CHAPTER EIGHT
Equilibrium Constant

8.1   Solubility = how many grams of $BaSO_4$ dissolve in a liter of water.
Molar solubility = how many moles of $BaSO_4$ dissolve in a liter of water.
Solubility product = $[Ba^{2+}][SO_4^{2-}]$. The solubility product is important since it stays constant; the molar solubility and solubility of barium sulfate depend on how much barium ion and sulfate ion exist in solution previously. The K_{sp} of barium sulfate is 1.1×10^{-10} M.

8.2   The solubility product is usually not quoted for a soluble ionic compound because it is soluble enough that it is easier to work with the solubility or molar solubility, since these are simpler quantities to think about.

8.3   a) $CuBr_{(s)} \longleftrightarrow Cu^+(aq) + Br^-(aq)$
$K_{sp} = [Cu^+][Br^-] = 4.2 \times 10^{-8}$
   b) $ZnC_2O_{4(s)} \longleftrightarrow Zn_2+(aq) + C_2O_4^{2-}(aq)$
$K_{sp} = [Zn^{2+}][C_2O_4^{2-}] =$
   c) $Ag_2CrO_{4(s)} \longleftrightarrow 2Ag^+(aq) + CrO_4^{2-}(aq)$
$K_{sp} = [Ag^+]^2[CrO_4^{2-}] =$
   d) $Hg_2Cl_{2(s)} \longleftrightarrow Hg_2^{2+}(aq) + 2Cl^-(aq)$
$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 3.5 \times 10^{-18}$
   e) $AuCl_{3(s)} \longleftrightarrow Au^{3+}(aq) + 3Cl^-(aq)$
$K_{sp} = [Au^{3+}][Cl^-]^3 =$
   f) $Mn_3(PO_4)_{2(s)} \longleftrightarrow 3 Mn^{2+}(aq) + 2PO_4^{3-}(aq)$
$K_{sp} = [Mn^{2+}]^3[PO_4^{3-}]^2 =$

8.4 $A_xB_y \longleftrightarrow XA^+ + YB^-$
$K_{sp} = [A^+]^x[B^-]^y$

8.5   We can predict whether a precipitate will form when two solutions are mixed by utilizing the solubility rules and the solubility products listed in Table 16.2.

8.6   No, this is not true. The molar solubility of silver(I) chloride is 1.3×10^{-5}, and the molar solubility of silver(I) carbonate is 2.0×10^{-4}.

**8.7**   **(a)**   The solubility equilibrium is given by the equation

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$
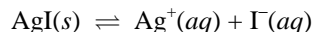
The expression for K_{sp} is given by

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

The value of K_{sp} can be found in Table 16.2 of the text. If the equilibrium concentration of silver ion is the value given, the concentration of iodide ion must be

$$[I^-] = \frac{K_{sp}}{[Ag^+]} = \frac{8.3 \times 10^{-17}}{9.1 \times 10^{-9}} = 9.1 \times 10^{-9} \ M$$

(b)   The value of K_{sp} for aluminum hydroxide can be found in Table 16.2 of the text. The equilibrium expressions are:

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$
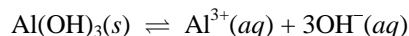
$$K_{sp} = [Al^{3+}][OH^-]^3$$

Using the given value of the hydroxide ion concentration, the equilibrium concentration of aluminum ion is:

$$[Al^{3+}] = \frac{K_{sp}}{[OH^-]^3} = \frac{1.8 \times 10^{-33}}{(2.9 \times 10^{-9})^3} = 7.4 \times 10^{-8} \ M$$

What is the pH of this solution? Will the aluminum concentration change if the pH is altered?

8.8 In each case, we first calculate the number of moles of compound dissolved in one liter of solution (the molar solubility).

(a) $\left(\dfrac{7.3 \times 10^{-2} \text{ g SrF}_2}{1 \text{ L soln}} \right) \times \left(\dfrac{1 \text{ mol SrF}_2}{125.6 \text{ g SrF}_2} \right) = 5.8 \times 10^{-4} \text{ mol/L}$

Step 1: Write the equilibrium reaction. Then, from the equilibrium equation, write the solubility product expression.

$$SrF_2 \ (s) \ \rightleftharpoons \ Sr^{2+} \ (aq) \ + \ 2 \ F^- \ (aq)$$
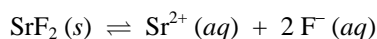
$$K_{sp} \ = \ [Sr^{2+}][F^-]^2$$

Step 2: The molar solubility is the amount of SrF_2 that dissolves. From the stoichiometry of the equilibrium equation, you should find that

$$[Sr^{2+}] \ = \ [SrF_2] \ = \ 5.8 \times 10^{-4} \ M$$

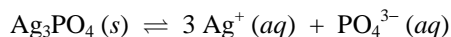and

$$[F^-] \ = \ 2[SrF_2] \ = \ 1.16 \times 10^{-3} \ M$$

Step 3: Substitute the equilibrium concentrations of Sr^{2+} and F^- into the solubility product expression to calculate K_{sp}.

$$K_{sp} \ = \ [Sr^{2+}][F^-]^2 \ = \ (5.8 \times 10^{-4})(1.16 \times 10^{-3})^2 \ = \ 7.8 \times 10^{-10}$$

(b) $\left(\dfrac{6.7 \times 10^{-3} \text{ g Ag}_3\text{PO}_4}{1 \text{ L soln}} \right) \times \left(\dfrac{1 \text{ mol Ag}_3\text{PO}_4}{418.7 \text{ g Ag}_3\text{PO}_4} \right) = 1.6 \times 10^{-5} \text{ mol/L}$

(b) is solved in a similar manner to (a)

The equilibrium equation is:

$$Ag_3PO_4 \ (s) \ \rightleftharpoons \ 3 \ Ag^+ \ (aq) \ + \ PO_4^{3-} \ (aq)$$

$$K_{sp} \ = \ [Ag^+]^3[PO_4^{3-}] \ = \ [3 \times (1.6 \times 10^{-5})]^3(1.6 \times 10^{-5}) \ = \ 1.8 \times 10^{-18}$$

8.9 For $MnCO_3$ dissolving, we write

$$MnCO_3(s) \ \rightleftharpoons \ Mn^{2+}(aq) + CO_3^{2-}(aq)$$
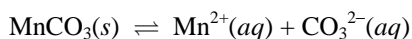
For every mole of $MnCO_3$ that dissolves, one mole of Mn^{2+} will be produced and one mole of CO_3^{2-} will be produced. If the molar solubility of $MnCO_3$ is s mol/L, then the concentrations of Mn^{2+} and CO_3^{2-} are:

$$[Mn^{2+}] = [CO_3^{2-}] = s = 4.2 \times 10^{-6}\ M$$

$$K_{sp} = [Mn^{2+}][CO_3^{2-}] = s^2 = (4.2 \times 10^{-6})^2 = \mathbf{1.8 \times 10^{-11}}$$

8.10   First, we can convert the solubility of MX in g/L to mol/L.

$$\left(\frac{4.63 \times 10^{-3}\ \text{g MX}}{1\ \text{L soln}} \right) \times \left(\frac{1\ \text{mol MX}}{346\ \text{g MX}} \right) = 1.34 \times 10^{-5}\ \text{mol/L} = s\ \text{(molar solubility)}$$
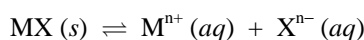
The equilibrium reaction is:

$$MX\ (s) \rightleftharpoons M^{n+}\ (aq) + X^{n-}\ (aq)$$

Since the mole ratio of MX to each of the ions is 1:1, the equilibrium concentrations of each of the ions can also be represented by s. Solving for K_{sp},

$$K_{sp} = [M^{n+}][X^{n-}] = s^2 = (1.34 \times 10^{-5})^2 = \mathbf{1.80 \times 10^{-10}}$$

8.11   The charges of the M and X ions are +3 and −2, respectively (are other values possible?). We first calculate the number of moles of M_2X_3 that dissolve in 1.0 L of water

$$\text{Moles } M_2X_3 = (3.6 \times 10^{-17}\ \text{g}) \left(\frac{1\ \text{mol}}{288\ \text{g}} \right) = 1.3 \times 10^{-19}\ \text{mol}$$

The molar solubility, s, of the compound is therefore $1.3 \times 10^{-19}\ M$. At equilibrium the concentration of M^{3+} must be $2s$ and that of X^{2-} must be $3s$. (See Table 16.3 of the text.)

$$K_{sp} = [M^{3+}]^2[X^{2-}]^3 = [2s]^2[3s]^3 = 108s^5$$

Since these are equilibrium concentrations, the value of K_{sp} can be found by simple substitution

$$K_{sp} = 108s^5 = 108(1.3 \times 10^{-19})^5 = \mathbf{4.0 \times 10^{-93}}$$

8.12   *Step 1:* Write the equilibrium reaction. Then, from the equilibrium equation, write the solubility product expression.

$$CaF_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2\,F^-\ (aq)$$
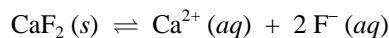
$$K_{sp} = [Ca^{2+}][F^-]^2$$

Step 2: A certain amount of calcium fluoride will dissociate in solution. Let's represent this amount as $-s$. Since one unit of CaF_2 yields one Ca^{2+} ion and two F^- ions, at equilibrium $[Ca^{2+}]$ is s and $[F^-]$ is $2s$. We summarize the changes in concentration as follows:

	$CaF_2\ (s)$	$\rightleftharpoons$	$Ca^{2+}\ (aq)$	$+$	$2\,F^-\ (aq)$
Initial (*M*):			0		0
Change (*M*):	$-s$		$+s$		$+2s$
Equilibrium (*M*):			s		$2s$

Recall, that the concentration of a pure solid does not enter into an equilibrium constant expression. Therefore, the concentration of CaF_2 is not important.

Step 3: Substitute the value of K_{sp} and the concentrations of Ca^{2+} and F^- in terms of s into the solubility product expression to solve for s, the molar solubility.

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

$$4.0 \times 10^{-11} = (s)(2s)^2$$

$$4.0 \times 10^{-11} = 4s^3$$

$$s = \text{molar solubility} = \mathbf{2.2 \times 10^{-4} \, mol/L}$$

The molar solubility indicates that 2.2×10^{-4} mol of CaF_2 will dissolve in 1 L of an aqueous solution.

8.13   Let s be the molar solubility of $Zn(OH)_2$. The equilibrium concentrations of the ions are then

$$[Zn^{2+}] = s \text{ and } [OH^-] = 2s$$

$$K_{sp} = [Zn^{2+}][OH^-]^2 = (s)(2s)^2 = 4s^3 = 1.8 \times 10^{-14}$$

$$s = \left[\frac{1.8 \times 10^{-14}}{4}\right]^{1/3} = 1.7 \times 10^{-5}$$

$$[OH^-] = 2s = 3.4 \times 10^{-5} \, M \text{ and pOH} = 4.47$$

$$\mathbf{pH} = 14.00 - 4.47 = \mathbf{9.53}$$

If the K_{sp} of $Zn(OH)_2$ were smaller by many more powers of ten, would $2s$ still be the hydroxide ion concentration in the solution?

8.14   First we can calculate the OH^- concentration from the pH.

$$pOH = 14.00 - pH$$

$$pOH = 14.00 - 9.68 = 4.32$$

$$[OH^-] = 10^{-pOH} = 10^{-4.32} = 4.8 \times 10^{-5} \, M$$

The equilibrium equation is:

$$MOH \, (s) \rightleftharpoons M^+ \, (aq) + OH^- \, (aq)$$
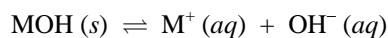
From the balanced equation we know that $[M^+] = [OH^-]$

$$\mathbf{K_{sp}} = [M^+][OH^-] = (4.8 \times 10^{-5})^2 = \mathbf{2.3 \times 10^{-9}}$$

8.15   According to the solubility rules, the only precipitate that might form is $BaCO_3$.

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$
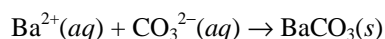
The number of moles of Ba^{2+} present in the original 20.0 mL of $Ba(NO_3)_2$ solution is

$$20.0 \text{ mL} \times \frac{0.10 \text{ mol Ba}^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.0 \times 10^{-3} \text{ mol Ba}^{2+}$$

The total volume after combining the two solutions is 70.0 mL. The concentration of Ba^{2+} in 70 mL is

$$[Ba^{2+}] = \frac{2.0 \times 10^{-3} \text{ mol Ba}^{2+}}{70.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} = 2.9 \times 10^{-2} \text{ } M$$

The number of moles of CO_3^{2-} present in the original 50.0 mL Na_2CO_3 solution is

$$50.0 \text{ mL} \times \frac{0.10 \text{ mol CO}_3^{2-}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 5.0 \times 10^{-3} \text{ mol CO}_3^{2-}$$

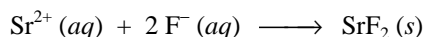The concentration of CO_3^{2-} in the 70.0 mL of combined solution is

$$[CO_3^{2-}] = \frac{5.0 \times 10^{-3} \text{ mol CO}_3^{2-}}{70.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} = 7.1 \times 10^{-2} \text{ } M$$

Now we must compare Q and K_{sp}. From Table 16.2 of the text, the K_{sp} for $BaCO_3$ is 8.1×10^{-9}. As for Q,

$$Q = [Ba^{2+}][CO_3^{2-}] = (2.9 \times 10^{-2})(7.1 \times 10^{-2}) = 2.1 \times 10^{-3}$$

Since $(2.1 \times 10^{-3}) > (8.1 \times 10^{-9})$, then $Q > K_{sp}$. Therefore, $BaCO_3$ will precipitate.

8.16   The net ionic equation is:

$$Sr^{2+} (aq) + 2 F^- (aq) \longrightarrow SrF_2 (s)$$

Let's find the limiting reagent in the precipitation reaction.

$$\text{Moles F}^- = 75 \text{ mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.060 \text{ mol}}{1 \text{ L}}\right) = 0.0045 \text{ mol}$$

$$\text{Moles Sr}^{2+} = 25 \text{ mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.15 \text{ mol}}{1 \text{ L}}\right) = 0.0038 \text{ mol}$$

From the stoichiometry of the balanced equation, twice as many moles of F^- are required to react with Sr^{2+}. This would require 0.0076 mol of F^-, but we only have 0.0045 mol. Thus, F^- is the limiting reagent.

Let's assume that the above reaction goes to completion. Then, we will consider the equilibrium that is established when SrF_2 partially dissociates into ions.

	$Sr^{2+} (aq)$	$+ 2 F^- (aq)$	$\longrightarrow SrF_2 (s)$
Initial (mol)	0.0038	0.0045	0
Change (mol)	−0.00225	−0.0045	+0.00225
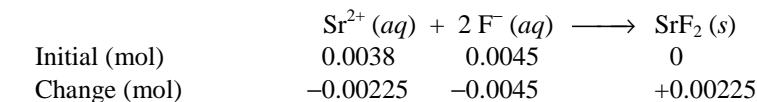
After reaction (mol)   0.00155   0   0.00225

Now, let's establish the equilibrium reaction. The total volume of the solution is 100 mL $=$ 0.100 L. Divide the above moles by 0.100 L to convert to molar concentration.

$$SrF_2\ (s)\ \rightleftharpoons\ Sr^{2+}\ (aq)\ +\ 2\ F^-\ (aq)$$

	$SrF_2\ (s)$	$Sr^{2+}\ (aq)$	$2\ F^-\ (aq)$
Initial (M)	0.0225	0.0155	0
Change (M)	$-x$	$+x$	$+2x$
Equilibrium (M)	$0.0225 - x$	$0.0155 + x$	$2x$

Write the solubility product expression, then solve for x.

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

$$2.0 \times 10^{-10}\ =\ (0.0155 + x)(2x)^2\ \approx\ (0.0155)(2x)^2$$

$$x\ =\ 5.7 \times 10^{-5}\ M$$

$$[F^-]\ =\ 2x\ =\ \mathbf{1.1 \times 10^{-4}\ M}$$

$$[Sr^{2+}]\ =\ 0.0155 + x\ =\ \mathbf{0.016\ M}$$

Both sodium ions and nitrate ions are spectator ions and therefore do not enter into the precipitation reaction.

$$[NO_3^-]\ =\ \frac{2(0.0038)\ \text{mol}}{0.10\ \text{L}}\ =\ \mathbf{0.076\ M}$$

$$[Na^+]\ =\ \frac{0.0045\ \text{mol}}{0.10\ \text{L}}\ =\ \mathbf{0.045\ M}$$

8.17   The presence of a common ion decreases the solubility of weakly soluble ionic compounds. The presence of carbonate anion in a sodium carbonate solution will lower the solubility of calcium carbonate. Le Chatelier's principle explains this by noting the following equilibrium: $CaCO_3$ $\rightarrow$ / $\leftarrow$ $Ca^{2+} + CO_3^{2+}$
Adding carbonate anion will shift this equilibrium to the left, lowering the solubility of calcium carbonate.

8.18   B is reasonable. D is reasonable. None of the others are reasonable statements.

8.19   First let s be the molar solubility of $CaCO_3$ in this solution.

$$CaCO_3(s)\ \rightleftharpoons\ Ca^{2+}(aq)\ +\ CO_3^{2-}(aq)$$

	$CaCO_3(s)$	$Ca^{2+}(aq)$	$CO_3^{2-}(aq)$
Initial (M):		0.050	0
Change (M):		$+s$	$+s$
Equilibrium (M):		$(0.050 + s)$	s

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = (0.050 + s)s = 8.7 \times 10^{-9}$$

We can assume $0.050 + s \approx 0.050$, then

$$s = \frac{8.7 \times 10^{-9}}{0.050} = 1.7 \times 10^{-7} \ M$$

The mass of $CaCO_3$ can then be found.

$$3.0 \times 10^2 \ mL \left(\frac{1 \ L}{1000 \ mL} \right) \left(\frac{1.7 \times 10^{-7} \ mol}{1 \ L} \right) \left(\frac{100.1 \ g \ CaCO_3}{1 \ mol} \right) = \mathbf{5.1 \times 10^{-6} \ g \ CaCO_3}$$

8.20 **(a)** Set up a table to find the equilibrium concentrations in pure water.

	$PbBr_2 \ (s)$	$\rightleftharpoons$	$Pb^{2+} \ (aq)$	$+ \ 2 \ Br^- \ (aq)$
Initial (M)			0	0
Change (M)	$-s$		$+s$	$+2s$
Equilibrium (M)			s	$2s$

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

$$8.9 \times 10^{-6} = (s)(2s)^2$$

$$s = \text{molar solubility} = \mathbf{0.013 \ M}$$

(b) Set up a table to find the equilibrium concentrations in 0.20 M KBr. KBr is a soluble salt that ionizes completely giving a initial concentration of $Br^- = 0.20 \ M$.

	$PbBr_2 \ (s)$	$\rightleftharpoons$	$Pb^{2+} \ (aq)$	$+ \ 2 \ Br^- \ (aq)$
Initial (M)			0	0.20
Change (M)	$-s$		$+s$	$+2s$
Equilibrium (M)			s	$0.20 + 2s$

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

$$8.9 \times 10^{-6} = (s)(0.20 + 2s)^2$$

$$8.9 \times 10^{-6} \approx (s)(0.20)^2$$

$$s = \text{molar solubility} = \mathbf{2.2 \times 10^{-4} \ M}$$

Thus, the molar solubility of $PbBr_2$ is reduced from 0.013 M to $2.2 \times 10^{-4} \ M$ as a result of the common ion (Br^-) effect.

(c) Set up a table to find the equilibrium concentrations in 0.20 M $Pb(NO_3)_2$. $Pb(NO_3)_2$ is a soluble salt that dissociates completely giving an initial concentration of $[Pb^{2+}] = 0.20 \ M$.

	$PbBr_2 \ (s)$	$\rightleftharpoons$	$Pb^{2+} \ (aq)$	$+ \ 2 \ Br^- \ (aq)$
Initial (M):			0.20	0
Change (M):	$-s$		$+s$	$+2s$
Equilibrium (M):			$0.20 + s$	$2s$

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

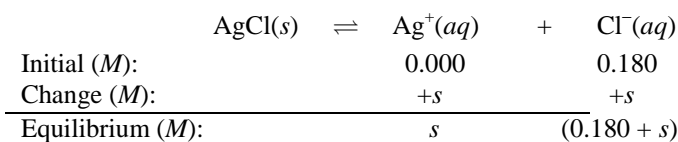$$8.9 \times 10^{-6} = (0.20 + s)(2s)^2$$

$$8.9 \times 10^{-6} \approx (0.20)(2s)^2$$

$$s = \text{molar solubility} = \mathbf{3.3 \times 10^{-3}}\,\boldsymbol{M}$$

Thus, the molar solubility of $PbBr_2$ is reduced from 0.013 M to 3.3×10^{-3} M as a result of the common ion (Pb^{2+}) effect.

8.21 We first calculate the concentration of chloride ion in the solution.

$$[Cl^-] = \left(\frac{10.0 \text{ g } CaCl_2}{1 \text{ L soln}}\right)\left(\frac{1 \text{ mol } CaCl_2}{111.0 \text{ g } CaCl_2}\right)\left(\frac{2 \text{ mol } Cl^-}{1 \text{ mol } CaCl_2}\right) = 0.180\ M$$
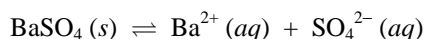
	$AgCl(s)$	$\rightleftharpoons$	$Ag^+(aq)$	$+$	$Cl^-(aq)$
Initial (M):			0.000		0.180
Change (M):			$+s$		$+s$
Equilibrium (M):			s		$(0.180 + s)$

If we assume that $(0.180 + s) \approx 0.180$, then

$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{0.180} = 8.9 \times 10^{-10}\ M = s$$

The molar solubility of AgCl is $\mathbf{8.9 \times 10^{-10}}\,\boldsymbol{M}$.

8.22 The equilibrium reaction is:

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

For both parts of the problem:

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

(a) In pure water, let $[Ba^{2+}] = [SO_4^{2-}] = s$

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

$$1.1 \times 10^{-10} = s^2$$

$$s = \mathbf{1.0 \times 10^{-5}}\,\boldsymbol{M}$$

The molar solubility of $BaSO_4$ in pure water is 1.0×10^{-5} mol/L.

(b) Assuming the molar solubility of $BaSO_4$ to be s, then

$$[Ba^{2+}] = s\ M \quad \text{and} \quad [SO_4^{2-}] = (1.0 + s)\ M \approx 1.0\ M$$

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

$$1.1 \times 10^{-10} = (s)(1.0)$$

$$s = 1.1 \times 10^{-10} \, M$$

Due to the common ion effect, the molar solubility of $BaSO_4$ decreases to 1.1×10^{-10} mol/L in
$1.0 \, M \, SO_4^{2-}(aq)$ compared to 1.0×10^{-5} mol/L in pure water.

8.23 In each entry a Lewis acid, such as Ag^+, joins with a Lewis base, such as NH_3. Acids and bases are attracted to each other, so these complexes have a high K_f.

8.24 The effect of complex ion formation will dramatically increase solubility of compounds, in most cases. As an example, silver(I) chloride will be quite soluble in a solution of potassium cyanide, due to sequestering of the silver ion by the basic cyanide anion. Silver(I) chloride is only sparingly soluble in deionized water.

8.25 First find the molarity of the copper(II) ion

$$\text{Moles CuSO}_4 = 2.50 \, \text{g} \left(\frac{1 \, \text{mol}}{159.6 \, \text{g}} \right) = 0.0157 \, \text{mol}$$

$$[Cu^{2+}] = \frac{0.0157 \, \text{mol}}{0.90 \, \text{L}} = 0.0174 \, M$$

As in Example 16.15 of the text, the position of equilibrium will be far to the right. We assume essentially all the copper ion is complexed with NH_3. The NH_3 consumed is $4 \times 0.0174 \, M = 0.0696 \, M$. The uncombined NH_3 remaining is $(0.30 - 0.0696) \, M$, or $0.23 \, M$. The equilibrium concentrations of $Cu(NH_3)_4^{2+}$ and NH_3 are therefore **0.0174 M** and **0.23 M**, respectively. We find $[Cu^{2+}]$ from the formation constant expression.

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 5.0 \times 10^{13} = \frac{0.0174}{[Cu^{2+}][0.23]^4}$$

$$\mathbf{[Cu^{2+}] = 1.2 \times 10^{-13} \, M}$$

8.26 In solution, Cd^{2+} ions will complex with CN^- ions. The concentration of Cd^{2+} will be determined by the following equilibrium

$$Cd^{2+}(aq) + 4 \, CN^-(aq) \rightleftharpoons Cd(CN)_4^{2-} \qquad K_f = 7.1 \times 10^{16}$$
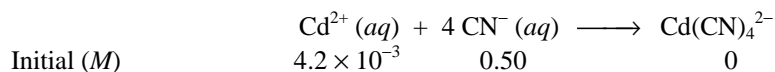
Since K_f is so large, this equilibrium lies far to the right. We can safely assume that all the Cd^{2+} reacts.

Step 1: Calculate the initial concentration of Cd^{2+} ions.

$$[Cd^{2+}]_0 = 0.50 \, \text{g} \times \frac{1 \, \text{mol Cd(NO}_3)_2}{236.42 \, \text{g Cd(NO}_3)_2} \times \frac{1 \, \text{mol Cd}}{1 \, \text{mol Cd(NO}_3)_2} \times \frac{1}{0.50 \, \text{L}} = 4.2 \times 10^{-3} \, M$$

Step 2: If we assume that the above equilibrium goes to completion, we can write

$$Cd^{2+}(aq) + 4 \, CN^-(aq) \longrightarrow Cd(CN)_4^{2-}$$

Initial (*M*) 4.2×10^{-3} 0.50   0

After reaction (M)   0   0.48 4.2×10^{-3}

Step 3: To find the concentration of free Cd^{2+} at equilibrium, use the formation constant expression.

$$K_f = \frac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4}$$

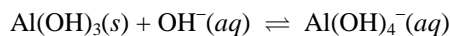Rearranging,

$$[Cd^{2+}] = \frac{[Cd(CN)_4^{2-}]}{K_f[CN^-]^4}$$

Substitute the equilibrium concentrations calculated above into the formation constant expression to calculate the equilibrium concentration of Cd^{2+}.

$$[\mathbf{Cd^{2+}}] = \frac{[Cd(CN)_4^{2-}]}{K_f[CN^-]^4} = \frac{4.2 \times 10^{-3}}{(7.1 \times 10^{16})(0.48)^4} = \mathbf{1.1 \times 10^{-18}} \, \boldsymbol{M}$$
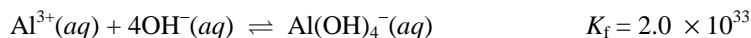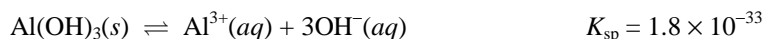
$$[\mathbf{CN^-}] = 0.48 \, M + (1.1 \times 10^{-18} \, M) = \mathbf{0.48} \, \boldsymbol{M}$$

$$[\mathbf{Cd(CN)_4^{2-}}] = (4.2 \times 10^{-3} \, M) - (1.1 \times 10^{-18}) = \mathbf{4.2 \times 10^{-3}} \, \boldsymbol{M}$$

8.27   The reaction

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$$

is the sum of the two known reactions

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \qquad\qquad K_{sp} = 1.8 \times 10^{-33}$$

$$Al^{3+}(aq) + 4OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq) \qquad\qquad K_f = 2.0 \times 10^{33}$$

The equilibrium constant is

$$K = K_{sp}K_f = (1.8 \times 10^{-33})(2.0 \times 10^{33}) = 3.6 = \frac{[Al(OH)_4^-]}{[OH^-]}$$

When pH = 14.00, $[OH^-] = 1.0 \, M$, therefore
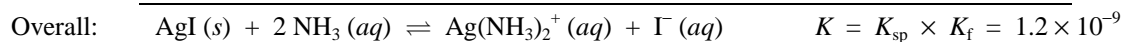
$$[Al(OH)_4^-] = K[OH^-] = 3.6 \times 1 = 3.6 \, M$$

This represents the maximum possible concentration of the complex ion at pH 14.00. Since this is much larger than the initial 0.010 M, the complex ion will be the predominant species.

8.28   Silver iodide is only slightly soluble. It dissociates to form a small amount of Ag^+ and I^- ions. The Ag^+ ions then complex with NH_3 in solution to form the complex ion $Ag(NH_3)_2^+$. The balanced equations are:

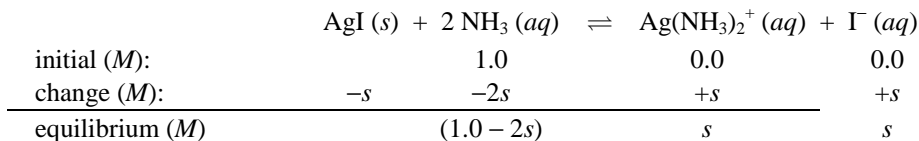$$AgI \, (s) \rightleftharpoons Ag^+ \, (aq) + I^- \, (aq) \qquad\qquad\qquad K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$$

$$\text{Ag}^+ (aq) + 2\,\text{NH}_3 (aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq) \qquad\qquad K_f =$$

$$\frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.5\times10^7$$

Overall: $\text{AgI} (s) + 2\,\text{NH}_3 (aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq) + \text{I}^- (aq) \qquad K = K_{sp} \times K_f = 1.2\times10^{-9}$

If s is the molar solubility of AgI then,

	AgI (s)	+ 2 NH$_3$ (aq)	$\rightleftharpoons$	Ag(NH$_3$)$_2^+$ (aq)	+ I$^-$ (aq)
initial (M):		1.0		0.0	0.0
change (M):	$-s$	$-2s$		$+s$	$+s$
equilibrium (M)		$(1.0 - 2s)$		s	s

Because K_f is large, we can assume all of the silver ions exist as Ag(NH$_3$)$_2^+$. Thus,

$$[\text{Ag(NH}_3)_2^+] = [\text{I}^-] = s$$
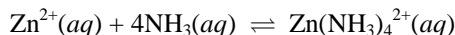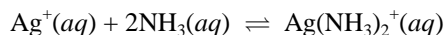
We can write the equilibrium constant expression for the above reaction, then solve for s.

$$K = 1.2\times10^{-9} = \frac{(s)(s)}{(1.0-2s)^2} \approx \frac{(s)(s)}{(1.0)^2}$$

$$s = 3.5\times10^{-5}\,M$$

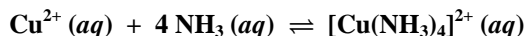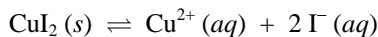At equilibrium, 3.5×10^{-5} moles of AgI dissolves in 1 L of 1.0 M NH$_3$ solution.

8.29   The balanced equations are:

$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)$$
$$\text{Zn}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Zn(NH}_3)_4^{2+}(aq)$$

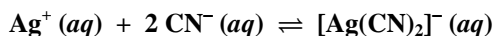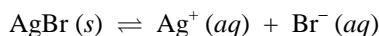Zinc hydroxide forms a complex ion with excess OH$^-$ and silver hydroxide does not; therefore, zinc hydroxide is soluble in 6 M NaOH.

8.30   **(a)**   The equations are as follows:

$$\text{CuI}_2 (s) \rightleftharpoons \text{Cu}^{2+} (aq) + 2\,\text{I}^- (aq)$$

$$\textbf{Cu}^{2+} \textbf{(aq)} + \textbf{4 NH}_3 \textbf{(aq)} \rightleftharpoons \textbf{[Cu(NH}_3)_4]^{2+} \textbf{(aq)}$$

The ammonia combines with the Cu^{2+} ions formed in the first step to form the complex ion [Cu(NH$_3$)$_4$]$^{2+}$, effectively removing the Cu^{2+} ions, causing the first equilibrium to shift to the right (resulting in more CuI$_2$ dissolving).

(b)   Similar to part (a):

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

$$\textbf{Ag}^+ \textbf{(aq)} + \textbf{2 CN}^- \textbf{(aq)} \rightleftharpoons \textbf{[Ag(CN)}_2]^- \textbf{(aq)}$$

(c) Similar to parts (a) and (b).

$$HgCl_2 \ (s) \ \rightleftharpoons \ Hg^{2+} \ (aq) \ + \ 2Cl^- \ (aq)$$

$$\mathbf{Hg^{2+} \ (aq) \ + \ 4Cl^- \ (aq) \ \rightleftharpoons \ [HgCl_4]^{2-} \ (aq)}$$
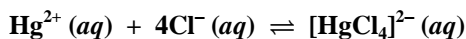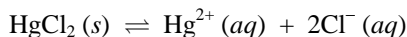
8.31 First, calculate the pH of the 2.00 M weak acid (HNO_2) solution before any NaOH is added.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{2.00 - x}$$

$$x = [H^+] = 0.030 \ M$$

$$pH = -\log(0.030) = 1.52$$

Since the pH after the addition is 1.5 pH units greater, the new pH $= 1.52 + 1.50 = 3.02$.

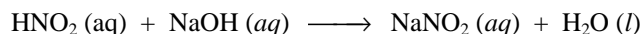From this new pH, we can calculate the $[H^+]$ in solution.

$$[H^+] = 10^{-pH} = 10^{-3.02} = 9.55 \times 10^{-4} \ M$$

When the NaOH is added, we dilute our original 2.00 M HNO_2 solution to:

$$M_I V_I = M_F V_F$$
$$(2.00 \ M)(400 \ mL) = M_F(600 \ mL)$$
$$M_F = 1.33 \ M$$

Since we have not reached the equivalence point, we have a buffer solution. The reaction between HNO_2 and NaOH is:

$$HNO_2 \ (aq) \ + \ NaOH \ (aq) \ \longrightarrow \ NaNO_2 \ (aq) \ + \ H_2O \ (l)$$

Since the mole ratio between HNO_2 and NaOH is 1:1, the decrease in $[HNO_2]$ is the same as the decrease in [NaOH].

We can calculate the decrease in $[HNO_2]$ by setting up the weak acid equilibrium. From the pH of the solution, we know that the $[H^+]$ at equilibrium is $9.55 \times 10^{-4} \ M$.

	$HNO_2 \ (aq)$	$\rightleftharpoons$	$H^+ \ (aq)$	+	$NO_2^- \ (aq)$
Initial (M)	1.33		0		0
Change (M)	$-x$				$+x$
Equilibrium (M)	$1.33 - x$		9.55×10^{-4}		x

We can calculate x from the equilibrium constant expression.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$$4.5 \times 10^{-4} = \frac{(9.55 \times 10^{-4})(x)}{1.33 - x}$$

$$x = 0.426 \ M$$

Thus, x is the decrease in [HNO$_2$] which equals the concentration of added OH$^-$. However, this is the concentration of NaOH after it has been diluted to 600 mL. We need to correct for the dilution from
200 mL to 600 mL to calculate the concentration of the original NaOH solution.

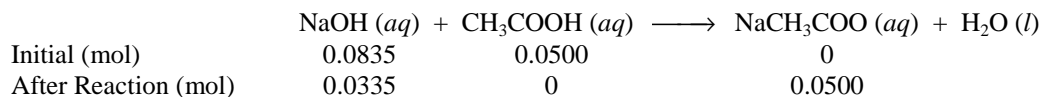$$M_I V_I = M_F V_F$$
$$M_I(200 \ \text{mL}) = (0.426 \ M)(600 \ \text{mL})$$
$$\textbf{[NaOH]} = M_I = \textbf{1.28} \ \textbf{\textit{M}}$$

8.32   The resulting solution is not a buffer system. There is excess NaOH and the neutralization is well past the equivalence point. We have a solution of sodium acetate and sodium hydroxide.

$$\text{Moles NaOH} = 0.500 \ \text{L} \left(\frac{0.167 \ \text{mol}}{1 \ \text{L}} \right) = 0.0835 \ \text{mol}$$

$$\text{Moles CH}_3\text{COOH} = 0.500 \text{L} \left(\frac{0.100 \ \text{mol}}{1 \ \text{L}} \right) = 0.0500 \ \text{mol}$$

The reaction between sodium hydroxide and acetic acid is:

	NaOH (*aq*) + CH$_3$COOH (*aq*) $\longrightarrow$ NaCH$_3$COO (*aq*) + H$_2$O (*l*)		
Initial (mol)	0.0835	0.0500	0
After Reaction (mol)	0.0335	0	0.0500

Since the total volume of the solution is 1.00 L, we can convert the number of moles directly to molarity.

$$\textbf{[OH}^-\textbf{]} = \textbf{0.0335} \ \textbf{\textit{M}}$$
$$\textbf{[Na}^+\textbf{]} = \textbf{0.0335} \ \textbf{\textit{M}} + \textbf{0.0500} \ \textbf{\textit{M}} = \textbf{0.0835} \ \textbf{\textit{M}}$$
$$\textbf{[CH}_3\textbf{COO}^-\textbf{]} = \textbf{0.0500} \ \textbf{\textit{M}}$$

We can calculate the [H$^+$] from the [OH$^-$].

$$\textbf{[H}^+\textbf{]} = \frac{K_w}{\textbf{[OH}^-\textbf{]}} = \frac{1.00 \times 10^{-14}}{0.0335} = \textbf{2.99} \times \textbf{10}^{-13} \ \textbf{\textit{M}}$$

Finally, we can calculate the acetic acid concentration from the K_a expression.

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

or,

$$[\text{CH}_3\text{COOH}] = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{K_a}$$

$$\textbf{[CH}_3\textbf{COOH]} = \frac{(2.99 \times 10^{-13})(0.0500)}{1.8 \times 10^{-5}} = \textbf{8.3} \times \textbf{10}^{-10} \ \textbf{\textit{M}}$$

8.33   A solubility equilibrium is an equilibrium between a solid (reactant) and its components (products: ions, neutral molecules, etc.) in solution. Only **(d)** represents a solubility equilibrium.

Consider part (b). Can you write the equilibrium constant for this reaction in terms of K_{sp} for calcium phosphate?

8.34   Since equal volumes of the two solutions were used, the initial molar concentrations will be halved.

$$[Ag^+] = \frac{0.12\ M}{2} = 0.060\ M$$

$$[Cl^-] = \frac{2(0.14\ M)}{2} = 0.14\ M$$

Let's assume that the Ag^+ ions and Cl^- ions react completely to form AgCl (s). Then, we will reestablish the equilibrium between AgCl, Ag^+, and Cl^-.

	Ag^+ (aq)	+	Cl^- (aq)	$\longrightarrow$	AgCl (s)
Initial (*M*)	0.060		0.14		0
Change (*M*)	−0.060		−0.060		+0.060
After reaction (*M*)	0		0.080		0.060

Now, setting up the equilibrium,

	AgCl(s)	$\rightleftharpoons$	Ag^+(aq)	+	Cl^-(aq)
Initial (*M*):	0.060		0		0.080
Change (*M*):	−*s*		+*s*		+*s*
Equilibrium (*M*):	0.060 − *s*		*s*		0.080 + *s*

Set up the K_{sp} expression to solve for *s*.

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

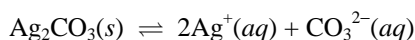$$1.6 \times 10^{-10} = (s)(0.080 + s)$$

$$s = 2.0 \times 10^{-9}\ M$$

$$[Ag^+] = s = \mathbf{2.0 \times 10^{-9}\ M}$$
$$[Cl^-] = 0.080\ M - s = \mathbf{0.080\ M}$$
$$[Zn^{2+}] = \frac{0.14\ M}{2} = \mathbf{0.070\ M}$$
$$[NO_3^-] = \frac{0.12\ M}{2} = \mathbf{0.060\ M}$$

8.35   First we find the molar solubility and then convert moles to grams. The solubility equilibrium for silver carbonate is:

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = (2s)^2(s) = 4s^3 = 8.1 \times 10^{-12}$$

$$s = \left(\frac{8.1 \times 10^{-12}}{4}\right)^{1/3} = 1.3 \times 10^{-4} \ M$$

Converting from mol/L to g/L:

$$\left(\frac{1.3 \times 10^{-4} \text{ mol}}{1 \text{ L soln}}\right)\left(\frac{275.8 \text{ g}}{1 \text{ mol}}\right) = \textbf{0.036 g/L}$$

8.36   The equilibrium reaction is:

	$Pb(IO_3)_2 \ (aq)$	$\rightleftharpoons$	$Pb^{2+} \ (aq)$	+	$2 \ IO_3^- \ (aq)$
Initial (M)			0		0.10
Change (M)	-2.4×10^{-11}		$+2.4 \times 10^{-11}$		$+2(2.4 \times 10^{-11})$
Equilibrium (M)			2.4×10^{-11}		≈ 0.10

Substitute the equilibrium concentrations into the solubility product expression to calculate K_{sp}.

$$K_{sp} = [Pb^{2+}][IO_3^-]^2$$

$$K_{sp} = (2.4 \times 10^{-11})(0.10)^2 = \textbf{2.4} \times \textbf{10}^{-13}$$

8.37 $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$

$$[Ba^{2+}] = 1.0 \times 10^{-5} \ M$$

In 5.0 L, the number of moles of Ba^{2+} is

$$(5.0 \text{ L})(1.0 \times 10^{-5} \text{ mol/L}) = 5.0 \times 10^{-5} \text{ mol } Ba^{2+} = 5.0 \times 10^{-5} \text{ mol } BaSO_4$$

The number of grams of $BaSO_4$ dissolved is

$$5.0 \times 10^{-5} \text{ mol } BaSO_4 \times \frac{233.4 \text{ g } BaSO_4}{1 \text{ mol } BaSO_4} = 0.012 \text{ g } BaSO_4$$

In practice, even less $BaSO_4$ will dissolve because the $BaSO_4$ is not in contact with the entire volume of blood. $Ba(NO_3)_2$ is too soluble to be used for this purpose.

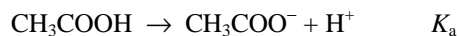**8.38**   **(a)** $H^+ + OH^- \rightarrow H_2O$ $K = 1.0 \times 10^{14}$

(b) $H^+ + NH_3 \rightarrow NH_4^+$

$$K = \frac{1}{K_a} = \frac{1}{5.6 \times 10^{-10}} = 1.8 \times 10^9$$

(c) $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Broken into 2 equations:

$CH_3COOH \rightarrow CH_3COO^- + H^+$ K_a

$H^+ + OH^- \rightarrow H_2O$ $1/K_w$

$$K = \frac{K_a}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^{9}$$

(d) $CH_3COOH + NH_3 \rightarrow CH_3COONH_4$

Broken into 2 equations:

$CH_3COOH \rightarrow CH_3COO^- + H^+$ $\qquad\qquad K_a$

$NH_3 + H^+ \rightarrow NH_4^+$ $\qquad\qquad\qquad \dfrac{1}{K_a'}$
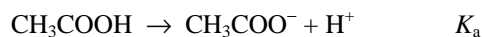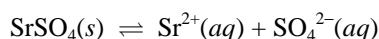
$$K = \frac{K_a}{K_a'} = \frac{1.8 \times 10^{-5}}{5.6 \times 10^{-10}} = 3.2 \times 10^{4}$$

8.39 Strontium sulfate is the more soluble of the two compounds. Therefore, we can assume that all of the SO_4^{2-} ions come from $SrSO_4$.

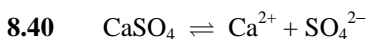$$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Sr^{2+}][SO_4^{2-}] = s^2 = 3.8 \times 10^{-7}$$

$$s = [Sr^{2+}] = [SO_4^{2-}] = \sqrt{3.8 \times 10^{-7}} = \mathbf{6.2 \times 10^{-4}\ M}$$
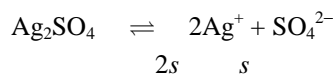
For $BaSO_4$:

$$[\mathbf{Ba^{2+}}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{1.1 \times 10^{-10}}{6.2 \times 10^{-4}} = \mathbf{1.8 \times 10^{-7}\ M}$$

8.40 $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$

$$s^2 = 2.4 \times 10^{-5}$$

$$s = 4.9 \times 10^{-3}\ M$$

Solubility: $4.9 \times 10^{-3}\ \dfrac{mol}{L} \times \dfrac{136.2\ g}{1\ mol} = \mathbf{0.67\ g/L}$

$Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$
$\qquad\qquad\quad 2s \qquad s$

$$1.4 \times 10^{-5} = 4s^3$$

$$s = 0.015\ M$$

Solubility: $0.015\ \dfrac{mol}{L} \times \dfrac{311.1\ g}{1\ mol} = \mathbf{4.7\ g/L}$

Note: Ag_2SO_4 has a larger solubility.

8.41 **(a)** This is a common ion (CO_3^{2-}) problem.

The dissociation of Na_2CO_3 is:

$$\text{Na}_2\text{CO}_3 \ (s) \ \xrightarrow{\ \text{H}_2\text{O}\ } \ 2 \ \text{Na}^+ \ (aq) \ + \ \text{CO}_3^{2-} \ (aq)$$
$$\qquad\qquad\qquad\qquad 2(0.050 \ M) \qquad 0.050 \ M$$
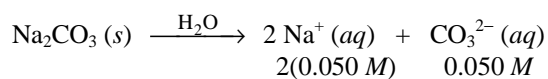
Let s be the molar solubility of CaCO_3 in Na_2CO_3 solution. We summarize the changes as:

	$\text{CaCO}_3 \ (s)$	$\rightleftharpoons$	$\text{Ca}^{2+} \ (aq)$	$+ \ \text{CO}_3^{2-}$
Initial (M)			0.00	0.050
Change (M)			$+s$	$+s$
Equil. (M)			$+s$	$0.050 + s$

$$K_{sp} \ = \ [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$8.7 \times 10^{-9} \ = \ s(0.050 + s)$$

Since s is small, we can assume that $0.050 + s \approx 0.050$
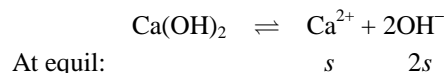
$$8.7 \times 10^{-9} \ = \ 0.050s$$

$$s \ = \ \mathbf{1.7 \times 10^{-7} \ M}$$

Thus, the addition of washing soda to permanent hard water removes most of the Ca^{2+} ions as a result of the common ion effect.

(b) Mg^{2+} is not removed by this procedure, because MgCO_3 is fairly soluble ($K_{sp} = 4.0 \times 10^{-5}$).

(c) The K_{sp} for Ca(OH)_2 is 8.0×10^{-6}.

$$\text{Ca(OH)}_2 \ \rightleftharpoons \ \text{Ca}^{2+} + 2\text{OH}^-$$
$$\text{At equil:} \qquad\qquad\qquad s \qquad 2s$$

$$K_{sp} \ = \ 8.0 \times 10^{-6} \ = \ [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$4s^3 \ = \ 8.0 \times 10^{-6}$$

$$s \ = \ 0.0126 \ M$$

$$[\text{OH}^-] \ = \ 2s \ = \ 0.0252 \ M$$

$$\text{pOH} \ = \ -\log(0.0252) \ = \ 1.60$$

$$\textbf{pH} \ = \ \mathbf{12.40}$$

(d) The $[\text{OH}^-]$ calculated above is $0.0252 \ M$. At this rather high concentration of OH^-, most of the Mg^{2+} will be removed as Mg(OH)_2. The small amount of Mg^{2+} remaining in solution is due to the following equilibrium:

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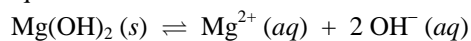
$$K_{sp} \ = \ [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.2 \times 10^{-11} \ = \ [\text{Mg}^{2+}](0.0252)^2$$

$$\mathbf{[\text{Mg}^{2+}] \ = \ 1.9 \times 10^{-8} \ M}$$

(e) Remove Ca^{2+} first because it is present in larger amounts.