}} = 9\underline{0}.9$$

Because K for the fluoride ion is relatively larger, more BaF_2 will dissolve in acid than $BaSO_4$.

18.54   Calculate the value of K for the reaction of H_3O^+ with both the SO_4^{2-} and PO_4^{3-} anions as they form by the slight dissolving of the insoluble salts. These constants are the reciprocals of the K_a values of the conjugate acids of these anions.
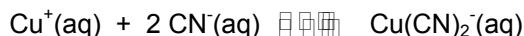
$$PO_4^{3-}(aq) + H_3O^+(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$$

$$K = \frac{1}{K_{a3}} = \frac{1}{4.8 \times 10^{-13}} = 2.\underline{0}8 \times 10^{12}$$

$$SO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HSO_4^-(aq) + H_2O(l)$$

$$K = \frac{1}{K_{a2}} = \frac{1}{1.1 \times 10^{-2}} = 9\underline{0}.9$$
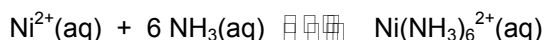
Because K for the phosphate ion is relatively larger, more $Ca_3(PO_4)_2$ will dissolve in acid than $CaSO_4$.

18.55   The equation is

$$Cu^+(aq) \ + \ 2 \ CN^-(aq) \ \rightleftharpoons \ Cu(CN)_2^-(aq)$$

The K_f expression is

$$K_f \ = \ \frac{[Cu(CN)_2^-]}{[Cu^+][CN^-]^2} \ = \ 1.0 \times 10^{16}$$

18.56   The equation is

$$Ni^{2+}(aq) \ + \ 6 \ NH_3(aq) \ \rightleftharpoons \ Ni(NH_3)_6^{2+}(aq)$$

The K_f expression is

$$K_f \ = \ \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} \ = \ 5.6 \times 10^8$$

18.57   Assume the only $[Ag^+]$ is that in equilibrium with the $Ag(CN)_2^-$ formed from Ag^+ and CN^-. (In other words, assume all the 0.015 M Ag^+ reacts with CN^- to form 0.015 M $Ag(CN)_2^-$.) Subtract the CN^- that forms the 0.015 M $Ag(CN)_2^-$ from the initial 0.100 M CN^-. Use this as the starting concentration of CN^- for the usual concentration table.

[0.100 M NaCN - (2 x 0.015 M)] = 0.070 M starting CN^-

Conc. (M)	$Ag(CN)_2^-$	$\rightleftharpoons$	Ag^+	+	$2CN^-$
Starting	0.015		0		0.070
Change	-x		+x		+2x
Equilibrium	0.015 - x		x		0.070 + 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 the exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 0.015 and 2x is negligible compared to 0.070.

$$K_f \ = \ \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} \ = \ \frac{(0.015 \ - \ x)}{(x)(0.070 \ + \ 2x)^2} \ \cong \ \frac{(0.015)}{(x)(0.070)^2} \ \cong \ 5.6 \times 10^{18}$$

Rearrange and solve for x = $[Ag^+]$:

$$x \ \cong \ (0.015) \ \div \ [(5.6 \times 10^{18})(0.070)^2] \ \cong \ 5.\underline{4}6 \times 10^{-19} \ = \ 5.5 \times 10^{-19} \ M$$

18.58 You can make a rough assumption that most of the $Zn(OH)_4^{2-}$ that dissociates forms Zn^{2+} and OH^- ions. Assemble the usual concentration table, using 0.20 M as the starting concentration for $Zn(OH)_4^{2-}$ and assuming the starting concentrations of Zn^{2+} and OH^- ions are zero.

Conc. (M)	$Zn(OH)_4^{2-}$	⇌	Zn^{2+}	+	$4OH^-$
Starting	0.20		0		0
Change	-x		+x		+4x
Equilibrium	0.20 - x		x		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 the exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 0.20.

$$K_f = \frac{[Zn(OH)_4^{2-}]}{[Zn^{2+}][OH^-]^4} = \frac{(0.20 - x)}{(x)(4x)^4} \cong \frac{(0.20)}{(x)(4x)^4} \cong 2.8 \times 10^{15}$$

Rearrange and solve for $x = [Zn^{2+}]$:

$$x \cong \sqrt[5]{\frac{(0.20)}{256 \times (2.8 \times 10^{15})}} = 1.\underline{9}4 \times 10^{-4} = 1.9 \times 10^{-4} \text{ M}$$

18.59 Start by calculating the $[Cd^{2+}]$ in equilibrium with the $Cd(NH_3)_4^{2+}$ formed from Cd^{2+} and NH_3. Then, use the $[Cd^{2+}]$ to decide whether or not CdC_2O_4 will precipitate by calculating the ion product and comparing it with the K_{sp} of 1.5×10^{-8} for CdC_2O_4. Assume all the 0.0020 M Cd^{2+} reacts with NH_3 to form 0.0020 M $Cd(NH_3)_4^{2+}$, and calculate the remaining NH_3. Use these as the starting concentrations for the usual concentration table.

$$[0.10 \text{ M NH}_3 - (4 \times 0.0020 \text{ M})] = 0.0\underline{9}2 \text{ M starting NH}_3$$

Conc. (M)	$Cd(NH_3)_4^{2+}$	⇌	Cd^{2+}	+	$4NH_3$
Starting	0.0020		0		0.092
Change	-x		+x		+4x
Equilibrium	0.0020 - x		x		0.092 + 4x

(continued)

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all the exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 0.0020 and 4x is negligible compared to 0.092.

$$K_f = \frac{[Cd(NH_3)_4{}^{2+}]}{[Cd^{2+}][NH_3]^4} = \frac{(0.0020 - x)}{(x)(0.092 + 4x)^4} \cong \frac{(0.0020)}{(x)(0.092)^4} \cong 1.0 \times 10^7$$

Rearrange and solve for x:

$$x \cong (0.0020) \div [(1.0 \times 10^7)(0.092)^4] \cong \underline{2}.79 \times 10^{-6} \, M \cong [Cd^{2+}]$$

Now, calculate the ion product for CdC_2O_4:

$$Q_c = [Cd^{2+}][C_2O_4{}^{2-}] = (2.79 \times 10^{-6})(0.010) = 2.\underline{7}9 \times 10^{-8}$$

Because Q_c is greater than the K_{sp} of 1.5×10^{-8}, the solution is supersaturated before equilibrium. At equilibrium, a precipitate will form, and the solution will be saturated.

18.60   Start by calculating the $[Ni^{2+}]$ in equilibrium with the $Ni(NH_3)_6{}^{2+}$ formed from Ni^{2+} and NH_3. Then, use the $[Ni^{2+}]$ to decide whether or not $Ni(OH)_2$ will precipitate by calculating the ion product and comparing it with the K_{sp} of 2.0×10^{-15} for $Ni(OH)_2$. Assume all the 0.0020 M Ni^{2+} reacts with NH_3 to form 0.0020 M $Ni(NH_3)_6{}^{2+}$, and calculate the remaining NH_3. Use these as starting concentrations for the usual concentration table.

$$[0.10 \, M \, NH_3 - (6 \times 0.0020 \, M)] = 0.0\underline{8}8 \, M \, \text{starting } NH_3$$

Conc. (M)	$Ni(NH_3)_6{}^{2+}$	⇌	Ni^{2+}	+	$6NH_3$
Starting	0.0020		0		0.088
Change	-x		+x		+6x
Equilibrium	0.0020 - x		x		0.088 + 6x

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all the exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming that x is negligible compared to 0.0020 and 6x is negligible compared to 0.088.

$$K_f = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = \frac{(0.0020 - x)}{(x)(0.088 + 6x)^6} \cong \frac{(0.0020)}{(x)(0.088)^6} \cong 5.60 \times 10^8$$
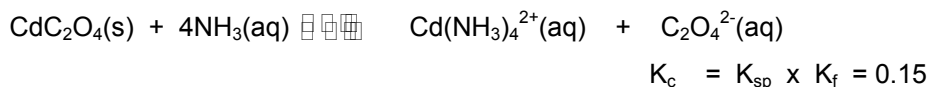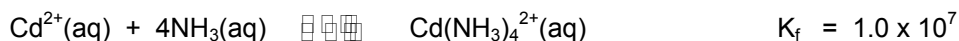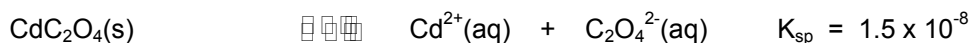
Rearrange and solve for x:

$$x \cong (0.0020) \div [5.6 \times 10^8 \times (0.088)^6] \cong \underline{7}.69 \times 10^{-6}\ M \cong [Ni^{2+}]$$

Now, calculate the ion product for $Ni(OH)_2$:

$$Q_c = [Ni^{2+}][OH^-]^2 = (7.69 \times 10^{-6})(0.010)^2 = \underline{7}.69 \times 10^{-10}$$

Because Q_c is greater than the K_{sp} of 2.0×10^{-15}, the solution is supersaturated before equilibrium. At equilibrium, a precipitate will form, and the solution will be saturated.

18.61 Using the rule from Chapter 15, 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.

$CdC_2O_4(s)$ ⇌ $Cd^{2+}(aq) + C_2O_4^{2-}(aq)$		$K_{sp} = 1.5 \times 10^{-8}$
$Cd^{2+}(aq) + 4NH_3(aq)$ ⇌ $Cd(NH_3)_4^{2+}(aq)$		$K_f = 1.0 \times 10^7$

$$CdC_2O_4(s) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq) + C_2O_4^{2-}(aq)$$

$$K_c = K_{sp} \times K_f = 0.15$$

Assemble the usual table using 0.10 M as the starting concentration of NH_3 and x as the unknown concentration of $Cd(NH_3)_4^{2+}$ formed.

Conc. (M)	$CdC_2O_4(s)$	+	$4NH_3$	⇌	$Cd(NH_3)_4^{2+}$	+	$C_2O_4^{2-}$
Starting			0.10		0		0
Change			-4x		+x		+x
Equilibrium			0.10 - 4x		x		x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression.

$$K_c = \frac{[Cd(NH_3)_4^{2+}][C_2O_4^{2-}]}{[NH_3]^4} = \frac{(x)^2}{(0.10 - 4x)^4} = 0.15$$

Take the square root of both sides of the two right-hand terms, rearrange into a quadratic equation, and solve for x:

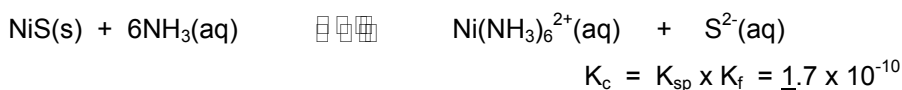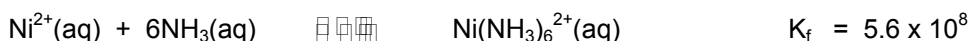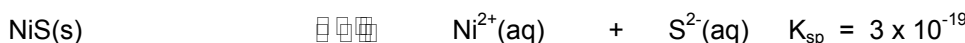$$\frac{x}{(0.10 - 4x)^2} = 0.3\underline{8}7$$

$$16x^2 - 3.38x + 0.010 = 0$$

$$x = \frac{3.38 \pm \sqrt{(-3.38)^2 - 4(16)(0.010)}}{2(16)} = 0.208 \text{ (too large) and } 3.\underline{0}01 \times 10^{-3}$$

Using the smaller root, $x = 3.\underline{0}01 \times 10^{-3} = 3.0 \times 10^{-3}$ M (molar solubility of CdC_2O_4)

18.62 Using the rule from Chapter 15, 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.

$NiS(s)$ ⇌ $Ni^{2+}(aq)$ + $S^{2-}(aq)$ $K_{sp} = 3 \times 10^{-19}$

$Ni^{2+}(aq) + 6NH_3(aq)$ ⇌ $Ni(NH_3)_6^{2+}(aq)$ $K_f = 5.6 \times 10^8$

$NiS(s) + 6NH_3(aq)$ ⇌ $Ni(NH_3)_6^{2+}(aq)$ + $S^{2-}(aq)$

$$K_c = K_{sp} \times K_f = \underline{1}.7 \times 10^{-10}$$

Assemble the usual table using 0.10 M as the starting concentration of NH_3 and x as the unknown concentration of $Ni(NH_3)_6^{2+}$ formed.

Conc (M)	NiS(s)	+	6NH₃	⇌	Ni(NH₃)₆²⁺	+	S²⁻
Starting			0.10		0		0
Change			-6x		+x		+x
Equilibrium			0.10 - 6x		x		x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression. It will be necessary to simplify the exact equation to obtain a solution without using a higher-order equation.

$$K_c = \frac{[Ni(NH_3)_6^{2+}][S^{2-}]}{[NH_3]^6} = \frac{(x)^2}{(0.10 - 6x)^6} = 1.7 \times 10^{-10}$$

Take the square root of both sides of the two right-hand terms. Note that the resulting equation contains an x^3 term and an x term.

$$\frac{x}{(0.10 - 6x)^3} = \underline{1}.3 \times 10^{-5}$$

Assume $6x$ is negligible compared to 0.10 M, and solve the above equation for x:

$$\frac{x}{(0.10)^3} = \underline{1}.3 \times 10^{-5}$$

$$x = \underline{1}.3 \times 10^{-8} = 1 \times 10^{-8} \text{ M} \text{ (molar solubility of NiS in 0.10 M NH}_3\text{)}$$

18.63   The Pb^{2+}, Cd^{2+}, and Sr^{2+} ions can be separated in two steps: (1) Add HCl to precipitate only the Pb^{2+} as $PbCl_2$, leaving the others in solution. (2) After pouring the solution away from the precipitate, add 0.3 M HCl and H_2S to precipitate only the CdS away from the Sr^{2+} ion, whose sulfide is soluble under these conditions.

18.64   The Hg^{2+}, Ca^{2+}, and Na^+ ions can be separated in two steps: (1) Add 0.3 M HCl and H_2S to precipitate only the HgS, leaving the others in solution. (2) After pouring the solution away from the precipitate, add NH_3 and $(NH_4)_2HPO_4$ to precipitate only the $Ca_3(PO_4)_2$ away from the Na^+ ion, whose phosphate is soluble under these conditions.

18.65 a. Ag^+ is not possible because no precipitate formed with HCl.

   b. Ca^{2+} is not possible if the compound contains only one cation because Mn^{2+} is indicated by the evidence. However, if the compound consists of two or more cations, Ca^{2+} is possible because no reactions were described involving Ca^{2+}.

   c. Mn^{2+} is possible because a precipitate was obtained with basic sulfide ion.

   d. Cd^{2+} is not possible because no precipitate was obtained with acidic sulfide solution.

18.66 $PbCrO_4$ is not the compound formed from H_2S because it doesn't contain sulfide ion. CdS is possible because it contains sulfide ion and precipitates in acidic sulfide (Analytical Group II). Neither MnS nor Ag_2S is possible because neither falls into Analytical Group II.

■ Solutions to General Problems

18.67 Assemble the usual concentration table. Let x equal the molar solubility of $PbSO_4$. When x mol $PbSO_4$ dissolves in one L of solution, x mol Pb^{2+} and x mol SO_4^{2-} form.

Conc. (M)	$PbSO_4(s)$	⇌	Pb^{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.

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 1.7 \times 10^{-8}$$

$$x = \sqrt{(1.7 \times 10^{-8})} = 1.\underline{3}03 \times 10^{-4} = 1.3 \times 10^{-4} \text{ M}$$

18.68 Assemble the usual concentration table. Let x equal the molar solubility of HgS. When x mol HgS dissolves in one L of solution, x mol Hg^{2+} and x mol S^{2-} form.

Conc. (M)	HgS(s)	⇌	Hg^{2+}	+	S^{2-}
Starting			0		0
Change			+x		+x
Equilibrium			x		x

Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x.

$$[Hg^{2+}][S^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 1.6 \times 10^{-52}$$

$$x = \sqrt{(1.6 \times 10^{-52})} = 1.\underline{2}6 \times 10^{-26} = 1.3 \times 10^{-26} \text{ M}$$

18.69 Let x equal the molar solubility of Hg_2Cl_2. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$Hg_2Cl_2(s)$	⇌	Hg_2^{2+}	+	$2Cl^-$
Starting			0		0
Change			+x		+2x
Equilibrium			x		2x

$[Hg_2^{2+}][Cl^-]^2 = K_{sp}$

$(x)(2x)^2 = 4x^3 = 1.3 \times 10^{-18}$

$x = \sqrt[3]{\dfrac{1.3 \times 10^{-18}}{4}} = 6.\underline{8}7 \times 10^{-7}$ M

a. Molar solubility = $6.\underline{8}7 \times 10^{-7} = 6.9 \times 10^{-7}$ M

b. $\dfrac{6.87 \times 10^{-7} \text{ mol}}{L} \times \dfrac{472.1 \text{ g } Hg_2Cl_2}{1 \text{ mol}} = 3.\underline{2}4 \times 10^{-4} = 3.2 \times 10^{-4}$ g/L

18.70 Let x equal the molar solubility of $MgNH_4PO_4$. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$MgNH_4PO_4(s)$	⇌	Mg^{2+}	+	NH_4^+	+	PO_4^{3-}
Starting			0		0		0
Change			+x		+x		+x
Equilibrium			x		x		x

$[Mg^{2+}][NH_4^+][PO_4^{3-}] = K_{sp}$

$(x)(x)(x) = x^3 = 2.5 \times 10^{-13}$

$x = \sqrt[3]{2.5 \times 10^{-13}} = 6.\underline{2}99 \times 10^{-5}$ M

a. Molar solubility = $6.\underline{2}99 \times 10^{-5} = 6.3 \times 10^{-5}$ M

b. $\dfrac{6.299 \times 10^{-5} \text{ mol}}{L} \times \dfrac{137.3 \text{ g } MgNH_4PO_4}{1 \text{ mol}} = 8.\underline{6}48 \times 10^{-3} = 8.6 \times 10^{-3}$ g/L

18.71 Let x equal the molar solubility of $Ce(OH)_3$. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$Ce(OH)_3(s)$	⇌	Ce^{3+}	+	$3OH^-$
Starting			0		0
Change			+x		+3x
Equilibrium			x		3x

$[Ce^{3+}][OH^-]^3 = K_{sp}$

$(x)(3x)^3 = 27x^4 = 2.0 \times 10^{-20}$

$x = \sqrt[4]{\dfrac{2.0 \times 10^{-20}}{27}} = 5.\underline{2}16 \times 10^{-6}$ M

a. Molar solubility $= 5.\underline{2}16 \times 10^{-6} = 5.2 \times 10^{-6}$ M

b. $[OH^-] = 3x = 1.\underline{5}6 \times 10^{-5}$ M

   $pOH = 4.8\underline{0}54 = 4.81$

18.72 Let x equal the molar solubility of $Cu_2Fe(CN)_6$. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$Cu_2Fe(CN)_6$ (s)	⇌	$2Cu^{2+}$	+	$Fe(CN)_6^{4-}$
Starting			0		0
Change			+2x		+x
Equilibrium			2x		x

$[Cu^{2+}]^2[Fe(CN)_6^{4-}] = K_{sp}$

$(2x)^2(x) = 4x^3 = 1.3 \times 10^{-16}$

$x = \sqrt[3]{\dfrac{1.3 \times 10^{-16}}{4}} = 3.\underline{1}9 \times 10^{-6}$ M

a. Molar solubility $= 3.\underline{1}9 \times 10^{-6} = 3.2 \times 10^{-6}$ M

b. $\dfrac{3.19 \times 10^{-6} \text{ mol}}{L} \times \dfrac{339.0 \text{ g } Cu_2Fe(CN)_6}{1 \text{ mol}} = 1.\underline{0}8 \times 10^{-3} = 1.1 \times 10^{-3}$ g/L

18.73   Calculate the pOH from the pH, and then convert pOH to [OH⁻]. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$pOH = 14.00 - 8.80 = 5.20$

$[OH^-] = $ antilog $(-pOH) = $ antilog $(-5.20) = 6.\underline{3}09 \times 10^{-6}$ M

Conc. (M)	$Mg(OH)_2(s)$	⇌	Mg^{2+}	+	$2OH^-$
Starting			0		0
Change			+x		—
Equilibrium			x		6.309×10^{-6}

$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(6.309 \times 10^{-6})^2 = 1.8 \times 10^{-11}$

$$x = \frac{1.8 \times 10^{-11}}{(6.309 \times 10^{-6})^2} = 0.4\underline{5}2 = 0.45 \text{ M}$$

$$\frac{0.452 \text{ mol}}{L} \times \frac{58.3 \text{ g Mg(OH)}_2}{1 \text{mol}} = 2\underline{6}.3 = 26 \text{ g/L}$$

18.74   Calculate the pOH from the pH, and then convert pOH to [OH⁻]. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. Let 2x equal the molar solubility of the Ag^+ ion because you are seeking x, the molar solubility of Ag_2O.

$pOH = 14.00 - 10.50 = 3.50$

$[OH^-] = $ antilog $(-pOH) = $ antilog $(-3.50) = 3.\underline{1}6 \times 10^{-4}$ M

Conc. (M)	$Ag_2O(s)$ + $2H_2O$	⇌	$2Ag^+$	+	$2OH^-$
Starting			0		0
Change	x		+2x		—
Equilibrium			2x		3.16×10^{-4}

$K_c = [Ag^+]^2[OH^-]^2 = (2x)^2(3.16 \times 10^{-4})^2 = 2.0 \times 10^{-8}$

$$x = \sqrt{\frac{2.0 \times 10^{-8}}{4 \times (3.16 \times 10^{-4})^2}} = 0.2\underline{2}4 = 0.22 \text{ M}$$

$$\frac{0.224 \text{ mol}}{\text{L}} \times \frac{231.7 \text{ g Ag}_2\text{O}}{1 \text{ mol}} = 5\underline{1}.9 = 52 \text{ g/L}$$

18.75 Let x equal the change in M of Mg^{2+} and 0.10 M equal the starting OH^- concentration. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. Assume 2x is negligible compared to 0.10 M, and perform an approximate calculation.

Conc. (M)	$Mg(OH)_2(s)$	⇌	Mg^{2+}	+	$2OH^-$
Starting			0		0.10
Change			+x		+2x
Equilibrium			x		0.10 + 2x

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(0.10 + 2x)^2 \cong (x)(0.10)^2 \cong 1.8 \times 10^{-11}$$

$$x = \frac{1.8 \times 10^{-11}}{(0.10)^2} = 1.\underline{8}0 \times 10^{-9} = 1.8 \times 10^{-9} \text{ M}$$

18.76 Let x equal the change in M of Al^{3+} and 0.0010 M equal the starting OH^- concentration. Then, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. Assume 3x is negligible compared to 0.0010 M, and perform an approximate calculation.

Conc. (M)	$Al(OH)_3(s)$	⇌	Al^{3+}	+	$3OH^-$
Starting			0		0.0010
Change			+x		+3x
Equilibrium			x		0.0010 + 3x

$$K_{sp} = [Al^{3+}][OH^-]^3 = (x)(0.0010 + 3x)^3 \cong (x)(0.0010)^3 \cong 4.6 \times 10^{-33}$$

$$x = \frac{4.6 \times 10^{-33}}{(0.0010)^3} = 4.\underline{6}0 \times 10^{-24} = 4.6 \times 10^{-24} \text{ M}$$

18.77   To begin precipitation, you must add just slightly more sulfate ion than that required to give a saturated solution. Use the K_{sp} expression to calculate the $[SO_4^{2-}]$ needed to just begin precipitating the 0.0030 M Ca^{2+}.

$$[Ca^{2+}][SO_4^{2-}] = K_{sp} = 2.4 \times 10^{-5}$$

$$[SO_4^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{2.4 \times 10^{-5}}{3.0 \times 10^{-3}} = 8.\underline{0}0 \times 10^{-3} \text{ M}$$

When the sulfate ion concentration slightly exceeds 8.0×10^{-3} M, precipitation begins.

18.78   To begin precipitation, you must add just slightly more chromate ion than that required to give a saturated solution. Use the K_{sp} expression to calculate the $[CrO_4^{2-}]$ needed to just begin precipitating the 0.0025 M Sr^{2+}.

$$[Sr^{2+}][CrO_4^{2-}] = K_{sp} = 3.5 \times 10^{-5}$$

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Sr^{2+}]} = \frac{3.5 \times 10^{-5}}{2.5 \times 10^{-3}} = 1.\underline{4}0 \times 10^{-2} \text{ M}$$

When the chromate ion concentration slightly exceeds 1.4×10^{-2} M, precipitation begins.

18.79   Calculate the concentrations of Pb^{2+} and Cl^-. Use a total volume of 3.20 L + 0.80 L, or 4.00 L.

$$[Pb^{2+}] = \frac{\dfrac{1.25 \times 10^{-3} \text{ mol}}{L} \times 3.20 \text{ L}}{4.00 \text{ L}} = 1.0\underline{0} \times 10^{-3} \text{ M}$$

$$[Cl^-] = \frac{\dfrac{5.0 \times 10^{-1} \text{ mol}}{L} \times 0.80 \text{ L}}{4.00 \text{ L}} = 1.0\underline{0} \times 10^{-1} \text{ M}$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = [Pb^{2+}][Cl^-]^2 = (1.00 \times 10^{-3})(1.00 \times 10^{-1})^2 = 1.\underline{0}0 \times 10^{-5} \text{ M}^3$$

Because the Q_c is less than the K_{sp} of 1.6×10^{-5}, no precipitation occurs, and the solution is not saturated.

18.80 Rounded answer: Q_c equals 1.8×10^{-11} (equals K_{sp}, so solution is saturated).
Calculate the concentrations of Mg^{2+} and OH^-. Use a total volume of 0.150 L + 0.050 L,
or 0.200 L.

$$[Mg^{2+}] = \frac{\dfrac{2.4 \times 10^{-5} \text{ mol}}{L} \times 0.150 \text{ L}}{0.200 \text{ L}} = 1.\underline{8}0 \times 10^{-5} \text{ M}$$

$$[OH^-] = \frac{\dfrac{4.0 \times 10^{-3} \text{ mol}}{L} \times 0.050 \text{ L}}{0.200 \text{ L}} = 1.\underline{0}0 \times 10^{-3} \text{ M}$$

Calculate the ion product and compare it to K_{sp}.

$$Q_c = [Mg^{2+}][OH^-]^2 = (1.80 \times 10^{-5})(1.00 \times 10^{-3})^2 = 1.\underline{8}0 \times 10^{-11}$$

Because Q_c equals the K_{sp} of 1.8×10^{-11}, no precipitation occurs, and the solution is
saturated.

18.81 A mixture of $AgNO_3$ and NaCl can precipitate only AgCl because $NaNO_3$ is soluble.
Use the K_{sp} expression to calculate the [Cl⁻] needed to prepare a saturated solution
(just before precipitating the 0.0015 M Ag^+). Then, convert to moles and finally to
grams.

$$[Ag^+][Cl^-] = K_{sp} = 1.8 \times 10^{-10}$$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.5 \times 10^{-3}} = 1.\underline{2}0 \times 10^{-7} \text{ M}$$

The number of moles and grams in 0.785 L (785 mL) of this chloride-containing
solution is

$$0.785 \text{ L} \times (1.20 \times 10^{-7} \text{ mol/L}) = 9.\underline{4}2 \times 10^{-8} \text{ mol Cl}^- = 9.\underline{4}2 \times 10^{-8} \text{ mol NaCl}$$

$$(9.42 \times 10^{-7} \text{ mol NaCl}) \times (58.5 \text{ g NaCl/1mol}) = 5.\underline{5}1 \times 10^{-6} = 5.5 \times 10^{-6} \text{ g NaCl}$$

This amount of NaCl is too small to weigh on a balance.

18.82 A mixture of $BaCl_2$ and Na_2SO_4 can precipitate only $BaSO_4$ because NaCl is soluble. Use the K_{sp} expression to calculate the $[SO_4^{2-}]$ needed to prepare a saturated solution (just before precipitating the 0.0028 M Ba^{2+}). Then, convert to moles and finally to grams.

$$[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.1 \times 10^{-10}$$

$$[SO_4^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.1 \times 10^{-10}}{2.8 \times 10^{-3}} = 3.\underline{9}3 \times 10^{-8} \text{ M}$$

The number of moles and grams in 0.435 L of this sulfate-containing solution is
$(0.435 \text{ L} \times 3.93 \times 10^{-8} \text{ mol/L}) = 1.\underline{7}09 \times 10^{-8} \text{ mol } SO_4^{2-} = 1.\underline{7}09 \times 10^{-8} \text{ mol } Na_2SO_4$

$$(1.709 \times 10^{-8} \text{ mol } Na_2SO_4) \times (142 \text{ g/1 mol } Na_2SO_4)$$
$$= 2.\underline{4}2 \times 10^{-6} = 2.4 \times 10^{-6} \text{ g } Na_2SO_4$$

18.83 From the magnitude of K_f, assume Fe^{3+} and SCN^- react essentially completely to form 2.00 M $Fe(SCN)^{2+}$ at equilibrium. Use 2.00 M as the starting concentration of $Fe(SCN)^{2+}$ for the usual concentration table.

Conc. (M)	Fe^{3+}	+	SCN^-	⇌	$FeSCN^{2+}$
Starting	0		0		2.00
Change	+x		+x		-x
Equilibrium	x		x		2.00 - x

Substitute all the exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 2.00 M.

$$K_f = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(2.00 - x)}{(x)(x)} \cong \frac{(2.00)}{x^2} \cong 9.0 \times 10^2$$

Rearrange and solve for x:

$$x = \sqrt{\frac{2.00}{9.0 \times 10^2}} = 4.\underline{7}1 \times 10^{-2} = 4.7 \times 10^{-2} \text{ M}$$

Fraction dissociated $= [(4.\underline{7}1 \times 10^{-2}) \div (2.00)] \times 100\%$

$$= 0.02\underline{3}5 \text{ (< 0.03, so acceptable)}$$

18.84 From the magnitude of K_f, assume Co^{2+} and SCN^- react essentially completely to form 2.00 M $Co(SCN)^+$ at equilibrium. Use 2.00 M as the starting concentration of $Co(SCN)^+$ for the usual concentration table.

Conc. (M)	Co^{2+}	+	SCN^-	⇌	$CoSCN^+$
Starting	0		0		2.00
Change	+x		+x		-x
Equilibrium	x		x		2.00 - x

Substitute all the exact equilibrium concentrations into the formation-constant expression; then, simplify the exact equation by assuming x is negligible compared to 2.00 M.
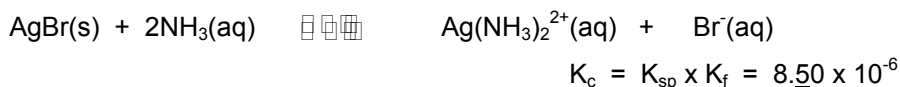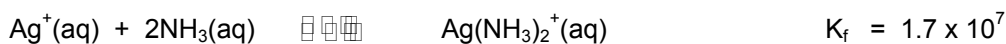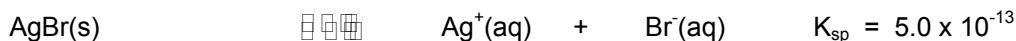
$$K_f = \frac{[CoSCN^+]}{[Co^{2+}][SCN^-]} = \frac{(2.00 - x)}{(x)(x)} \cong \frac{(2.00)}{x^2} \cong 1.0 \times 10^2$$

Rearrange and solve for x:

$$x = \sqrt{\frac{2.00}{1.0 \times 10^2}} = 0.1\underline{4}1 = 0.14 \text{ M}$$

The value of x = 0.14 affects the term 2.00 - x slightly in the second significant figure. From the quadratic formula, you obtain x = 0.1$\underline{3}$7, which also rounds to 0.14.

18.85 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:

$AgBr(s)$	⇌	$Ag^+(aq)$	+	$Br^-(aq)$		$K_{sp} = 5.0 \times 10^{-13}$
$Ag^+(aq) + 2NH_3(aq)$	⇌	$Ag(NH_3)_2^+(aq)$				$K_f = 1.7 \times 10^7$

$AgBr(s) + 2NH_3(aq)$ ⇌ $Ag(NH_3)_2^{2+}(aq)$ + $Br^-(aq)$

$$K_c = K_{sp} \times K_f = 8.\underline{5}0 \times 10^{-6}$$

Assemble the usual table using 5.0 M as the starting concentration of NH_3 and x as the unknown concentration of $Ag(NH_3)_2^+$ formed.

(continued)

Conc. (M)	AgBr(s)	+	$2NH_3$	⇌	$Ag(NH_3)_2^+$	+	Br^-
Starting			5.0		0		0
Change			-2x		+x		+x
Equilibrium			5.0 - 2x		x		x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression; it will not be necessary to simplify the equation because taking the square root of both sides removes the x^2 term.

$$K_c = \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2} = \frac{x^2}{(5.0 - 2x)^2} = 8.\underline{5}0 \times 10^{-6}$$
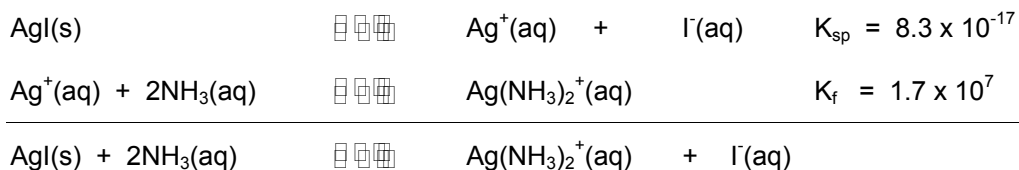
Take the square root of both sides of the two right-hand terms and solve for x.

$$\frac{x}{(5.0 - 2x)} = 2.\underline{9}15 \times 10^{-3}$$

$$x + (5.8 \times 10^{-3}) x = 1.\underline{4}575 \times 10^{-2}$$

$$x = 1.\underline{4}49 \times 10^{-2} = 1.4 \times 10^{-2} \text{ M} \text{ (the molar solubility of AgBr in 5.0 M } NH_3)$$

18.86 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:

AgI(s)		⇌	$Ag^+(aq)$	+	$I^-(aq)$	$K_{sp} = 8.3 \times 10^{-17}$
$Ag^+(aq) + 2NH_3(aq)$		⇌	$Ag(NH_3)_2^+(aq)$			$K_f = 1.7 \times 10^7$
$AgI(s) + 2NH_3(aq)$		⇌	$Ag(NH_3)_2^+(aq)$	+	$I^-(aq)$	

$$K_c = K_{sp} \times K_f = 1.\underline{4}1 \times 10^{-9}$$

Assemble the usual table using 2.0 M as the starting concentration of NH_3 and x as the unknown concentration of $Ag(NH_3)_2^+$ formed.

Conc. (M)	AgI(s) +	2NH$_3$	⇌	Ag(NH$_3$)$_2^+$ +	I$^-$
Starting		2.0		0	0
Change		-2x		+x	+x
Equilibrium		2.0 - 2x		x	x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression; it will not be necessary to simplify the equation because taking the square root of both sides removes the x^2 term.

$$K_c = \frac{[Ag(NH_3)_2^+][I^-]}{[NH_3]^2} = \frac{x^2}{(2.0 - 2x)^2} = 1.\underline{4}1 \times 10^{-9}$$

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

$$\frac{x}{(2.0 - 2x)} = 3.\underline{7}5 \times 10^{-5}$$

$$x + (7.5 \times 10^{-5})x = 7.\underline{5}0 \times 10^{-5}$$

$$x = 7.\underline{4}99 \times 10^{-5} = 7.5 \times 10^{-5} \text{ M} \text{ (the molar solubility of AgI in 2.0 M NH}_3)$$

18.87 Start by recognizing that, because each zinc oxalate produces one oxalate ion, the solubility of zinc oxalate equals the oxalate concentration:

$$ZnC_2O_4(s) + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + C_2O_4^{2-}$$

Thus, the $[C_2O_4^{2-}] = 3.6 \times 10^{-4}$ M. Now, calculate the $[Zn^{2+}]$ in equilibrium with the oxalate ion using the K_{sp} expression for zinc oxalate.

$$K_{sp} = [Zn^{2+}][C_2O_4^{2-}] = 1.5 \times 10^{-9}$$

$$[Zn^{2+}] = \frac{1.5 \times 10^{-9}}{3.6 \times 10^{-4}} = 4.\underline{1}6 \times 10^{-6} = 4.2 \times 10^{-6} \text{ M}$$

To calculate K_f, the $[Zn(NH_3)_4{}^{2+}]$ term must be calculated. This can be done by recognizing that the molar solubility of ZnC_2O_4 is the sum of the concentration of Zn^{2+} and $Zn(NH_3)_4{}^{2+}$ ions:

Molar solubility of ZnC_2O_4 = $[Zn^{2+}]$ + $[Zn(NH_3)_4{}^{2+}]$

3.6×10^{-4} = (4.16×10^{-6}) + $[Zn(NH_3)_4{}^{2+}]$

$[Zn(NH_3)_4{}^{2+}]$ = (3.6×10^{-4}) - (4.16×10^{-6}) = $3.\underline{5}58 \times 10^{-4}$ M

Now, the $[NH_3]$ term must be calculated by subtracting the ammonia in $[Zn(NH_3)_4{}^{2+}]$ from the starting NH_3 of 0.0150 M:

$[NH_3]$ = 0.0150 - $4[Zn(NH_3)_4{}^{2+}]$ = 0.0150 - $4(3.558 \times 10^{-4})$ = $0.013\underline{5}7$ M

Solve for K_f by substituting the known concentrations into the K_f expression:

$$K_f = \frac{[Zn(NH_3)_4{}^{2+}]}{[Zn^{2+}][NH_3]^4} = \frac{3.558 \times 10^{-4}}{(4.16 \times 10^{-6})(0.01357)^4} = 2.\underline{5}2 \times 10^9 = 2.5 \times 10^9$$

18.88 Start by recognizing that, because each cadmium oxalate produces one oxalate ion, the solubility of cadmium oxalate equals the oxalate concentration:

$CdC_2O_4(s)$ + $4NH_3$ ⇌ $Cd(NH_3)_4{}^{2+}$ + $C_2O_4{}^{2-}$

Thus, the $[C_2O_4{}^{2-}]$ = 6.1×10^{-3} M. Now, calculate the $[Cd^{2+}]$ in equilibrium with the oxalate ion using the K_{sp} expression for cadmium oxalate.

K_{sp} = $[Cd^{2+}][C_2O_4{}^{2-}]$ = 1.5×10^{-8}

$$[Cd^{2+}] = \frac{1.5 \times 10^{-8}}{6.1 \times 10^{-3}} = 2.\underline{4}6 \times 10^{-6} = 2.5 \times 10^{-6} \text{ M}$$

To calculate K_f, the $[Cd(NH_3)_4{}^{2+}]$ term must be calculated. This can be done by recognizing that the molar solubility of CdC_2O_4 is the sum of the concentration of Cd^{2+} and $Cd(NH_3)_4{}^{2+}$ ions:

Molar solubility of CdC_2O_4 = $[Cd^{2+}]$ + $[Cd(NH_3)_4{}^{2+}]$

6.1×10^{-3} = (2.46×10^{-6}) + $[Cd(NH_3)_4{}^{2+}]$

$[Cd(NH_3)_4{}^{2+}] = (6.1 \times 10^{-3}) - (2.46 \times 10^{-6}) \cong 6.1 \times 10^{-3}$ M

Now the $[NH_3]$ term must be calculated by subtracting the ammonia in $[Cd(NH_3)_4{}^{2+}]$ from the starting NH_3 of 0.0150 M:

$[NH_3] = 0.150 - 4[Cd(NH_3)_4{}^{2+}] = 0.150 - 4(6.1 \times 10^{-3}) = 0.12\underline{5}6$ M

Solve for K_f by substituting the known concentrations into the K_f expression:

$$K_f = \frac{[Cd(NH_3)_4{}^{2+}]}{[Cd^{2+}][NH_3]^4} = \frac{6.1 \times 10^{-3}}{(2.46 \times 10^{-6})(0.1256)^4} = 9.\underline{9}6 \times 10^6 = 1.0 \times 10^7$$

18.89   The OH^- formed by ionization of NH_3 (to $NH_4{}^+$ and OH^-) is a common ion that will precipitate Mg^{2+} as the slightly soluble $Mg(OH)_2$ salt. The simplest way to treat the problem is to calculate the $[OH^-]$ of 0.10 M NH_3 before the soluble Mg^{2+} salt is added. As the soluble Mg^{2+} salt is added, the $[Mg^{2+}]$ will increase until the solution is saturated with respect to $Mg(OH)_2$ (the next Mg^{2+} ions to be added will precipitate). Calculate the $[Mg^{2+}]$ at the point at which precipitation begins.

To calculate the $[OH^-]$ of 0.10 M NH_3, let x equal the mol/L of NH_3 that ionize, forming x mol/L of $NH_4{}^+$ and x mol/L of OH^- and leaving $(0.10 - x)$ M NH_3 in solution. We can summarize the situation in tabular form:

Conc. (M)	NH_3	+	H_2O	$\rightleftharpoons$	$NH_4{}^+$	+	OH^-
Starting	0.10				~0		0
Change	-x				+x		+x
Equilibrium	0.10 - x				x		x

The equilibrium-constant equation is:

$$K_c = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = \frac{x^2}{(0.10 - x)} \cong \frac{x^2}{(0.10)}$$

The value of x can be obtained by rearranging and taking the square root:

$$[OH^-] \cong \sqrt{1.8 \times 10^{-5} \times 0.10} = 1.\underline{3}4 \times 10^{-3}$$ M

Note that $(0.10 - x)$ is not significantly different from 0.10, so x can be ignored in the $(0.10 - x)$ term.

Now, use the K_{sp} of $Mg(OH)_2$ to calculate the $[Mg^{2+}]$ of a saturated solution of $Mg(OH)_2$, which essentially will be the Mg^{2+} ion concentration when $Mg(OH)_2$ begins to precipitate.

$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(1.34 \times 10^{-3})^2} = 1.\underline{0}0 \times 10^{-5} = 1.0 \times 10^{-5} \text{ M}$$

18.90 The OH^- formed by ionization of N_2H_4 (to $N_2H_5^+$ and OH^-) is a common ion that will precipitate Mg^{2+} as the slightly soluble $Mg(OH)_2$ salt. The simplest way to treat the problem is to calculate the $[OH^-]$ of 0.20 M N_2H_4 before the soluble Mg^{2+} salt is added. As the soluble Mg^{2+} salt is added, the $[Mg^{2+}]$ will increase until the solution is saturated with respect to $Mg(OH)_2$ (the next Mg^{2+} ions to be added will precipitate). Calculate the $[Mg^{2+}]$ at the point at which precipitation begins.

To calculate the $[OH^-]$ of 0.20 M N_2H_4, let x equal the mol/L of N_2H_4 that ionizes, forming x mol/L of N_2H_5 and x mol/L of OH^- and leaving $(0.20 - x)$ M N_2H_4 in solution. We can summarize the situation in tabular form:

Conc. (M)	N_2H_4	+	H_2O	⇌	$N_2H_5^+$	+	OH^-
Starting	0.20				~0		0
Change	-x				+x		+x
Equilibrium	0.20 - x				x		x

The equilibrium-constant equation is:

$$K_c = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = \frac{x^2}{(0.20 - x)} \cong \frac{x^2}{(0.20)}$$

The value of x can be obtained by rearranging and taking the square root:

$$[OH^-] \cong \sqrt{1.7 \times 10^{-6} \times 0.20} = 5.\underline{8}3 \times 10^{-4} \text{ M}$$

Note that (0.20 - x) is not significantly different from 0.10, so x can be ignored in the (0.20 - x) term.

Now, use the K_{sp} of $Mg(OH)_2$ to calculate the $[Mg^{2+}]$ of a saturated solution of $Mg(OH)_2$, which essentially will be the Mg^{2+} ion concentration when $Mg(OH)_2$ begins to precipitate.
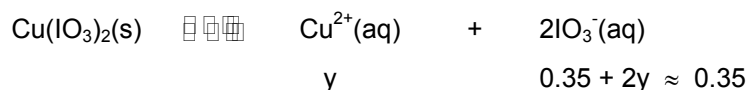
$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(5.83 \times 10^{-4})^2} = 5.\underline{2}9 \times 10^{-5} = 5.3 \times 10^{-5} \text{ M}$$

18.91 a. Use the solubility information to calculate K_{sp}. The reaction is

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) \quad + \quad 2IO_3^-(aq)$$
$$2.7 \times 10^{-3} \qquad 2 \times (2.7 \times 10^{-3})$$
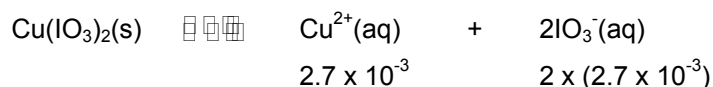
$$K_{sp} = [Cu^{2+}][IO_3^-]^2 = [2.7 \times 10^{-3}][2 \times (2.7 \times 10^{-3})]^2 = 7.\underline{8}7 \times 10^{-8}$$

Set up an equilibrium. The reaction is

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) \quad + \quad 2IO_3^-(aq)$$
$$y \qquad 0.35 + 2y \approx 0.35$$

$$K_{sp} = [y][0.35]^2 = 7.87 \times 10^{-8}$$

Molar solubility $= y = 6.\underline{4}2 \times 10^{-7} = 6.4 \times 10^{-7}$ M
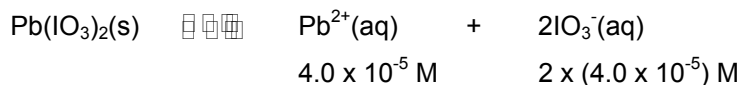
b. Set up an equilibrium. The reaction is

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) \quad + \quad 2IO_3^-(aq)$$
$$y + 0.35 \approx 0.35 \qquad 2y$$
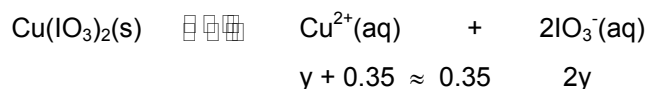
$$K_{sp} = [0.35][2y]^2 = 7.87 \times 10^{-8}$$

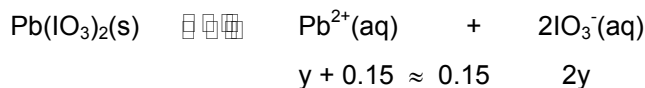Molar solubility $= y = 2.\underline{3}7 \times 10^{-4} = 2.4 \times 10^{-4}$ M

c. Yes, $Cu(IO_3)_2$ is a 1:2 electrolyte. It takes two IO_3^- ions to combine with one Cu^{2+} ion. The IO_3^- ion is involved as a square term in the K_{sp} expression.

18.92 a. Use the solubility information to calculate K_{sp}. The reaction is

$$Pb(IO_3)_2(s) \quad \rightleftharpoons \quad Pb^{2+}(aq) \quad + \quad 2IO_3^-(aq)$$

$$4.0 \text{ x } 10^{-5} \text{ M} \qquad 2 \text{ x } (4.0 \text{ x } 10^{-5}) \text{ M}$$

$$K_{sp} = [Pb^{2+}][IO_3^-]^2 = [4.0 \text{ x } 10^{-5}][2 \text{ x } (4.0 \text{ x } 10^{-5})]^2 = 2.\underline{5}6 \text{ x } 10^{-13}$$

Set up an equilibrium. The reaction is

$$Pb(IO_3)_2(s) \quad \rightleftharpoons \quad Pb^{2+}(aq) \quad + \quad 2IO_3^-(aq)$$

$$y + 0.15 \approx 0.15 \qquad 2y$$

$$K_{sp} = [0.15][2y]^2 = 2.56 \text{ x } 10^{-13}$$

Molar solubility = y = $6.\underline{5}3 \text{ x } 10^{-7}$ = $6.5 \text{ x } 10^{-7}$ M

b. Because of the common ion effect or a consideration of Le Chatelier's principle, the molar solubility would be less.

18.93 a. Set up an equilibrium. The reaction and equilibrium-constant expression are

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \qquad K_{sp} = [Pb^{2+}][I^-]^2 = 6.5 \text{ x } 10^{-9}$$
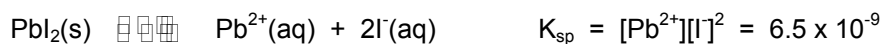
The Pb^{2+} ion concentration is 0.0150 M. Plug this in, and solve for the iodine ion concentration.

$$[I^-] = \sqrt{\frac{6.5 \text{ x } 10^{-9}}{0.0150}} = 6.\underline{5}8 \text{ x } 10^{-4} = 6.6 \text{ x } 10^{-4} \text{M}$$
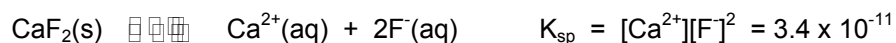
b. Solve the equilibrium-constant expression for the lead ion concentration.

$$[Pb^{2+}] = \frac{6.5 \text{ x } 10^{-9}}{(2.0 \text{ x } 10^{-3})^2} = 1.\underline{6}3 \text{ x } 10^{-3} \text{ M}$$

The percent of the lead(II) ion remaining in solution is

$$\text{Percent } Pb^{2+} \text{ remaining} = \frac{1.63 \text{ x } 10^{-3}}{0.0150} \text{ x } 100\% = 1\underline{0}.9 = 11 \text{ percent}$$

18.94 a. Set up an equilibrium. The reaction and equilibrium-constant expression are

$$CaF_2(s) \; \rightleftharpoons \; Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Ca^{2+}][F^-]^2 = 3.4 \times 10^{-11}$$

Solve the equilibrium-constant expression for the fluoride ion concentration. The calcium ion concentration is 0.00750 M.

$$[F^-] = \sqrt{\frac{3.4 \times 10^{-11}}{0.00750}} = 6.\underline{7}3 \times 10^{-5} = 6.7 \times 10^{-5} \; M$$

b. Solve the equilibrium-constant expression for the calcium ion concentration. The fluoride ion concentration is 9.5×10^{-4} M.

$$[Ca^{2+}] = \frac{3.4 \times 10^{-11}}{(9.5 \times 10^{-4})^2} = 3.\underline{7}7 \times 10^{-5} \; M$$

The percent of the calcium ion precipitated is

$$Percent \; Ca^{2+} \; precipitated = \frac{0.00750 - 3.77 \times 10^{-5}}{0.00750} \times 100\% = 99.4$$

$$= 99 \; percent$$

18.95 a. The reaction and equilibrium-constant expression are

$$Co(OH)_2(s) \; \rightleftharpoons \; Co^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Co^{2+}][OH^-]^2$$

From the molar solubility, $[Co^{2+}] = 5.4 \times 10^{-6}$ M and $[OH^-] = 2 \times (5.4 \times 10^{-6})$ M. Therefore,

$$K_{sp} = [5.4 \times 10^{-6}][2 \times (5.4 \times 10^{-6})]^2 = 6.\underline{3}0 \times 10^{-16} = 6.3 \times 10^{-16}$$

b. From the pOH (14 - pH), the $[OH^-] = 10^{-3.57} = 2.\underline{6}9 \times 10^{-4}$ M. The molar solubility is equal to the cobalt ion concentration at equilibrium.

$$[Co^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{6.3 \times 10^{-16}}{(2.69 \times 10^{-4})^2} = 8.\underline{7}1 \times 10^{-9} = 8.7 \times 10^{-9} \; M$$

c. The common ion effect (OH⁻) in part (b) decreases the solubility of Co^{2+}.
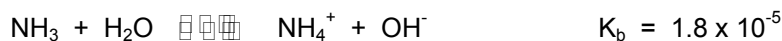
18.96 a. The reaction and equilibrium-constant expression are

$$Be(OH)_2(s) \rightleftharpoons Be^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Be^{2+}][OH^-]^2$$

From the molar solubility, $[Be^{2+}] = 8.6 \times 10^{-7}$ M and $[OH^-] = 2 \times (8.6 \times 10^{-7})$ M. Therefore,

$$K_{sp} = [8.6 \times 10^{-7}][2 \times (8.6 \times 10^{-7})]^2 = 2.\underline{5}4 \times 10^{-18} = 2.5 \times 10^{-18}$$

b. This is a buffer system. The reaction is

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = 1.8 \times 10^{-5}$$

Set up the equilibrium, and calculate the OH^- ion concentration.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.25)[OH^-]}{(1.50)} = 1.8 \times 10^{-5}$$

$$[OH^-] = 1.\underline{0}8 \times 10^{-4} \text{ M}$$

The molar solubility is equal to the beryllium ion concentration at equilibrium.

$$[Be^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{2.5 \times 10^{-18}}{(1.08 \times 10^{-4})^2} = 2.\underline{1}4 \times 10^{-10} = 2.1 \times 10^{-10} \text{ M}$$

c. The common ion effect (a Le Chatelier stress) decreases the solubility of Be^{2+}.

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

$\underline{Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad\qquad K_f = 1.7 \times 10^7}$

$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$
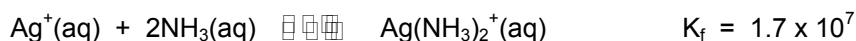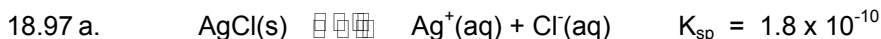
$K = K_{sp} \times K_f = (1.8 \times 10^{-10})(1.7 \times 10^7) = 3.\underline{0}6 \times 10^{-3} = 3.1 \times 10^{-3}$
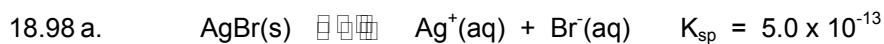
b. The equilibrium-constant expression is

$$\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \frac{y^2}{(0.80)^2} = 3.06 \times 10^{-3}$$

$y = [Ag(NH_3)_2^+] = 0.04\underline{4}3 = 0.044\ M$

mol AgCl dissolved $=$ mol $Ag(NH_3)_2^+ = 0.044\ mol/L \times 1.00\ L = 0.044\ mol$

mol NH_3 reacted $= 0.0443\ mol\ Ag(NH_3)_2^+ \times \dfrac{2\ mol\ NH_3}{1\ mol\ Ag(NH_3)_2^+} = 0.08\underline{8}6\ mol$

The total moles of NH_3 added $= 0.80\ M \times 1.00\ L + 0.0886 = 0.8\underline{8}9 = 0.89\ mol$

18.98 a.　　$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$　　$K_{sp} = 5.0 \times 10^{-13}$

$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}$　　　$K_f = 2.9 \times 10^{13}$

$\overline{\qquad\qquad AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)\qquad\qquad}$

$K = K_{sp} \times K_f = (5.0 \times 10^{-13})(2.9 \times 10^{13}) = 1\underline{4}.5 = 15$

mol $AgBr = 2.5\ g\ AgBr \times \dfrac{1\ mol\ AgBr}{187.77\ g\ AgBr} = 0.01\underline{3}3\ mol$

mol $Ag(S_2O_3)_2^{3-} =$ mol $AgBr = 0.0133\ mol$

$$\frac{[Ag(S_2O_3)_2^{2-}][Br^-]}{[S_2O_3^{2-}]^2} = \frac{(0.0133)^2}{[S_2O_3^{2-}]^2} = 14.5$$

Take the square root of both sides to obtain the moles of $S_2O_3^{2-}$ at equilibrium.

$$\frac{0.0133}{[S_2O_3^{2-}]} = \sqrt{14.5}$$

$[S_2O_3^{2-}] = 0.003\underline{4}9\ mol/L$

The moles of $S_2O_3^{2-}$ in $Ag(S_2O_3)_2^{3-}$ = 2 x 0.0133 = 0.0266 mol

Total moles of $S_2O_3^{2-}$ = 0.0266 + 0.00349 = 0.0301 = 0.030 mol

The moles of $Na_2S_2O_3$ added = moles of $S_2O_3^{2-}$ = 0.030 mol

18.99 a. The moles of NH_4Cl (molar mass 53.49 g/mol) are given by

$$\text{mol } NH_4Cl = 26.7 \text{ g} \times \frac{1 \text{ mol } NH_4Cl}{53.49 \text{ g } NH_4Cl} = 0.4992 \text{ mol}$$

The reaction and equilibrium-constant expression are

$$NH_3 + H_2O \ \rightleftharpoons \ NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Solve the equilibrium-constant expression for [OH⁻]. The molarity of the NH_4Cl is 0.4992 mol/1.0 L = 0.4992 M.

$$[OH^-] = \frac{(1.8 \times 10^{-5})(4.2)}{(0.4992)} = 1.51 \times 10^{-4} = 1.5 \times 10^{-4} \text{ M}$$

b. The reaction and equilibrium-constant expression are

$$Mg(OH)_2 \ \rightleftharpoons \ Mg^{2+} + 2OH^- \qquad K_{sp} = [Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$$

Solving for $[Mg^{2+}]$ gives

$$[Mg^{2+}] = \frac{(1.8 \times 10^{-11})}{(1.51 \times 10^{-4})^2} = 7.89 \times 10^{-4} = 7.9 \times 10^{-4} \text{ M}$$

The percent Mg^{2+} that has been removed is given by

$$\text{Percent } Mg^{2+} \text{ removed} = \frac{0.075 - 7.89 \times 10^{-4}}{0.075} \times 100\% = 98.9 = 99 \text{ percent}$$

18.100 a. The moles of $(NH_4)_2SO_4$ (molar mass 132.15 g/mol) are given by

$$\text{mol } (NH_4)_2SO_4 = 75.8 \text{ g } \times \frac{1 \text{ mol } (NH_4)_2SO_4}{132.15 \text{ g } (NH_4)_2SO_4} = 0.57\underline{3}6 \text{ mol}$$

The moles of $NH_4^+ = 2 \times 0.5736 = 1.1\underline{4}7$ mol. The reaction and equilibrium-constant expression are

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Solve the equilibrium-constant expression for $[OH^-]$. The molarity of the NH_4Cl is 1.1$\underline{4}$7 mol/1.0 L = 1.1$\underline{4}$7 M.

$$[OH^-] = \frac{(1.8 \times 10^{-5})(1.6)}{(1.147)} = 2.\underline{5}1 \times 10^{-5} = 2.5 \times 10^{-5} \text{ M}$$

b. The reaction and equilibrium-constant expression are

$$Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2OH^- \qquad K_{sp} = [Mn^{2+}][OH^-]^2 = 4.6 \times 10^{-14}$$
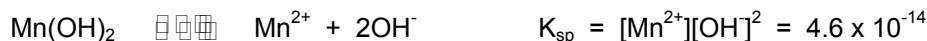
Solving for $[Mn^{2+}]$ gives

$$[Mn^{2+}] = \frac{(4.6 \times 10^{-14})}{(2.51 \times 10^{-5})^2} = 7.\underline{3}0 \times 10^{-5} = 7.3 \times 10^{-5} \text{ M}$$

The percent Mn^{2+} that has been removed is given by

$$\text{Percent } Mn^{2+} \text{ removed} = \frac{0.058 - 7.30 \times 10^{-5}}{0.058} \times 100\% = 9\underline{9}.9 \text{ percent}$$

Nearly 100 percent of the Mn^{2+} has been removed.

■ Solutions to Cumulative-Skills Problems

18.101 Using the K_{sp} of 1.1×10^{-21} for ZnS, calculate the $[S^{2-}]$ needed to maintain a saturated solution (without precipitation):

$$[S^{2-}] = \frac{1.1 \times 10^{-21}}{1.5 \times 10^{-4} \text{ M } Zn^{2+}} = 7.\underline{3}3 \times 10^{-18} \text{ M}$$

Next, use the overall H_2S ionization expression to calculate the $[H_3O^+]$ needed to achieve this $[S^{2-}]$ level:

$$[H_3O^+] = \sqrt{\frac{1.1 \times 10^{-20}\ (0.10\ M)}{7.33 \times 10^{-18}\ M}} = 1.\underline{2}25 \times 10^{-2}\ M$$

Finally, calculate the buffer ratio of $[SO_4^{2-}]/[HSO_4^-]$ from the H_2SO_4 K_{a2} expression where K_{a2} has the value 1.1×10^{-2}:

$$\frac{[SO_4^{2-}]}{[HSO_4^-]} = \frac{K_{a2}}{[H_3O^+]} = \frac{1.1 \times 10^{-2}}{1.225 \times 10^{-2}} = \frac{0.8979}{1.000}$$

If $[HSO_4^-] = 0.20\ M$, then

$$[SO_4^{2-}] = 0.8979 \times 0.20\ M = 0.1\underline{7}95 = 0.18\ M$$

18.102 Using the K_{sp} of 4×10^{-21} for CoS, calculate the $[S^{2-}]$ needed to maintain a saturated solution (without precipitation):

$$[S^{2-}] = \frac{4 \times 10^{-21}}{1.8 \times 10^{-4}\ M\ Co^{2+}} = 2.\underline{2}2 \times 10^{-17}\ M$$

Next, use the overall H_2S ionization expression to calculate the $[H_3O^+]$ needed to achieve this $[S^{2-}]$ level:

$$[H_3O^+] = \sqrt{\frac{1.1 \times 10^{-20}\ (0.10\ M)}{2.22 \times 10^{-17}\ M}} = 7.\underline{0}4 \times 10^{-3}\ M$$

Finally, calculate the buffer ratio of $[SO_4^{2-}]/[HSO_4^-]$ from the H_2SO_4 K_{a2} expression where K_{a2} has the value 1.1×10^{-2}:

$$\frac{[SO_4^{2-}]}{[HSO_4^-]} = \frac{K_{a2}}{[H_3O^+]} = \frac{1.1 \times 10^{-2}}{7.04 \times 10^{-3}} = \frac{1.56}{1.000}$$
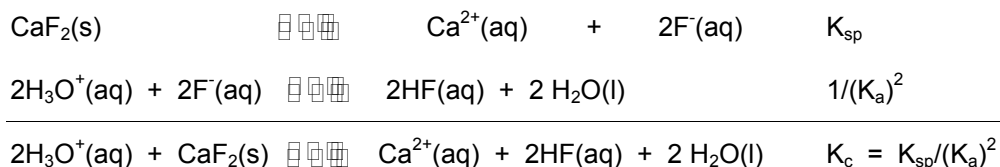
If $[HSO_4^-] = 0.20\ M$, then

$$[SO_4^{2-}] = \underline{1}.56 \times 0.20\ M = 0.\underline{3}12 = 0.3\ M$$

18.103   Begin by solving for $[H_3O^+]$ in the buffer. Ignoring changes in $[HCHO_2]$ as a result of ionization in the buffer, you obtain

$$[H_3O^+] \cong 1.7 \times 10^{-4} \times \frac{0.45\,M}{0.20\,M} = 3.\underline{8}25 \times 10^{-4}\,M$$

You should verify that this approximation is valid (you obtain the same result from the Henderson-Hasselbalch equation). The equilibrium for the dissolution of CaF_2 in acidic solution is obtained by subtracting twice the acid ionization of HF from the solubility equilibrium of CaF_2:

$CaF_2(s)$	⇌	$Ca^{2+}(aq)$ + $2F^-(aq)$	K_{sp}
$2H_3O^+(aq) + 2F^-(aq)$ ⇌		$2HF(aq) + 2\,H_2O(l)$	$1/(K_a)^2$
$2H_3O^+(aq) + CaF_2(s)$ ⇌		$Ca^{2+}(aq) + 2HF(aq) + 2\,H_2O(l)$	$K_c = K_{sp}/(K_a)^2$

Therefore, $K_c = (3.4 \times 10^{-11}) \div (6.8 \times 10^{-4})^2 = 7.\underline{3}5 \times 10^{-5}$. In order to solve the equilibrium-constant equation, you require the concentration of HF, which you obtain from the acid-ionization constant for HF.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$6.8 \times 10^{-4} = 3.825 \times 10^{-4} \times \frac{[F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = 1.778, \text{ or } [F^-] = 1.\underline{7}78\,[HF]$$

Let x be the solubility of CaF_2 in the buffer. Then, $[Ca^{2+}] = x$ and $[F^-] + [HF] = 2x$. Substituting from the previous equation, you obtain

$$2x = 1.778[HF] + [HF] = 2.778[HF], \text{ or } [HF] = 2x/2.\underline{7}78$$

You can now substitute for $[H_3O^+]$ and $[HF]$ into the equation for K_c.

$$K_c = \frac{[Ca^{2+}][HF]^2}{[H_3O^+]^2} = \frac{x(2x/2.778)^2}{(3.825 \times 10^{-4})^2} = 7.35 \times 10^{-5}$$

$$7.35 \times 10^{-5} = (3.543 \times 10^6)x^3$$

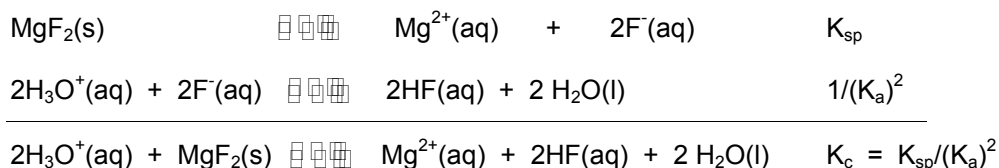$$x^3 = 2.075 \times 10^{-11}$$

$$x = 2.\underline{7}48 \times 10^{-4} = 2.7 \times 10^{-4}\,M$$

18.104   Begin by solving for $[H_3O^+]$ in the buffer. Ignoring changes in $[HC_2H_3O_2]$ as a result of ionization in the buffer, you obtain

$$[H_3O^+] \cong 1.7 \times 10^{-5} \times \frac{0.45\,M}{0.20\,M} = 3.\underline{8}25 \times 10^{-5}\,M$$

You should verify that this approximation is valid (you obtain the same result from the Henderson-Hasselbalch equation). The equilibrium for the dissolution of MgF_2 in acidic solution is obtained by subtracting twice the acid ionization of HF from the solubility equilibrium of MgF_2:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq) \qquad K_{sp}$$

$$2H_3O^+(aq) + 2F^-(aq) \rightleftharpoons 2HF(aq) + 2\,H_2O(l) \qquad 1/(K_a)^2$$

$$2H_3O^+(aq) + MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2HF(aq) + 2\,H_2O(l) \qquad K_c = K_{sp}/(K_a)^2$$

Therefore, $K_c = (6.5 \times 10^{-9}) \div (6.8 \times 10^{-4})^2 = 1.\underline{4}06 \times 10^{-2}$. In order to solve the equilibrium-constant equation, you require the concentration of HF, which you obtain from the acid-ionization constant for HF.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$6.8 \times 10^{-4} = 3.825 \times 10^{-5} \times \frac{[F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = 17.78, \text{ or } [F^-] = 1\underline{7}.78\,[HF]$$

Let x be the solubility of MgF_2 in the buffer. Then, $[Mg^{2+}] = x$ and $[F^-] + [HF] = 2x$. Substituting from the previous equation, you obtain

$$2x = 17.78[HF] + [HF] = 18.78[HF], \text{ or } [HF] = 2x/1\underline{8}.78$$
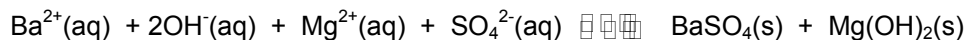
You can now substitute for $[H_3O^+]$ and $[HF]$ into the equation for K_c.

$$K_c = \frac{[Mg^{2+}][HF]^2}{[H_3O^+]^2} = \frac{x(2x/18.78)^2}{(3.825 \times 10^{-5})^2} = 1.406 \times 10^{-2}$$

$$1.406 \times 10^{-2} = (7.752 \times 10^6)x^3$$

$$x^3 = 1.812 \times 10^{-9}$$

$$x = 1.\underline{2}19 \times 10^{-3} = 1.2 \times 10^{-3}\,M$$

18.105 The net ionic equation is

$$Ba^{2+}(aq) + 2OH^-(aq) + Mg^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons BaSO_4(s) + Mg(OH)_2(s)$$

Start by calculating the mol/L of each ion after mixing and before precipitation. Use a total volume of 0.0450 + 0.0670 L = 0.112 L.

M of SO_4^{2-} and Mg^{2+} = (0.350 mol/L x 0.0670 L) ÷ 0.112 L = 0.20$\underline{9}$4 M

M of Ba^{2+} = (0.250 mol/L x 0.0450 L) ÷ 0.112 L = 0.10$\underline{0}$4 M

M of OH^- = (2 x 0.250 mol/L x 0.0450 L) ÷ 0.112 L = 0.200$\underline{8}$9 M

Assemble a table showing the precipitation of $BaSO_4$ and $Mg(OH)_2$.

Conc. (M)	Ba^{2+}	+	SO_4^{2-}	+	Mg^{2+}	+	$2OH^-$
					$\rightleftharpoons$		$BaSO_4(s) + Mg(OH)_2(s)$
Starting	0.1004		0.2094		0.2094		0.20089
Change	-0.1004		-0.1004		-0.1004		-0.20089
Equilibrium	0.0000		0.1090		0.1090		0.0000

To calculate $[Ba^{2+}]$, use the K_{sp} expression for $BaSO_4$.

$$[Ba^{2+}] = \frac{1.1 \times 10^{-10}}{0.10\underline{9}0 \, M \, SO_4^{2-}} = 1.\underline{0}09 \times 10^{-9} = 1.0 \times 10^{-9} \, M$$

$$[SO_4^{2-}] = 0.10\underline{9}0 = 0.109 \, M$$

Calculate the $[OH^-]$ using the K_{sp} expression for $Mg(OH)_2$:

$$[OH^-] = \sqrt{\frac{1.8 \times 10^{-11}}{0.1090 \, M \, Mg^{2+}}} = 1.\underline{2}8 \times 10^{-5} = 1.3 \times 10^{-5} \, M$$

$$[Mg^{2+}] = 0.10\underline{9}0 = 0.109 \, M$$

18.106   The net ionic equation is

$$Pb^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2AgCl(s)$$

Start by calculating the mol/L of each ion after mixing and before precipitation. Use a total volume of 0.0250 + 0.0500 L = 0.0750 L.

M of SO_4^{2-} = (0.0150 mol/L x 0.0500 L) ÷ 0.0750 L = 0.0100̲0 M

M of Pb^{2+} = (0.0100 mol/L x 0.0250 L) ÷ 0.0750 L = 0.00333̲3 M

M of Ag^+ = (2 x 0.0150 mol/L x 0.0500 L) ÷ 0.0750 L = 0.0200̲0 M

M of Cl^- = (2 x 0.0100 mol/L x 0.0250 L) ÷ 0.07500 = 0.00666̲6 M

Assemble a table showing the precipitation of $PbSO_4$ and $AgCl$.

Conc. (M)	Pb^{2+}	+	SO_4^{2-}	+	Ag^+	+	Cl^-
					$\rightleftharpoons$		$PbSO_4(s) + AgCl(s)$
Starting	0.003333		0.01000		0.02000		0.006667
Change	-0.003333		-0.003333		-0.006667		-0.006667
Equilibrium	0.000000		0.006̲667		0.0133̲33		0.000000

To calculate $[Pb^{2+}]$, use the K_{sp} expression for $PbSO_4$.

$$[Pb^{2+}] = \frac{1.7 \times 10^{-8}}{0.006667 \text{ M } SO_4^{2-}} = 2.5̲49 \times 10^{-6} = 2.50 \times 10^{-6} \text{ M}$$

$[SO_4^{2-}]$ = 0.006̲667 = 0.0067M

Calculate the $[Cl^-]$ using the K_{sp} expression for AgCl:

$$[Cl^-] = \frac{1.8 \times 10^{-10}}{0.01333 \text{ M } Ag^+} = 1.3̲503 \times 10^{-8} = 1.4 \times 10^{-8} \text{ M}$$

$[Ag^+]$ = 0.0133̲3 = 0.0133 M

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