CHAPTER 16

SOLUBILITY AND COMPLEX ION EQUILIBRIA

Questions

9. K_{sp} values can only be compared to determine relative solubilities when the salts produce the same number of ions. Here, Ag_2S and CuS do not produce the same number of ions when they dissolve, so each has a different mathematical relationship between the K_{sp} value and the molar solubility. To determine which salt has the larger molar solubility, you must do the actual calculations and compare the two molar solubility values.

10. The solubility product constant (K_{sp}) is an equilibrium constant that has only one value for a given solid at a given temperature. Solubility, on the other hand, can have many values for a given solid at a given temperature. In pure water, the solubility is some value, yet the solubility is another value if a common ion is present. And the actual solubility when a common ion is present varies according to the concentration of the common ion. However, in all cases the product of the ion concentrations must satisfy the K_{sp} expression and give that one unique K_{sp} value at that particular temperature.

11. i. This is the result when you have a salt that breaks up into two ions. Examples of these salts include AgCl, $SrSO_4$, $BaCrO_4$, and $ZnCO_3$.

    ii. This is the result when you have a salt that breaks up into three ions, either two cations and one anion or one cation and two anions. Some examples are SrF_2, Hg_2I_2, and Ag_2SO_4.

    iii. This is the result when you have a salt that breaks up into four ions, either three cations and one anion (Ag_3PO_4) or one cation and three anions (ignoring the hydroxides, there are no examples of this type of salt in Table 16.1).

    iv. This is the result when you have a salt that breaks up into five ions, either three cations and two anions [$Sr_3(PO_4)_2$] or two cations and three anions (no examples of this type of salt are in Table 16.1).

12. The obvious choice is that the metal ion reacts with PO_4^{3-} and forms an insoluble phosphate salt. The other possibility is due to the weak base properties of PO_4^{3-} (PO_4^{3-} is the conjugate base of the weak acid HPO_4^{2-}, so it is a weak base). Because PO_4^{3-} is a weak base in water, OH^- ions are present at a fairly large concentration. Hence the other potential precipitate is the metal ion reacting with OH^- to form an insoluble hydroxide salt.

13. For the K_{sp} reaction of a salt dissolving into its respective ions, a common ion would be one of the ions in the salt added from an outside source. When a common ion (a product in the K_{sp} reaction) is present, the K_{sp} equilibrium shifts to the left, resulting in less of the salt dissolving into its ions (solubility decreases).

14. S^{2-} is a very basic anion and reacts significantly with H^+ to form HS^- ($S^{2-} + H^+ \rightleftharpoons HS^-$). The actual concentration of S^{2-} in solution depends on the amount of H^+ present. In basic solutions, little H^+ is present, which shifts the above reaction to the left. In basic solutions, the S^{2-} concentration is relatively high. So, in basic solutions, a wider range of sulfide salts will precipitate. However, in acidic solutions, added H^+ shifts the equilibrium to the right resulting in a lower S^{2-} concentration. In acidic solutions, only the least soluble sulfide salts will precipitate out of solution.

15. Some people would automatically think that an increase in temperature would increase the solubility of a salt. This is not always the case as some salts show a decrease in solubility as temperature increases. The two major methods used to increase solubility of a salt both involve removing one of the ions in the salt by reaction. If the salt has an ion with basic properties, adding H^+ will increase the solubility of the salt because the added H^+ will react with the basic ion, thus removing it from solution. More salt dissolves in order to to make up for the lost ion. Some examples of salts with basic ions are AgF, $CaCO_3$, and $Al(OH)_3$. The other way to remove an ion is to form a complex ion. For example, the Ag^+ ion in silver salts forms the complex ion $Ag(NH_3)_2^+$ as ammonia is added. Silver salts increase their solubility as NH_3 is added because the Ag^+ ion is removed through complex ion formation.

16. Because the formation constants are generally very large numbers, the stepwise reactions can be assumed to essentially go to completion. Thus an equilibrium mixture of a metal ion and a specific ligand will mostly contain the final complex ion in the stepwise formation reactions.

17. In 2.0 *M* NH_3, the soluble complex ion $Ag(NH_3)_2^+$ forms, which increases the solubility of AgCl(s). The reaction is $AgCl(s) + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$. In 2.0 *M* NH_4NO_3, NH_3 is only formed by the dissociation of the weak acid NH_4^+. There is not enough NH_3 produced by this reaction to dissolve AgCl(s) by the formation of the complex ion.

18. Unlike AgCl(s), $PbCl_2(s)$ shows a significant increase in solubility with an increase in temperature. Hence add NaCl to the solution containing the metal ion to form the chloride salt precipitate, and then heat the solution. If the precipitate disappears, then $PbCl_2$ is present, and the metal ion is Pb^{2+}. If the precipitate does not dissolve with an increase in temperature, then AgCl is the precipitate, and Ag^+ is the metal ion present.

Exercises

Solubility Equilibria

19. a. $AgC_2H_3O_2(s) \rightleftharpoons Ag^+(aq) + C_2H_3O_2^-(aq)$ $K_{sp} = [Ag^+]\,[C_2H_3O_2^-]$

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

c. $Ca_3(PO_4)_2(s) \rightleftharpoons 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq)$ $K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2$

20. a. $Ag_2CO_3(s) \rightleftharpoons 2\ Ag^+(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Ag^+]^2\,[CO_3^{2-}]$

b. $Ce(IO_3)_3(s) \rightleftharpoons Ce^{3+}(aq) + 3\ IO_3^-\ (aq)$ $K_{sp} = [Ce^{3+}]\ [IO_3^-]^3$

c. $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\ F^-(aq)$ $K_{sp} = [Ba^{2+}]\ [F^-]^2$

21. In our setup, s = solubility of the ionic solid in mol/L. This is defined as the maximum amount of a salt that can dissolve. Because solids do not appear in the K_{sp} expression, we do not need to worry about their initial and equilibrium amounts.

a.

	$CaC_2O_4(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$
Initial			0		0
	s mol/L of $CaC_2O_4(s)$ dissolves to reach equilibrium				
Change	$-s$	$\rightarrow$	$+s$		$+s$
Equil.			s		s

From the problem, $s = 4.8 \times 10^{-5}$ mol/L.

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = (s)(s) = s^2$, $K_{sp} = (4.8 \times 10^{-5})^2 = 2.3 \times 10^{-9}$

b.

	$BiI_3(s)$	$\rightleftharpoons$	$Bi^{3+}(aq)$	+	$3\ I^-(aq)$
Initial			0		0
	s mol/L of $BiI_3(s)$ dissolves to reach equilibrium				
Change	$-s$	$\rightarrow$	$+s$		$+3s$
Equil.			s		$3s$

$K_{sp} = [Bi^{3+}][I^-]^3 = (s)(3s)^3 = 27\ s^4$, $K_{sp} = 27(1.32 \times 10^{-5})^4 = 8.20 \times 10^{-19}$

22. a.

	$Pb_3(PO_4)_2(s)$	$\rightleftharpoons$	$3\ Pb^{2+}(aq)$	+	$2\ PO_4^{3-}(aq)$
Initial			0		0
	s mol/L of $Pb_3(PO_4)_2(s)$ dissolves to reach equilibrium = molar solubility				
Change	$-s$	$\rightarrow$	$+3s$		$+2s$
Equil.			$3s$		$2s$

$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2 = (3s)^3(2s)^2 = 108\ s^5$, $K_{sp} = 108(6.2 \times 10^{-12})^5 = 9.9 \times 10^{-55}$

b.

	$Li_2CO_3(s)$	$\rightleftharpoons$	$2\ Li^+(aq)$	+	$CO_3^{2-}(aq)$
Initial	s = solubility (mol/L)		0		0
Equil.			$2s$		s

$K_{sp} = [Li^+]^2[CO_3^{2-}] = (2s)^2(s) = 4s^3$, $K_{sp} = 4(7.4 \times 10^{-2})^3 = 1.6 \times 10^{-3}$

23.
$$\text{Solubility} = s = \frac{0.14\ \text{g Ni(OH)}_2}{\text{L}} \times \frac{1\ \text{mol Ni(OH)}_2}{92.71\ \text{g Ni(OH)}_2} = 1.5 \times 10^{-3}\ \text{mol/L}$$

	$Ni(OH)_2(s)$	$\rightleftharpoons$	$Ni^{2+}(aq)$	+	$2OH^-(aq)$
Initial			0		1.0×10^{-7} *M* (from water)
	s mol/L of $Ni(OH)_2$ dissolves to reach equailibrium				
Change	$-s$	$\rightarrow$	$+s$		$+2s$
Equil.			s		$1.0 \times 10^{-7} + 2s$

From the calculated molar solubility, $1.0 \times 10^{-7} + 2s \approx 2s$.

$K_{sp} = [Ni^{2+}][OH^-]^2 = s(2s)^2 = 4s^3$, $K_{sp} = 4(1.5 \times 10^{-3})^3 = 1.4 \times 10^{-8}$

24. $M_2X_3(s) \rightleftharpoons 2\,M^{3+}(aq) + 3\,X^{2-}(aq) \qquad K_{sp} = [M^{3+}]^2[X^{2-}]^3$

	$M_2X_3(s)$	$2\,M^{3+}(aq)$	$3\,X^{2-}(aq)$
Initial	*s* = solubility (mol/L)	0	0
	s mol/L of $M_2X_3(s)$ dissolves to reach equilibrium		
Change	$-s$	$+2s$	$+3s$
Equil.		$2s$	$3s$

$$K_{sp} = (2s)^2(3s)^3 = 108s^5\,;\quad s = \frac{3.60 \times 10^{-7}\ \text{g}}{\text{L}} \times \frac{1\ \text{mol}\ M_2X_3}{288\ \text{g}} = 1.25 \times 10^{-9}\ \text{mol/L}$$

$K_{sp} = 108(1.25 \times 10^{-9})^5 = 3.30 \times 10^{-43}$

25. $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Br^-(aq)$

	$PbBr_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	$2\,Br^-(aq)$
Initial			0	0
	s mol/L of $PbBr_2(s)$ dissolves to reach equilibrium			
Change	$-s$	$\rightarrow$	$+s$	$+2s$
Equil.			s	$2s$

From the problem, $s = [Pb^{2+}] = 2.14 \times 10^{-2}\ M$. So:

$K_{sp} = [Pb^{2+}][Br^-]^2 = s(2s)^2 = 4s^3$, $K_{sp} = 4(2.14 \times 10^{-2})^3 = 3.92 \times 10^{-5}$

26. $Ag_2C_2O_4(s) \rightleftharpoons 2\,Ag^+(aq) + C_2O_4^{2-}(aq)$

	$Ag_2C_2O_4(s)$	$2\,Ag^+(aq)$	$C_2O_4^{2-}(aq)$
Initial	*s* = solubility (mol/L)	0	0
Equil.		$2s$	s

From problem, $[Ag^+] = 2s = 2.2 \times 10^{-4}\ M$, $s = 1.1 \times 10^{-4}\ M$

$K_{sp} = [Ag^+]^2[C_2O_4^{2-}] = (2s)^2(s) = 4s^3 = 4(1.1 \times 10^{-4})^3 = 5.3 \times 10^{-12}$

27. In our setup, *s* = solubility in mol/L. Because solids do not appear in the K_{sp} expression, we do not need to worry about their initial or equilibrium amounts.

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

Initial			0	0
	s mol/L of $Ag_3PO_4(s)$ dissolves to reach equilibrium			
Change	$-s$	$\rightarrow$	$+3s$	$+s$
Equil.			$3s$	s

$K_{sp} = 1.8 \times 10^{-18} = [Ag^+]^3[PO_4^{3-}] = (3s)^3(s) = 27\ s^4$

$27s^4 = 1.8 \times 10^{-18}$, $s = (6.7 \times 10^{-20})^{1/4} = 1.6 \times 10^{-5}$ mol/L = molar solubility

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

Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = 8.7 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] = s^2$, $s = 9.3 \times 10^{-5}$ mol/L

c. $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

Initial	s = solubility (mol/L)	0	0
Equil.		s	$2s$

$K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2 = (s)(2s)^2 = 4s^3$, $s = 6.5 \times 10^{-7}$ mol/L

28. a. $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$

Initial	s = solubility (mol/L)	0	0
Equil.		s	$2s$

$K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2 = s(2s)^2 = 4s^3$

$s = (1.4 \times 10^{-8}/4)^{1/3} = 1.5 \times 10^{-3}$ mol/L = molar solubility

b. $CdCO_3(s) \rightleftharpoons Cd^{2+}(aq) + CO_3^{2-}(aq)$

Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = 5.2 \times 10^{-12} = [Cd^{2+}][CO_3^{2-}] = s^2$, $s = 2.3 \times 10^{-6}$ mol/L

c. $Sr_3(PO_4)_2(s) \rightleftharpoons 3\ Sr^{2+}(aq) + 2\ PO_4^{3-}(aq)$

Initial	s = solubility (mol/L)	0	0
Equil.		$3s$	$2s$

$K_{sp} = 1 \times 10^{-31} = [Sr^{2+}]^3[PO_4^{3-}]^2 = (3s)^3(2s)^2 = 108\ s^5$, $s = 2 \times 10^{-7}$ mol/L

29. $$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$$

Initial	s = solubility (mol/L)	0	1.0×10^{-7} *M* (from water)
Equil.		s	$1.0 \times 10^{-7} + 2s$

$K_{sp} = [Mg^{2+}][OH^-]^2 = s(1.0 \times 10^{-7} + 2s)^2$; assume that $1.0 \times 10^{-7} + 2s \approx 2s$, then:

$$K_{sp} = 8.9 \times 10^{-12} = s(2s)^2 = 4s^3, \quad s = 1.3 \times 10^{-4} \text{ mol/L}$$

Assumption is good (1.0×10^{-7} is 0.04% of $2s$). Molar solubility = 1.3×10^{-4} mol/L

30. $$Cd(OH)_2(s) \rightleftharpoons Cd^{2+}(aq) + 2\ OH^-(aq) \qquad K_{sp} = 5.9 \times 10^{-15}$$

Initial	s = solubility (mol/L)	0	1.0×10^{-7} *M*
Equil.		s	$1.0 \times 10^{-7} + 2s$

$K_{sp} = [Cd^{2+}][OH^-]^2 = s(1.0 \times 10^{-7} + 2s)^2$; assume that $1.0 \times 10^{-7} + 2s \approx 2s$, then:

$$K_{sp} = 5.9 \times 10^{-15} = s(2s)^2 = 4s^3, \quad s = 1.1 \times 10^{-5} \text{ mol/L}$$

Assumption is good (1.0×10^{-7} is 0.4% of $2s$). Molar solubility = 1.1×10^{-5} mol/L

31. Let s = solubility of $Al(OH)_3$ in mol/L. *Note*: Because solids do not appear in the K_{sp} expression, we do not need to worry about their initial or equilibrium amounts.

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

Initial			0	1.0×10^{-7} *M* (from water)
	s mol/L of $Al(OH)_3(s)$ dissolves to reach equilibrium = molar solubility			
Change	$-s$	→	$+s$	$+3s$
Equil.			s	$1.0 \times 10^{-7} + 3s$

$K_{sp} = 2 \times 10^{-32} = [Al^{3+}][OH^-]^3 = (s)(1.0 \times 10^{-7} + 3s)^3 \approx s(1.0 \times 10^{-7})^3$

$$s = \frac{2 \times 10^{-32}}{1.0 \times 10^{-21}} = 2 \times 10^{-11} \text{ mol/L; \quad assumption good } (1.0 \times 10^{-7} + 3s \approx 1.0 \times 10^{-7}).$$

32. Let s = solubility of $Co(OH)_3$ in mol/L.

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

Initial			0	1.0×10^{-7} *M* (from water)
	s mol/L of $Co(OH)_3(s)$ dissolves to reach equilibrium = molar solubility			
Change	$-s$	→	$+s$	$+3s$
Equil.			s	$1.0 \times 10^{-7} + 3s$

$K_{sp} = 2.5 \times 10^{-43} = [Co^{3+}][OH^-]^3 = (s)(1.0 \times 10^{-7} + 3s)^3 \approx s(1.0 \times 10^{-7})^3$

$s = \dfrac{2.5 \times 10^{-43}}{1.0 \times 10^{-21}} = 2.5 \times 10^{-22}$ mol/L; assumption good ($1.0 \times 10^{-7} + 3s \approx 1.0 \times 10^{-7}$).

33. a. Because both solids dissolve to produce three ions in solution, we can compare values of K_{sp} to determine relative solubility. Because the K_{sp} for CaF_2 is the smallest, $CaF_2(s)$ has the smallest molar solubility.

b. We must calculate molar solubilities because each salt yields a different number of ions when it dissolves.

$$\begin{array}{llcccl} & Ca_3(PO_4)_2(s) & \rightleftharpoons & 3\,Ca^{2+}(aq) & + \; 2\,PO_4^{3-}(aq) & K_{sp} = 1.3 \times 10^{-32} \\ \text{Initial} & s = \text{solubility (mol/L)} & & 0 & 0 & \\ \text{Equil.} & & & 3s & 2s & \end{array}$$

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5$, $s = (1.3 \times 10^{-32}/108)^{1/5} = 1.6 \times 10^{-7}$ mol/L

$$\begin{array}{llcccl} & FePO_4(s) & \rightleftharpoons & Fe^{3+}(aq) & + \; PO_4^{3-}(aq) & K_{sp} = 1.0 \times 10^{-22} \\ \text{Initial} & s = \text{solubility (mol/L)} & & 0 & 0 & \\ \text{Equil.} & & & s & s & \end{array}$$

$K_{sp} = [Fe^{3+}][PO_4^{3-}] = s^2$, $s = \sqrt{1.0 \times 10^{-22}} = 1.0 \times 10^{-11}$ mol/L

$FePO_4$ has the smallest molar solubility.

34. a.

$$\begin{array}{llccc} & FeC_2O_4(s) & \rightleftharpoons & Fe^{2+}(aq) & + \; C_2O_4^{2-}(aq) \\ \text{Equil.} & s = \text{solubility (mol/L)} & & s & s \end{array}$$

$K_{sp} = 2.1 \times 10^{-7} = [Fe^{2+}][C_2O_4^{2-}] = s^2$, $s = 4.6 \times 10^{-4}$ mol/L

$$\begin{array}{llcccc} & Cu(IO_4)_2(s) & \rightleftharpoons & Cu^{2+}(aq) & + \; 2\,IO_4^-(aq) & \\ \text{Equil.} & & & s & 2s & (1.4 \times 10^{-7}/4)^{1/3} \end{array}$$

$K_{sp} = 1.4 \times 10^{-7} = [Cu^{2+}][IO_4^-]^2 = s(2s)^2 = 4s^3$, $s = (1.4 \times 10^{-7}/4)^{1/3} = 3.3 \times 10^{-3}$ mol/L

By comparing calculated molar solubilities, $FeC_2O_4(s)$ is less soluble (in mol/L).

b. Each salt produces three ions in solution, so we can compare K_{sp} values to determine relative molar solubilities. Therefore, $Mn(OH)_2(s)$ will be less soluble (in mol/L) because it has a smaller K_{sp} value.

35. a.

$$\begin{array}{llccc} & Fe(OH)_3(s) & \rightleftharpoons & Fe^{3+}(aq) & + \; 3\,OH^-(aq) \\ \text{Initial} & & & 0 & 1 \times 10^{-7}\,M \text{ (from water)} \\ & \multicolumn{4}{l}{s \text{ mol/L of } Fe(OH)_3(s) \text{ dissolves to reach equilibrium = molar solubility}} \\ \text{Change} & -s & \rightarrow & +s & +3s \\ \text{Equil.} & & & s & 1 \times 10^{-7} + 3s \end{array}$$

$K_{sp} = 4 \times 10^{-38} = [Fe^{3+}][OH^-]^3 = (s)(1 \times 10^{-7} + 3s)^3 \approx s(1 \times 10^{-7})^3$

$s = 4 \times 10^{-17}$ mol/L; assumption good ($3s << 1 \times 10^{-7}$)

b. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$ pH = 5.0, $[OH^-] = 1 \times 10^{-9}\ M$

		Fe^{3+}	OH^-	
Initial		0	$1 \times 10^{-9}\ M$	(buffered)
	s mol/L dissolves to reach equilibrium			
Change	$-s$ →	$+s$		(assume no pH change in buffer)
Equil.		s	1×10^{-9}	

$K_{sp} = 4 \times 10^{-38} = [Fe^{3+}][OH^-]^3 = (s)(1 \times 10^{-9})^3$, $s = 4 \times 10^{-11}$ mol/L = molar solubility

c. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$ pH = 11.0, $[OH^-] = 1 \times 10^{-3}\ M$

		Fe^{3+}	OH^-	
Initial		0	$0.001\ M$	(buffered)
	s mol/L dissolves to reach equilibrium			
Change	$-s$ →	$+s$		(assume no pH change)
Equil.		s	0.001	

$K_{sp} = 4 \times 10^{-38} = [Fe^{3+}][OH^-]^3 = (s)(0.001)^3$, $s = 4 \times 10^{-29}$ mol/L = molar solubility

Note: As $[OH^-]$ increases, solubility decreases. This is the common ion effect.

36. $Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2\,OH^-(aq)$ pH = 11.00, $[OH^-] = 1.0 \times 10^{-3}\ M$

		Co^{2+}	OH^-	
Initial	s = solubility (mol/L)	0	1.0×10^{-3}	(buffered)
Equil.		s	1.0×10^{-3}	(assume no pH change)

$K_{sp} = 2.5 \times 10^{-16} = [Co^{2+}][OH^-]^2 = s(1.0 \times 10^{-3})^2$, $s = 2.5 \times 10^{-10}$ mol/L

37. a. $Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq)$

		Ag^+	SO_4^{2-}
Initial	s = solubility (mol/L)	0	0
Equil.		$2s$	s

$K_{sp} = 1.2 \times 10^{-5} = [Ag^+]^2[SO_4^{2-}] = (2s)^2s = 4s^3$, $s = 1.4 \times 10^{-2}$ mol/L

b. $Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq)$

		Ag^+	SO_4^{2-}
Initial	s = solubility (mol/L)	$0.10\ M$	0
Equil.		$0.10 + 2s$	s

$K_{sp} = 1.2 \times 10^{-5} = (0.10 + 2s)^2(s) \approx (0.10)^2(s)$, $s = 1.2 \times 10^{-3}$ mol/L; assumption good.

c.	$Ag_2SO_4(s)$	$\rightleftharpoons$	$2\ Ag^+(aq)$	$+$	$SO_4^{2-}(aq)$
Initial	s = solubility (mol/L)		0		0.20 M
Equil			$2s$		$0.20 + s$

$1.2 \times 10^{-5} = (2s)^2(0.20 + s) \approx 4s^2(0.20)$, $s = 3.9 \times 10^{-3}$ mol/L; assumption good.

Note: Comparing the solubilities of parts b and c to that of part a illustrates that the solubility of a salt decreases when a common ion is present.

38. a.	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	$+$	$2\ I^-(aq)$
Initial	s = solubility (mol/L)		0		0
Equil.			s		$2s$

$K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2 = 4s^3$, $s = 1.5 \times 10^{-3}$ mol/L

b.	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	$+$	$2\ I^-(aq)$
Initial	s = solubility (mol/L)		0.10 M		0
Equil.			$0.10 + s$		$2s$

$1.4 \times 10^{-8} = (0.10 + s)(2s)^2 \approx (0.10)(2s)^2 = (0.40)s^2$, $s = 1.9 \times 10^{-4}$ mol/L; assumption good.

c.	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	$+$	$2\ I^-(aq)$
Initial	s = solubility (mol/L)		0		0.010 M
Equil.			s		$0.010 + 2s$

$1.4 \times 10^{-8} = (s)(0.010 + 2s)^2 \approx (s)(0.010)^2$, $s = 1.4 \times 10^{-4}$ mol/L; assumption good.

Note that in parts b and c, the presence of a common ion decreases the solubility as compared to the solubility of $PbI_2(s)$ in water.

39.	$Ca_3(PO_4)_2(s)$	$\rightleftharpoons$	$3\ Ca^{2+}(aq)$	$+$	$2\ PO_4^{3-}(aq)$
Initial			0		0.20 M
	s mol/L of $Ca_3(PO_4)_2(s)$ dissolves to reach equilibrium				
Change	$-s$	$\rightarrow$	$+3s$		$+2s$
Equil.			$3s$		$0.20 + 2s$

$K_{sp} = 1.3 \times 10^{-32} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3s)^3(0.20 + 2s)^2$

Assuming $0.20 + 2s \approx 0.20$: $1.3 \times 10^{-32} = (3s)^3(0.20)^2 = 27s^3(0.040)$

s = molar solubility = 2.3×10^{-11} mol/L; assumption good.

40.	$Pb_3(PO_4)_2(s)$	$\rightleftharpoons$	$3\ Pb^{2+}(aq)$	$+$	$2\ PO_4^{3-}(aq)$	$K_{sp} = 1 \times 10^{-54}$
Initial	s = solubility (mol/L)		0.10 M		0	
Equil.			$0.10 + 3s$		$2s$	

$1 \times 10^{-54} = (0.10 + 3s)^3(2s)^2 \approx (0.10)^3(2s)^2$, $s = 2 \times 10^{-26}$ mol/L; assumptions good.

41.

		$Ce(IO_3)_3(s)$	$\rightleftharpoons$	$Ce^{3+}(aq)$	+	$3\ IO_3^-(aq)$
Initial	s = solubility (mol/L)			0		0.20 M
Equil.				s		$0.20 + 3s$

$K_{sp} = [Ce^{3+}][IO_3^-]^3 = s(0.20 + 3s)^3$

From the problem, $s = 4.4 \times 10^{-8}$ mol/L; solving for K_{sp}:

$$K_{sp} = (4.4 \times 10^{-8})[0.20 + 3(4.4 \times 10^{-8})]^3 = 3.5 \times 10^{-10}$$

42.

		$Pb(IO_3)_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2\ IO_3^-(aq)$
Initial	s = solubility (mol/L)			0		0.10 M
Equil.				s		$0.10 + 2s$

$K_{sp} = [Pb^{2+}][IO_3^-]^2 = (s)(0.10 + 2s)^2$

From the problem, $s = 2.6 \times 10^{-11}$ mol/L; solving for K_{sp}:

$$K_{sp} = (2.6 \times 10^{-11})[0.10 + 2(2.6 \times 10^{-11})]^2 = 2.6 \times 10^{-13}$$

43. If the anion in the salt can act as a base in water, the solubility of the salt will increase as the solution becomes more acidic. Added H^+ will react with the base, forming the conjugate acid. As the basic anion is removed, more of the salt will dissolve to replenish the basic anion. The salts with basic anions are Ag_3PO_4, $CaCO_3$, $CdCO_3$, and $Sr_3(PO_4)_2$. Hg_2Cl_2 and PbI_2 do not have any pH dependence since Cl^- and I^- are terrible bases (the conjugate bases of strong acids).

$$Ag_3PO_4(s) + H^+(aq) \rightarrow 3\ Ag^+(aq) + HPO_4^{2-}(aq) \xrightarrow{\text{excess } H^+} 3\ Ag^+(aq) + H_3PO_4(aq)$$

$$CaCO_3(s) + H^+ \rightarrow Ca^{2+} + HCO_3^- \xrightarrow{\text{excess } H^+} Ca^{2+} + H_2CO_3\ [H_2O(l) + CO_2(g)]$$

$$CdCO_3(s) + H^+ \rightarrow Cd^{2+} + HCO_3^- \xrightarrow{\text{excess } H^+} Cd^{2+} + H_2CO_3\ [H_2O(l) + CO_2(g)]$$

$$Sr_3(PO_4)_2(s) + 2\ H^+ \rightarrow 3\ Sr^{2+} + 2\ HPO_4^{2-} \xrightarrow{\text{excess } H^+} 3\ Sr^{2+} + 2\ H_3PO_4$$

44. a. AgF b. $Pb(OH)_2$ c. $Sr(NO_2)_2$ d. $Ni(CN)_2$

All these salts have anions that are bases. The anions of the other choices are conjugate bases of strong acids. They have no basic properties in water and, therefore, do not have solubilities that depend on pH.

Precipitation Conditions

45.

	$ZnS(s)$	$\rightleftharpoons$	Zn^{2+}	+	S^{2-}	$K_{sp} = [Zn^{2+}][S^{2-}]$
Initial	s = solubility (mol/L)		$0.050\ M$		0	
Equil.			$0.050 + s$		s	

$K_{sp} = 2.5 \times 10^{-22} = (0.050 + s)(s) \approx (0.050)s$, $s = 5.0 \times 10^{-21}$ mol/L; assumption good.

$$\text{Mass ZnS that dissolves} = 0.3000\ \text{L} \times \frac{5.0 \times 10^{-21}\ \text{mol ZnS}}{\text{L}} \times \frac{97.45\ \text{g ZnS}}{\text{mol}} = 1.5 \times 10^{-19}\ \text{g}$$

46. For 99% of the Mg^{2+} to be removed, we need, at equilibrium, $[Mg^{2+}] = 0.01(0.052\ M)$. Using the K_{sp} equilibrium constant, calculate the $[OH^-]$ required to reach this reduced $[Mg^{2+}]$.

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = 8.9 \times 10^{-12}$

$8.9 \times 10^{-12} = [Mg^{2+}][OH^-]^2 = [0.01(0.052\ M)]\,[OH^-]^2$, $[OH^-] = 1.3 \times 10^{-4}\ M$ (extra sig. fig.)

$pOH = -\log(1.3 \times 10^{-4}) = 3.89$; $pH = 10.11$; at a pH = 10.1, 99% of the Mg^{2+} in seawater will be removed as $Mg(OH)_2(s)$.

47. The formation of $Mg(OH)_2(s)$ is the only possible precipitate. $Mg(OH)_2(s)$ will form if $Q > K_{sp}$.

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = [Mg^{2+}][OH^-]^2 = 8.9 \times 10^{-12}$

$$[Mg^{2+}]_0 = \frac{100.0\ \text{mL} \times 4.0 \times 10^{-4}\ \text{mmol}\ Mg^{2+}/\text{mL}}{100.0\ \text{mL} + 100.0\ \text{mL}} = 2.0 \times 10^{-4}\ M$$

$$[OH^-]_0 = \frac{100.0\ \text{mL} \times 2.0 \times 10^{-4}\ \text{mmol}\ OH^-/\text{mL}}{200.0\ \text{mL}} = 1.0 \times 10^{-4}\ M$$

$$Q = [Mg^{2+}]_0[OH^-]_0^2 = (2.0 \times 10^{-4}\ M)(1.0 \times 10^{-4})^2 = 2.0 \times 10^{-12}$$

Because $Q < K_{sp}$, $Mg(OH)_2(s)$ will not precipitate, so no precipitate forms.

48. $AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$ $K_{sp} = 2.2 \times 10^{-12}$

$Q = [Ag^+]_0[CN^-]_0 = (1.0 \times 10^{-5})(2.0 \times 10^{-6}) = 2.0 \times 10^{-11}$

Because $Q > K_{sp}$, $AgCN(s)$ will form as a precipitate.

49. $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ F^-(aq)$ $K_{sp} = 4 \times 10^{-8}$

$$[Pb^{2+}]_0 = \frac{\text{mmol}\ Pb^{2+}(aq)}{\text{total mL solution}} = \frac{100.0\ \text{mL} \times \dfrac{1.0 \times 10^{-2}\ \text{mmol}\ Pb^{2+}}{\text{mL}}}{100.0\ \text{mL} + 100.0\ \text{mL}} = 5.0 \times 10^{-3}\ M$$

$$[F^-]_0 = \frac{\text{mmol } F^-}{\text{total mL solution}} = \frac{100.0 \text{ mL} \times \dfrac{1.0 \times 10^{-3} \text{ mmol } F^-}{\text{mL}}}{200.0 \text{ mL}} = 5.0 \times 10^{-4}\ M$$

$$Q = [Pb^{2+}]_0[F^-]_0^2 = (5.0 \times 10^{-3})(5.0 \times 10^{-4})^2 = 1.3 \times 10^{-9}$$

Because Q < K_{sp}, $PbF_2(s)$ will not form as a precipitate.

50. $Ce(IO_3)_3(s) \rightleftharpoons Ce^{3+}(aq) + 3\ IO_3^-(aq)$ $K_{sp} = 3.2 \times 10^{-10}$

$$Q = [Ce^{3+}]_0[IO_3^-]_0^3 = (2.0 \times 10^{-3})(1.0 \times 10^{-2})^3 = 2.0 \times 10^{-9}$$

Because Q > K_{sp}, $Ce(IO_3)_3(s)$ will form as a precipitate.

51. The concentrations of ions are large, so Q will be greater than K_{sp}, and $BaC_2O_4(s)$ will form. To solve this problem, we will assume that the precipitation reaction goes to completion; then we will solve an equilibrium problem to get the actual ion concentrations. This makes the math reasonable.

$$100.\text{ mL} \times \frac{0.200 \text{ mmol } K_2C_2O_4}{\text{mL}} = 20.0 \text{ mmol } K_2C_2O_4$$

$$150.\text{ mL} \times \frac{0.250 \text{ mmol BaBr}_2}{\text{mL}} = 37.5 \text{ mmol BaBr}_2$$

	$Ba^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$	$\rightarrow$	$BaC_2O_4(s)$	$K = 1/K_{sp} >> 1$
Before	37.5 mmol		20.0 mmol		0	
Change	−20.0		−20.0	$\rightarrow$	+20.0	Reacts completely (K is large).
After	17.5		0		20.0	

New initial concentrations (after complete precipitation) are:

$$[Ba^{2+}] = \frac{17.5 \text{ mmol}}{250.\text{ mL}} = 7.00 \times 10^{-2}\ M;\ [C_2O_4^{2-}] = 0\ M$$

$$[K^+] = \frac{2(20.0 \text{ mmol})}{250.\text{ mL}} = 0.160\ M;\ [Br^-] = \frac{2(37.5 \text{ mmol})}{250.\text{ mL}} = 0.300\ M$$

For K^+ and Br^-, these are also the final concentrations. We can't have 0 M $C_2O_4^{2-}$. For Ba^{2+} and $C_2O_4^{2-}$, we need to perform an equilibrium calculation.

	$BaC_2O_4(s)$	$\rightleftharpoons$	$Ba^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$	$K_{sp} = 2.3 \times 10^{-8}$
Initial			0.0700 M		0	
	s mol/L of $BaC_2O_4(s)$ dissolves to reach equilibrium					
Equil.			0.0700 + s		s	

$K_{sp} = 2.3 \times 10^{-8} = [Ba^{2+}][C_2O_4^{2-}] = (0.0700 + s)(s) \approx (0.0700)s$

$s = [C_2O_4^{2-}] = 3.3 \times 10^{-7}$ mol/L; $[Ba^{2+}] = 0.0700\ M$; assumption good ($s \ll 0.0700$).

52. $$[Ba^{2+}]_0 = \frac{75.0\text{ mL} \times \dfrac{0.020\text{ mmol}}{\text{mL}}}{200.\text{ mL}} = 7.5 \times 10^{-3}\ M$$

$$[SO_4^{2-}]_0 = \frac{125\text{ mL} \times \dfrac{0.040\text{ mmol}}{\text{mL}}}{200.\text{ mL}} = 2.5 \times 10^{-2}\ M$$

$Q = [Ba^{2+}]_0[SO_4^{2-}]_0 = (7.5 \times 10^{-3})(2.5 \times 10^{-2}) = 1.9 \times 10^{-4} > K_{sp}\ (1.5 \times 10^{-9})$

A precipitate of $BaSO_4(s)$ will form.

	$BaSO_4(s)$	$\rightleftharpoons$	Ba^{2+}	+	SO_4^{2-}	
Before			$0.0075\ M$		$0.025\ M$	
	Let 0.0075 mol/L Ba^{2+} react with SO_4^{2-} to completion because $K_{sp} \ll 1$.					
Change		$\leftarrow$	-0.0075		-0.0075	Reacts completely
After			0		0.0175	New initial (carry extra sig. fig.)
	s mol/L $BaSO_4$ dissolves to reach equilibrium					
Change	$-s$	$\rightarrow$	$+s$		$+s$	
Equil.			s		$0.0175 + s$	

$K_{sp} = 1.5 \times 10^{-9} = [Ba^{2+}][SO_4^{2-}] = (s)(0.0175 + s) \approx s(0.0175)$

$s = 8.6 \times 10^{-8}$ mol/L; $[Ba^{2+}] = 8.6 \times 10^{-8}\ M$; $[SO_4^{2-}] = 0.018\ M$; assumption good.

53. $50.0\text{ mL} \times 0.00200\ M = 0.100$ mmol Ag^+; $50.0\text{ mL} \times 0.0100\ M = 0.500$ mmol IO_3^-

From the small K_{sp} value, assume $AgIO_3(s)$ precipitates completely. After reaction, 0.400 mmol IO_3^- is remaining. Now, let some $AgIO_3(s)$ dissolve in solution with excess IO_3^- to reach equilibrium.

	$AgIO_3(s)$	$\rightleftharpoons$	$Ag^+(aq)$	+	$IO_3^-(aq)$
Initial			0		$\dfrac{0.400\text{ mmol}}{100.0\text{ mL}} = 4.00 \times 10^{-3}\ M$
	s mol/L $AgIO_3(s)$ dissolves to reach equilibrium				
Equil.			s		$4.00 \times 10^{-3} + s$

$K_{sp} = [Ag^+][IO_3^-] = 3.0 \times 10^{-8} = s(4.00 \times 10^{-3} + s) \approx s(4.00 \times 10^{-3})$

$s = 7.5 \times 10^{-6}$ mol/L $= [Ag^+]$; assumptions good.

54. 50.0 mL × 0.10 M = 5.0 mmol Pb^{2+}; 50.0 mL × 1.0 M = 50. mmol Cl^-. For this solution, Q > K_{sp}, so $PbCl_2$ precipitates. Assume precipitation of $PbCl_2(s)$ is complete. 5.0 mmol Pb^{2+} requires 10. mmol of Cl^- for complete precipitation, which leaves 40. mmol Cl^- in excess. Now, let some of the $PbCl_2(s)$ redissolve to establish equilibrium

	$PbCl_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2\ Cl^-(aq)$
Initial			0		$\frac{40.\ \text{mmol}}{100.0\ \text{mL}} = 0.40\ M$
	s mol/L of $PbCl_2(s)$ dissolves to reach equilibrium				
Equil.			s		$0.40 + 2s$

$K_{sp} = [Pb^{2+}][Cl^-]^2$, $1.6 \times 10^{-5} = s(0.40 + 2s)^2 \approx s(0.40)^2$

$s = 1.0 \times 10^{-4}$ mol/L; assumption good.

At equilibrium: $[Pb^{2+}] = s = 1.0 \times 10^{-4}$ mol/L; $[Cl^-] = 0.40 + 2s$, $0.40 + 2(1.0 \times 10^{-4})$
$= 0.40\ M$

55. $Ag_3PO_4(s) \rightleftharpoons 3\ Ag^+(aq) + PO_4^{3-}(aq)$; when Q is greater than K_{sp}, precipitation will occur. We will calculate the $[Ag^+]_0$ necessary for Q = K_{sp}. Any $[Ag^+]_0$ greater than this calculated number will cause precipitation of $Ag_3PO_4(s)$. In this problem, $[PO_4^{3-}]_0 = [Na_3PO_4]_0 = 1.0 \times 10^{-5}\ M$.

$K_{sp} = 1.8 \times 10^{-18}$; $Q = 1.8 \times 10^{-18} = [Ag^+]_0^3[PO_4^{3-}]_0 = [Ag^+]_0^3(1.0 \times 10^{-5}\ M)$

$$[Ag^+]_0 = \left(\frac{1.8 \times 10^{-18}}{1.0 \times 10^{-5}}\right)^{1/3},\quad [Ag^+]_0 = 5.6 \times 10^{-5}\ M$$

When $[Ag^+]_0 = [AgNO_3]_0$ is greater than $5.6 \times 10^{-5}\ M$, precipitation of $Ag_3PO_4(s)$ will occur.

56. $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\ OH^-(aq)$ $K_{sp} = 2 \times 10^{-32}$

$Q = 2 \times 10^{-32} = [Al^{3+}]_0[OH^-]_0^3 = (0.2)[OH^-]_0^3$, $[OH^-]_0 = 4.6 \times 10^{-11}$ (carrying extra sig. fig.)

pOH = $-\log(4.6 \times 10^{-11}) = 10.3$; when the pOH of the solution equals 10.3, K_{sp} = Q. For precipitation, we want Q > K_{sp}. This will occur when $[OH^-]_0 > 4.6 \times 10^{-11}$ or when pOH < 10.3. Because pH + pOH = 14.00, precipitation of $Al(OH)_3(s)$ will begin when pH > 3.7 because this translates to a solution with pOH < 10.3.

57. For each lead salt, we will calculate the $[Pb^{2+}]_0$ necessary for Q = K_{sp}. Any $[Pb^{2+}]_0$ greater than this value will cause precipitation of the salt (Q > K_{sp}).

$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ F^-(aq)$ $K_{sp} = 4 \times 10^{-8}$; $Q = 4 \times 10^{-8} = [Pb^{2+}]_0[F^-]_0^2$

$$[Pb^{2+}]_0 = \frac{4 \times 10^{-8}}{(1 \times 10^{-4})^2} = 4\ M$$

$PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq) \quad K_{sp} = 7 \times 10^{-29};\ Q = 7 \times 10^{-29} = [Pb^{2+}]_0[S^{2-}]_0$

$$[Pb^{2+}]_0 = \frac{7 \times 10^{-29}}{1 \times 10^{-4}} = 7 \times 10^{-25}\ M$$

$Pb_3(PO_4)_2(s) \rightleftharpoons 3\ Pb^{2+}(aq) + 2\ PO_4^{3-}(aq) \quad K_{sp} = 1 \times 10^{-54}$

$$Q = 1 \times 10^{-54} = [Pb^{2+}]_0^3[PO_4^{3-}]_0^2$$

$$[Pb^{2+}]_0 = \left[\frac{1 \times 10^{-54}}{(1 \times 10^{-4})^2}\right]^{1/3} = 5 \times 10^{-16}\ M$$

From the calculated $[Pb^{2+}]_0$, the least soluble salt is PbS(s), and it will form first. $Pb_3(PO_4)_2(s)$ will form second, and $PbF_2(s)$ will form last because it requires the largest $[Pb^{2+}]_0$ in order for precipitation to occur.

58. From Table 16.1, K_{sp} for $NiCO_3 = 1.4 \times 10^{-7}$ and K_{sp} for $CuCO_3 = 2.5 \times 10^{-10}$. From the K_{sp} values, $CuCO_3$ will precipitate first since it has the smaller K_{sp} value and will be the least soluble. For $CuCO_3(s)$, precipitation begins when:

$$[CO_3^{2-}] = \frac{K_{sp,\,CuCO_3}}{[Cu^{2+}]} = \frac{2.5 \times 10^{-10}}{0.25\ M} = 1.0 \times 10^{-9}\ M\ CO_3^{2-}$$

For $NiCO_3(s)$ to precipitate:

$$[CO_3^{2-}] = \frac{K_{sp,\,NiCO_3}}{[Ni^{2+}]} = \frac{1.4 \times 10^{-7}}{0.25\ M} = 5.6 \times 10^{-7}\ M\ CO_3^{2-}$$

Determining the $[Cu^{2+}]$ when $CuCO_3(s)$ begins to precipitate:

$$[Cu^{2+}] = \frac{K_{sp,\,CuCO_3}}{[CO_3^{2-}]} = \frac{2.5 \times 10^{-10}}{5.6 \times 10^{-7}\ M} = 4.5 \times 10^{-4}\ M\ Cu^{2+}$$

For successful separation, 1% Cu^{2+} or less of the initial amount of Cu^{2+} (0.25 *M*) must be present before $NiCO_3(s)$ begins to precipitate. The percent of Cu^{2+} present when $NiCO_3(s)$ begins to precipitate is:

$$\frac{4.5 \times 10^{-4}\ M}{0.25\ M} \times 100 = 0.18\%\ Cu^{2+}$$

Because less than 1% of the initial amount of Cu^{2+} remains, the metals can be separated through slow addition of $Na_2CO_3(aq)$.

Complex Ion Equilibria

59. a.

$$\begin{array}{rcl}
\mathrm{Ni^{2+} + CN^- \rightleftharpoons NiCN^+} & & K_1 \\
\mathrm{NiCN^+ + CN^- \rightleftharpoons Ni(CN)_2} & & K_2 \\
\mathrm{Ni(CN)_2 + CN^- \rightleftharpoons Ni(CN)_3^-} & & K_3 \\
\mathrm{Ni(CN)_3^- + CN^- \rightleftharpoons Ni(CN)_4^{2-}} & & K_4 \\
\hline
\mathrm{Ni^{2+} + 4\,CN^- \rightleftharpoons Ni(CN)_4^{2-}} & & K_f = K_1K_2K_3K_4
\end{array}$$

Note: The various K constants are included for your information. Each NH_3 adds with a corresponding K value associated with that reaction. The overall formation constant K_f for the overall reaction is equal to the product of all the stepwise K values.

b.

$$\begin{array}{rcl}
\mathrm{V^{3+} + C_2O_4^{2-} \rightleftharpoons VC_2O_4^+} & & K_1 \\
\mathrm{VC_2O_4^+ + C_2O_4^{2-} \rightleftharpoons V(C_2O_4)_2^-} & & K_2 \\
\mathrm{V(C_2O_4)_2^- + C_2O_4^{2-} \rightleftharpoons V(C_2O_4)_3^{3-}} & & K_3 \\
\hline
\mathrm{V^{3+} + 3\,C_2O_4^{2-} \rightleftharpoons V(C_2O_4)_3^{3-}} & & K_f = K_1K_2K_3
\end{array}$$

60. a.

$$\begin{array}{ll}
\mathrm{Co^{3+} + F^- \rightleftharpoons CoF^{2+}} & K_1 \\
\mathrm{CoF^{2+} + F^- \rightleftharpoons CoF_2^+} & K_2 \\
\mathrm{CoF_2^+ + F^- \rightleftharpoons CoF_3} & K_3 \\
\mathrm{CoF_3 + F^- \rightleftharpoons CoF_4^-} & K_4 \\
\mathrm{CoF_4^- + F^- \rightleftharpoons CoF_5^{2-}} & K_5 \\
\mathrm{CoF_5^{2-} + F^- \rightleftharpoons CoF_6^{3-}} & K_6 \\
\hline
\mathrm{Co^{3+} + 6\,F^- \rightleftharpoons CoF_6^{3-}} & K_f = K_1K_2K_3K_4K_5K_6
\end{array}$$

b.

$$\begin{array}{rcl}
\mathrm{Zn^{2+} + NH_3 \rightleftharpoons ZnNH_3^{2+}} & & K_1 \\
\mathrm{ZnNH_3^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_2^{2+}} & & K_2 \\
\mathrm{Zn(NH_3)_2^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_3^{2+}} & & K_3 \\
\mathrm{Zn(NH_3)_3^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}} & & K_4 \\
\hline
\mathrm{Zn^{2+} + 4\,NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}} & & K_f = K_1K_2K_3K_4
\end{array}$$

61. $\mathrm{Fe^{3+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}}$ $\qquad K = \dfrac{[\mathrm{Fe(CN)_6^{3-}}]}{[\mathrm{Fe^{3+}}][\mathrm{CN^-}]^6}$

$$K = \frac{1.5\times10^{-3}}{(8.5\times10^{-40})(0.11)^6} = 1.0 \times 10^{42}$$

62. $\mathrm{Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)}$ $\qquad K = \dfrac{[\mathrm{Cu(NH_3)_4^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{NH_3}]^4}$

$$K = \frac{1.0 \times 10^{-3}}{(1.8 \times 10^{-17})(1.5)^4} = 1.1 \times 10^{13}$$

63. $Hg^{2+}(aq) + 2\ I^-(aq) \rightarrow \underset{\text{orange ppt}}{HgI_2(s)}$; $HgI_2(s) + 2\ I^-(aq) \rightarrow \underset{\text{soluble complex ion}}{HgI_4^{2-}(aq)}$

64. $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$, white ppt.; $AgCl(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$

$Ag(NH_3)_2^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s) + 2\ NH_3(aq)$, pale yellow ppt.

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

$Ag(S_2O_3)_2^{3-}(aq) + I^-(aq) \rightleftharpoons AgI(s) + 2\ S_2O_3^{2-}(aq)$, yellow ppt.

The least soluble salt (smallest K_{sp} value) must be AgI because it forms in the presence of Cl^- and Br^-. The most soluble salt (largest K_{sp} value) must be AgCl since it forms initially but never re-forms. The order of K_{sp} values is K_{sp} (AgCl) > K_{sp} (AgBr) > K_{sp} (AgI).

65. The formation constant for HgI_4^{2-} is an extremely large number. Because of this, we will let the Hg^{2+} and I^- ions present initially react to completion and then solve an equilibrium problem to determine the Hg^{2+} concentration.

	$Hg^{2+}(aq)$	$+\ 4\ I^-(aq)$	$\rightleftharpoons$	$HgI_4^{2-}(aq)$	$K = 1.0 \times 10^{30}$
Before	0.010 *M*	0.78 *M*		0	
Change	−0.010	−0.040	→	+0.010	Reacts completely (K is large).
After	0	0.74		0.010	New initial
	x mol/L HgI_4^{2-} dissociates to reach equilibrium				
Change	$+x$	$+4x$	←	$-x$	
Equil.	x	$0.74 + 4x$		$0.010 - x$	

$$K = 1.0 \times 10^{30} = \frac{[HgI_4^{2-}]}{[Hg^{2+}][I^-]^4} = \frac{(0.010 - x)}{(x)(0.74 + 4x)^4}\text{; making normal assumptions:}$$

$$1.0 \times 10^{30} = \frac{(0.010)}{(x)(0.74)^4},\quad x = [Hg^{2+}] = 3.3 \times 10^{-32}\ M;\quad \text{assumptions good.}$$

Note: 3.3×10^{-32} mol/L corresponds to one Hg^{2+} ion per 5×10^7 L. It is very reasonable to approach this problem in two steps. The reaction does essentially go to completion.

66.

	$Ni^{2+}(aq)$	$+\ 6\ NH_3(aq)$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}(aq)$	$K = 5.5 \times 10^8$
Initial	0	3.0 *M*		0.10 mol/0.50 L = 0.20 *M*	
	x mol/L $Ni(NH_3)_6^{2+}$ dissociates to reach equilibrium				
Change	$+x$	$+6x$	←	$-x$	
Equil.	x	$3.0 + 6x$		$0.20 - x$	

$$K = 5.5 \times 10^8 = = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = \frac{(0.20 - x)}{(x)(3.0 + 6x)^6},\quad 5.5 \times 10^8 \approx \frac{(0.20)}{(x)(3.0)^6}$$

$x = [Ni^{2+}] = 5.0 \times 10^{-13}\ M$; $[Ni(NH_3)_6^{2+}] = 0.20\ M - x = 0.20\ M$; assumptions good.

67. $[X^-]_0 = 5.00\ M$ and $[Cu^+]_0 = 1.0 \times 10^{-3}\ M$ because equal volumes of each reagent are mixed.

Because the K values are much greater than 1, assume the reaction goes completely to CuX_3^{2-}, and then solve an equilibrium problem.

$$Cu^+(aq) + 3\,X^-(aq) \rightleftharpoons CuX_3^{2-}(aq) \qquad K = K_1 \times K_2 \times K_3 = 1.0 \times 10^9$$

	$Cu^+(aq)$	$3\,X^-(aq)$	$CuX_3^{2-}(aq)$	
Before	$1.0 \times 10^{-3}\ M$	$5.00\ M$	0	
After	0	$5.00 - 3(10^{-3}) \approx 5.00$	1.0×10^{-3}	Reacts completely
Equil.	x	$5.00 + 3x$	$1.0 \times 10^{-3} - x$	

$$K = \frac{(1.0 \times 10^{-3} - x)}{(x)(5.00 + 3x)^3} = 1.0 \times 10^9 \approx \frac{1.0 \times 10^{-3}}{(x)(5.00)^3}, \quad x = [Cu^+] = 8.0 \times 10^{-15}\ M;$$

assumptions good.

$[CuX_3^{2-}] = 1.0 \times 10^{-3} - 8.0 \times 10^{-15} = 1.0 \times 10^{-3}\ M$

$$K_3 = \frac{[CuX_3^{2-}]}{[CuX_2^-][X^-]} = 1.0 \times 10^3 = \frac{(1.0 \times 10^{-3})}{[CuX_2^-](5.00)}, \quad [CuX_2^-] = 2.0 \times 10^{-7}\ M$$

Summarizing:

$[CuX_3^{2-}] = 1.0 \times 10^{-3}\ M$ (answer a)
$[CuX_2^-] = 2.0 \times 10^{-7}\ M$ (answer b)
$[Cu^{2+}] = 8.0 \times 10^{-15}\ M$ (answer c)

68. $[Be^{2+}]_0 = 5.0 \times 10^{-5}\ M$ and $[F^-]_0 = 4.0\ M$ because equal volumes of each reagent are mixed, so all concentrations given in the problem are diluted by a factor of one-half.

Because the K values are large, assume all reactions go to completion, and then solve an equilibrium problem.

$$Be^{2+}(aq) + 4\,F^-(aq) \rightleftharpoons BeF_4^{2-}(aq) \qquad K = K_1K_2K_3K_4 = 7.5 \times 10^{12}$$

	$Be^{2+}(aq)$	$4\,F^-(aq)$	$BeF_4^{2-}(aq)$
Before	$5.0 \times 10^{-5}\ M$	$4.0\ M$	0
After	0	$4.0\ M$	$5.0 \times 10^{-5}\ M$
Equil.	x	$4.0 + 4x$	$5.0 \times 10^{-5} - x$

$$K = 7.5 \times 10^{12} = \frac{[BeF_4^{2-}]}{[Be^{2+}][F^-]^4} = \frac{5.0 \times 10^{-5} - x}{x(4.0 + 4x)^4} \approx \frac{5.0 \times 10^{-5}}{x(4.0)^4}$$

$x = [Be^{2+}] = 2.6 \times 10^{-20}\ M$; assumptions good. $[F^-] = 4.0\ M$; $[BeF_4^{2-}] = 5.0 \times 10^{-5}\ M$

Now use the stepwise K values to determine the other concentrtations.

$$K_1 = 7.9 \times 10^4 = \frac{[BeF^+]}{[Be^{2+}][F^-]} = \frac{[BeF^+]}{(2.6 \times 10^{-20})(4.0)},\ [BeF^+] = 8.2 \times 10^{-15}\ M$$

$$K_2 = 5.8 \times 10^3 = \frac{[BeF_2]}{[BeF^+][F^-]} = \frac{[BeF_2]}{(8.2 \times 10^{-15})(4.0)},\ [BeF_2] = 1.9 \times 10^{-10}\ M$$

$$K_3 = 6.1 \times 10^2 = \frac{[BeF_3^-]}{[BeF_2][F^-]} = \frac{[BeF_3^-]}{(1.9 \times 10^{-10})(4.0)},\ [BeF_3^-] = 4.6 \times 10^{-7}\ M$$

69. a. $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad K_{sp} = [Ag^+][I^-] = 1.5 \times 10^{-16}$

		Ag^+	I^-
Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = 1.5 \times 10^{-16} = s^2$, $s = 1.2 \times 10^{-8}$ mol/L

b.

$$\begin{array}{lll} AgI(s) \rightleftharpoons Ag^+ + I^- & & K_{sp} = 1.5 \times 10^{-16} \\ Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+ & & K_f = 1.7 \times 10^7 \\ \hline AgI(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + I^-(aq) & & K = K_{sp} \times K_f = 2.6 \times 10^{-9} \end{array}$$

	$AgI(s)$ +	$2\,NH_3$	$\rightleftharpoons$	$Ag(NH_3)_2^+$	+ I^-
Initial		3.0 M		0	0
	s mol/L of AgBr(s) dissolves to reach equilibrium = molar solubility				
Equil.		$3.0 - 2s$		s	s

$$K = \frac{[Ag(NH_3)_2^+][I^-]}{[NH_3]^2} = \frac{s^2}{(3.0 - 2s)^2} = 2.6 \times 10^{-9} \approx \frac{s^2}{(3.0)^2},\ s = 1.5 \times 10^{-4}\ \text{mol/L}$$

Assumption good.

c. The presence of NH_3 increases the solubility of AgI. Added NH_3 removes Ag^+ from solution by forming the complex ion, $Ag(NH_3)_2^+$. As Ag^+ is removed, more AgI(s) will dissolve to replenish the Ag^+ concentration.

70.

$$\begin{array}{lll} AgBr(s) \rightleftharpoons Ag^+ + Br^- & & K_{sp} = 5.0 \times 10^{-13} \\ Ag^+ + 2\,S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} & & K_f = 2.9 \times 10^{13} \\ \hline AgBr(s) + 2\,S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} + Br^- & & K = K_{sp} \times K_f = 14.5 \end{array}$$

(Carry extra sig. figs.)

	$AgBr(s)$	+	$2\,S_2O_3^{2-}(aq)$	$\rightleftharpoons$	$Ag(S_2O_3)_2^{3-}(aq)$	+	$Br^{-}aq)$
Initial			0.500 *M*		0		0
	s mol/L AgBr(*s*) dissolves to reach equilibrium						
Change	$-s$		$-2s$	→	$+s$		$+s$
Equil.			$0.500 - 2s$		s		s

$$K = \frac{s^2}{(0.500 - 2s)^2} = 14.5; \text{ taking the square root of both sides:}$$

$$\frac{s}{0.500 - 2s} = 3.81,\ \ s = 1.91 - (7.62)s,\ \ s = 0.222 \text{ mol/L}$$

$$1.00\ \text{L} \times \frac{0.222 \text{ mol AgBr}}{\text{L}} \times \frac{187.8 \text{ g AgBr}}{\text{mol AgBr}} = 41.7 \text{ g AgBr} = 42 \text{ g AgBr}$$

71.

$$\begin{array}{ll} AgCl(s) \rightleftharpoons Ag^+ + Cl^- & K_{sp} = 1.6 \times 10^{-10} \\ Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+ & K_f\ = 1.7 \times 10^7 \\ \hline AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) & K = K_{sp} \times K_f = 2.7 \times 10^{-3} \end{array}$$

	$AgCl(s)$ + $2NH_3$	$\rightleftharpoons$	$Ag(NH_3)_2^+$	+ Cl^-
Initial	1.0 *M*		0	0
	s mol/L of AgCl(s) dissolves to reach equilibrium = molar solubility			
Equil.	$1.0 - 2s$		s	s

$$K = 2.7 \times 10^{-3} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \frac{s^2}{(1.0 - 2s)^2};\ \ \text{taking the square root:}$$

$$\frac{s}{1.0 - 2s} = (2.7 \times 10^{-3})^{1/2} = 5.2 \times 10^{-2},\ \ s = 4.7 \times 10^{-2} \text{ mol/L}$$

In pure water, the solubility of AgCl(s) is $(1.6 \times 10^{-10})^{1/2} = 1.3 \times 10^{-5}$ mol/L. Notice how the presence of NH_3 increases the solubility of AgCl(s) by over a factor of 3500.

72. a.

	$CuCl(s)$	$\rightleftharpoons$	$Cu^+(aq)$	+	$Cl^-(aq)$
Initial	s = solubility (mol/L)		0		0
Equil.			s		s

$$K_{sp} = 1.2 \times 10^{-6} = [Cu^+][Cl^-] = s^2,\ \ s = 1.1 \times 10^{-3} \text{ mol/L}$$

b. Cu^+ forms the complex ion $CuCl_2^-$ in the presence of Cl^-. We will consider both the K_{sp} reaction and the complex ion reaction at the same time.

$$\begin{array}{ll} CuCl(s) \rightleftharpoons Cu^+(aq) + Cl^-(aq) & K_{sp} = 1.2 \times 10^{-6} \\ Cu^+(aq) + 2\,Cl^-(aq) \rightleftharpoons CuCl_2^-(aq) & K_f = 8.7 \times 10^4 \\ \hline CuCl(s) + Cl^-(aq) \rightleftharpoons CuCl_2^-(aq) & K = K_{sp} \times K_f = 0.10 \end{array}$$

	$CuCl(s)$ + Cl^-	⇌ $CuCl_2^-$	
Initial	0.10 M	0	
Equil.	$0.10 - s$	s	where s = solubility of CuCl(s) in mol/L

$$K = 0.10 = \frac{[CuCl_2^-]}{[Cl^-]} = \frac{s}{0.10 - s},\quad 1.0 \times 10^{-2} - 0.10\,s = s,\quad s = 9.1 \times 10^{-3}\ \text{mol/L}$$

73. Test tube 1: Added Cl^- reacts with Ag^+ to form a silver chloride precipitate. The net ionic equation is $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Test tube 2: Added NH_3 reacts with Ag^+ ions to form a soluble complex ion, $Ag(NH_3)_2^+$. As this complex ion forms, Ag^+ is removed from the solution, which causes the AgCl(s) to dissolve. When enough NH_3 is added, all the silver chloride precipitate will dissolve. The equation is $AgCl(s) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$. Test tube 3: Added H^+ reacts with the weak base, NH_3, to form NH_4^+. As NH_3 is removed from the $Ag(NH_3)_2^+$ complex ion, Ag^+ ions are released to solution and can then react with Cl^- to re-form AgCl(s). The equations are $Ag(NH_3)_2^+(aq) + 2\,H^+(aq) \rightarrow Ag^+(aq) + 2\,NH_4^+(aq)$ and $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$.

74. In NH_3, Cu^{2+} forms the soluble complex ion $Cu(NH_3)_4^{2+}$. This increases the solubility of $Cu(OH)_2(s)$ because added NH_3 removes Cu^{2+} from the equilibrium causing more $Cu(OH)_2(s)$ to dissolve. In HNO_3, H^+ removes OH^- from the K_{sp} equilibrium causing more $Cu(OH)_2(s)$ to dissolve. Any salt with basic anions will be more soluble in an acid solution. $AgC_2H_3O_2(s)$ will be more soluble in either NH_3 or HNO_3. This is because Ag^+ forms the complex ion $Ag(NH_3)_2^+$, and $C_2H_3O_2^-$ is a weak base, so it will react with added H^+. AgCl(s) will be more soluble only in NH_3 due to $Ag(NH_3)_2^+$ formation. In acid, Cl^- is a horrible base, so it doesn't react with added H^+. AgCl(s) will not be more soluble in HNO_3.

Connecting to Biochemistry

75.

	$Ca_5(PO_4)_3OH(s)$ ⇌	$5\,Ca^{2+}$ +	$3\,PO_4^{3-}$ +	OH^-
Initial	s = solubility (mol/L)	0	0	1.0×10^{-7} from water
Equil.		$5s$	$3s$	$s + 1.0 \times 10^{-7} \approx s$

$$K_{sp} = 6.8 \times 10^{-37} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-] = (5s)^5(3s)^3(s)$$

$$6.8 \times 10^{-37} = (3125)(27)s^9,\quad s = 2.7 \times 10^{-5}\ \text{mol/L};\quad \text{assumption is good.}$$

The solubility of hydroxyapatite will increase as the solution gets more acidic because both phosphate and hydroxide can react with H^+.

	$Ca_5(PO_4)_3F(s) \rightleftharpoons$	$5\ Ca^{2+}$ +	$3\ PO_4^{3-}$ +	F^-
Initial	s = solubility (mol/L)	0	0	0
Equil.		$5s$	$3s$	s

$K_{sp} = 1 \times 10^{-60} = (5s)^5(3s)^3(s) = (3125)(27)s^9,\ \ s = 6 \times 10^{-8}$ mol/L

The hydroxyapatite in tooth enamel is converted to the less soluble fluorapatite by fluoride-treated water. The less soluble fluorapatite is more difficult to remove, making teeth less susceptible to decay.

76. $\dfrac{1\ \text{mg F}^-}{\text{L}} \times \dfrac{1\ \text{g}}{1000\ \text{mg}} \times \dfrac{1\ \text{mol F}^-}{19.00\ \text{g F}^-} = 5.3 \times 10^{-5}\ M\ \text{F}^- = 5 \times 10^{-5}\ M\ \text{F}^-$

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$ $K_{sp} = [Ca^{2+}][F^-]^2 = 4.0 \times 10^{-11}$; precipitation will occur when $Q > K_{sp}$. Let's calculate $[Ca^{2+}]$ so that $Q = K_{sp}$.

$Q = 4.0 \times 10^{-11} = [Ca^{2+}]_0[F^-]_0^2 = [Ca^{2+}]_0(5 \times 10^{-5})^2,\ \ [Ca^{2+}]_0 = 2 \times 10^{-2}\ M$

$CaF_2(s)$ will precipitate when $[Ca^{2+}]_0 > 2 \times 10^{-2}\ M$. Therefore, hard water should have a calcium ion concentration of less than $2 \times 10^{-2}\ M$ in order to avoid $CaF_2(s)$ formation.

77. KBT dissolves to form the potassium ion (K^+) and the bitartrate ion (abbreviated as BT^-).

	$KBT(s) \rightleftharpoons$	$K^+(aq)$ +	$BT^-(aq)$	$K_{sp} = 3.8 \times 10^{-4}$
Initial	s = solubility (mol/L)	0	0	
Equil.		s	s	

$3.8 \times 10^{-4} = [K^+][BT^-] = s(s) = s^2,\ \ s = 1.9 \times 10^{-2}$ mol/L

$$0.2500\ \text{L} \times \frac{1.9 \times 10^{-2}\ \text{mol KBT}}{\text{L}} \times \frac{188.2\ \text{g KBT}}{\text{mol}} = 0.89\ \text{g KBT}$$

78.

	$BaSO_4(s) \rightleftharpoons$	$Ba^{2+}(aq)$ +	$SO_4^{2-}(aq)$	$K_{sp} = 1.5 \times 10^{-9}$
Initial	s = solubility (mol/L)	0	0	
Equil.		s	s	

$1.5 \times 10^{-9} = [Ba^{2+}][SO_4^{2-}] = s^2,\ \ s = 3.9 \times 10^{-5}$ mol/L

$$0.1000\ \text{L} \times \frac{3.9 \times 10^{-5}\ \text{mol BaSO}_4}{\text{L}} \times \frac{233.4\ \text{g BaSO}_4}{\text{mol}} = 9.1 \times 10^{-4}\ \text{g BaSO}_4$$

79. Molar solubility of $ZnSO_4$ = s = $\dfrac{54.0\text{ g }ZnSO_4}{0.1000\text{ L}} \times \dfrac{1\text{ mol }ZnSO_4}{161.45\text{ g}}$ = 3.34 mol/L

$$ZnSO_4(s) \rightleftharpoons Zn^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = [Zn^{2+}][SO_4^{2-}]$$

		Zn^{2+}	SO_4^{2-}
Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = s(s) = s^2 = (3.34)^2$, $K_{sp} = 11.2$

80. Because of the small K_{sp} value, $Mg(OH)_2$ is not very soluble; hence not very much of the 10.0 g of $Mg(OH)_2$ will dissolve. We need to perform an equilibrium problem to determine the solubility of $Mg(OH)_2$.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq) \qquad K_{sp} = 8.9 \times 10^{-12}$$

		Mg^{2+}	OH^-
Initial	s = solubility (mol/L)	0	$1.0 \times 10^{-7}\ M$ (from water)
Equil.		s	$1.0 \times 10^{-7} + 2s$

$8.9 \times 10^{-12} = [Mg^{2+}][OH^-]^2 = s(1.0 \times 10^{-7} + 2s)^2$

If $1.0 \times 10^{-7} + 2s \approx 2s$: $8.9 \times 10^{-12} = s(2s)^2 = 4s^3$, $s = 1.3 \times 10^{-4}$ mol/L; assumption good.

From above, $[OH^-] = 1.0 \times 10^{-7} + 2s \approx 2s = 2(1.3 \times 10^{-4}) = 2.6 \times 10^{-4}$ mol/L.

Mol OH^- = $0.5000\text{ L} \times \dfrac{2.6 \times 10^{-4}\text{ mol }OH^-}{\text{L}} = 1.3 \times 10^{-4}\text{ mol }OH^-$

OH^- reacts with the acid in the stomach. As OH^- is removed, more $Mg(OH)_2$ must dissolve in an attempt to get back to equilibrium. This shift in the K_{sp} reaction continues until all the $Mg(OH)_2$ is used up or when there is no more acid in the stomach for OH^- to react with.

81.

$$\begin{array}{ll} Mn^{2+} + C_2O_4^{2-} \rightleftharpoons MnC_2O_4 & K_1 = 7.9 \times 10^3 \\ MnC_2O_4 + C_2O_4^{2-} \rightleftharpoons Mn(C_2O_4)_2^{2-} & K_2 = 7.9 \times 10^1 \\ \hline Mn^{2+}(aq) + 2\ C_2O_4^{2-}(aq) \rightleftharpoons Mn(C_2O_4)_2^{2-}(aq) & K_f = K_1K_2 = 6.2 \times 10^5 \end{array}$$

82.

$$Cr^{3+} + H_2EDTA^{2-} \rightleftharpoons CrEDTA^- + 2\ H^+$$

	Cr^{3+}	H_2EDTA^{2-}		$CrEDTA^-$	H^+	
Before	$0.0010\ M$	$0.050\ M$		0	$1.0 \times 10^{-6}\ M$	(Buffer)
Change	-0.0010	-0.0010	$\rightarrow$	$+0.0010$	No change	Reacts completely
After	0	0.049		0.0010	1.0×10^{-6}	New initial

x mol/L $CrEDTA^-$ dissociates to reach equilibrium

	Cr^{3+}	H_2EDTA^{2-}		$CrEDTA^-$	H^+	
Change	$+x$	$+x$	$\leftarrow$	$-x$		
Equil.	x	$0.049 + x$		$0.0010 - x$	1.0×10^{-6}	(Buffer)

$$K_f = 1.0 \times 10^{23} = \frac{[\text{CrEDTA}^-][\text{H}^+]^2}{[\text{Cr}^{3+}][\text{H}_2\text{EDTA}^{2-}]} = \frac{(0.0010 - x)(1.0 \times 10^{-6})^2}{(x)(0.049 + x)}$$

$1.0 \times 10^{23} \approx \dfrac{(0.0010)(1.0 \times 10^{-12})}{x(0.049)}$, $x = [\text{Cr}^{3+}] = 2.0 \times 10^{-37}\ M$; assumptions good.

83. a.

	$Pb(OH)_2(s)$	$\rightleftharpoons$	Pb^{2+}	+	$2\ OH^-$
Initial	s = solubility (mol/L)		0		$1.0 \times 10^{-7}\ M$ from water
Equil.			s		$1.0 \times 10^{-7} + 2s$

$K_{sp} = 1.2 \times 10^{-15} = [Pb^{2+}][OH^-]^2 = s(1.0 \times 10^{-7} + 2s)^2 \approx s(2s^2) = 4s^3$

$s = [Pb^{2+}] = 6.7 \times 10^{-6}\ M$; assumption is good by the 5% rule.

b.

	$Pb(OH)_2(s)$	$\rightleftharpoons$	Pb^{2+}	+	$2\ OH^-$	
Initial			0		$0.10\ M$	pH = 13.00, $[OH^-] = 0.10\ M$
	s mol/L $Pb(OH)_2(s)$ dissolves to reach equilibrium					
Equil.			s		0.10	(Buffered solution)

$1.2 \times 10^{-15} = (s)(0.10)^2$, $s = [Pb^{2+}] = 1.2 \times 10^{-13}\ M$

c. We need to calculate the Pb^{2+} concentration in equilibrium with $EDTA^{4-}$. Since K is large for the formation of $PbEDTA^{2-}$, let the reaction go to completion and then solve an equilibrium problem to get the Pb^{2+} concentration.

	Pb^{2+}	+	$EDTA^{4-}$	$\rightleftharpoons$	$PbEDTA^{2-}$	$K = 1.1 \times 10^{18}$
Before	$0.010\ M$		$0.050\ M$		0	
	0.010 mol/L Pb^{2+} reacts completely (large K)					
Change	-0.010		-0.010	$\rightarrow$	$+0.010$	Reacts completely
After	0		0.040		0.010	New initial
	x mol/L $PbEDTA^{2-}$ dissociates to reach equilibrium					
Equil.	x		$0.040 + x$		$0.010 - x$	

$1.1 \times 10^{18} = \dfrac{(0.010 - x)}{(x)(0.040 + x)} \approx \dfrac{0.010}{x(0.040)}$, $x = [Pb^{2+}] = 2.3 \times 10^{-19}\ M$; assumptions good.

Now calculate the solubility quotient for $Pb(OH)_2$ to see if precipitation occurs. The concentration of OH^- is $0.10\ M$ since we have a solution buffered at pH = 13.00.

$Q = [Pb^{2+}]_0[OH^-]_0^2 = (2.3 \times 10^{-19})(0.10)^2 = 2.3 \times 10^{-21} < K_{sp}\ (1.2 \times 10^{-15})$

$Pb(OH)_2(s)$ will not form since Q is less than K_{sp}.

84. $C_7H_5BiO_4(s) + H_2O(l) \rightleftharpoons C_7H_4O_3^{2-}(aq) + Bi^{3+}(aq) + OH^-(aq)$

		$C_7H_4O_3^{2-}$	Bi^{3+}	OH^-
Initial	s = solubility (mol/L)	0	0	$1.0 \times 10^{-7}\ M$ (from water)
Equil.		s	s	$1.0 \times 10^{-7} + s$

$K = [C_7H_4O_3^{2-}][Bi^{3+}][OH^-] = s(s)(1.0 \times 10^{-7} + s)$; from the problem, $s = 3.2 \times 10^{-19}$ mol/L:

$$K = (3.2 \times 10^{-19})^2(1.0 \times 10^{-7} + 3.2 \times 10^{-19}) = 1.0 \times 10^{-44}$$

Additional Exercises

85. $$\text{Mol Ag}^+ \text{ added} = 0.200 \text{ L} \times \frac{0.24 \text{ mol AgNO}_3}{\text{L}} \times \frac{1 \text{ mol Ag}^+}{\text{mol AgNO}_3} = 0.048 \text{ mol Ag}^+$$

The added Ag^+ will react with the halogen ions to form a precipitate. Because the K_{sp} values are small, we can assume these precipitation reactions go to completion. The order of precipitation will be AgI(s) first (the least soluble compound since K_{sp} is the smallest), followed by AgBr(s), with AgCl(s) forming last [AgCl(s) is the most soluble compound listed since it has the largest K_{sp}].

Let the Ag^+ react with I^- to completion.

	$Ag^+(aq)$	+	$I^-(aq)$	→	$AgI(s)$	$K = 1/K_{sp} >> 1$
Before	0.048 mol		0.018 mol		0	
Change	−0.018		−0.018		+0.018	I^- is limiting.
After	0.030 mol		0		0.018 mol	

Let the Ag^+ remaining react next with Br^- to completion.

	$Ag^+(aq)$	+	$Br^-(aq)$	→	$AgBr(s)$	$K = 1/K_{sp} >> 1$
Before	0.030 mol		0.018 mol		0	
Change	−0.018		−0.018		+0.018	Br^- is limiting.
After	0.012 mol		0		0.018 mol	

Finally, let the remaining Ag^+ react with Cl^- to completion.

	$Ag^+(aq)$	+	$Cl^-(aq)$	→	$AgCl(s)$	$K = 1/K_{sp} >> 1$
Before	0.012 mol		0.018 mol		0	
Change	−0.012		−0.012		+0.012	Ag^+ is limiting.
After	0		0.006 mol		0.012 mol	

Some of the AgCl will redissolve to produce some Ag^+ ions; we can't have $[Ag^+] = 0$ *M*. Calculating how much AgCl(s) redissolves:

	$AgCl(s)$	→	$Ag^+(aq)$	+	$Cl^-(aq)$	$K_{sp} = 1.6 \times 10^{-10}$
Initial	s = solubility (mol/L)		0		0.006 mol/0.200 L = 0.03 *M*	
	s mol/L of AgCl dissolves to reach equilibrium					
Change	$-s$	→	$+s$		$+s$	
Equil.			s		$0.03 + s$	

$K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-] = s(0.03 + s) \approx (0.03)s$

$s = 5 \times 10^{-9}$ mol/L; the assumption that $0.03 + s \approx 0.03$ is good.

Mol AgCl present = 0.012 mol – 5×10^{-9} mol = 0.012 mol

$$\text{Mass AgCl present} = 0.012 \text{ mol AgCl} \times \frac{143.4 \text{ g}}{\text{mol AgCl}} = 1.7 \text{ g AgCl}$$

$[Ag^+] = s = 5 \times 10^{-9}$ mol/L

86. $AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq) \quad K_{sp} = [Ag^+][X^-]$

$AgY(s) \rightleftharpoons Ag^+(aq) + Y^-(aq) \quad K_{sp} = [Ag^+][Y^-]$

For conjugate acid-base pairs, the weaker the acid, the stronger is the conjugate base. Because HX is a stronger acid (has a larger K_a value) than HY, Y^- will be a stronger base than X^-. In acidic solution, Y^- will have a greater affinity for the H^+ ions. Therefore, AgY(s) will be more soluble in acidic solution because more Y^- will be removed through reaction with H^+, which will cause more AgY(s) to dissolve.

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

We need to determine the F^- concentration present in a 1.0 *M* HF solution. Solving the weak acid equilibrium problem:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \quad K_a = \frac{[H^+][F^-]}{[HF]}$$

	HF	H^+	F^-
Initial	1.0 *M*	~0	0
Equil.	$1.0 - x$	x	x

$K_a = 7.2 \times 10^{-4} = \dfrac{x(x)}{1.0 - x} \approx \dfrac{x^2}{1.0}$, $x = [F^-] = 2.7 \times 10^{-2}$ *M*; assumption good.

Next, calculate the Ca^{2+} concentration necessary for $Q = K_{sp,\,CaF_2}$.

$Q = [Ca^{2+}]_0[F^-]_0^2$, $4.0 \times 10^{-11} = [Ca^{2+}]_0(2.7 \times 10^{-2})^2$, $[Ca^{2+}]_0 = 5.5 \times 10^{-8}$ mol/L

$$\text{Mass } Ca(NO_3)_2 = 1.0 \text{ L} \times \frac{5.5 \times 10^{-8} \text{ mol } Ca^{2+}}{\text{L}} \times \frac{1 \text{ mol } Ca(NO_3)_2}{\text{mol } Ca^{2+}} \times \frac{164.10 \text{ g } Ca(NO_3)_2}{\text{mol}}$$

$$= 9.0 \times 10^{-6} \text{ g } Ca(NO_3)_2$$

For precipitation of $CaF_2(s)$ to occur, we need $Q > K_{sp}$. When 9.0×10^{-6} g $Ca(NO_3)_2$ has been added to 1.0 L of solution, $Q = K_{sp}$. So precipitation of $CaF_2(s)$ will begin to occur when just over 9.0×10^{-6} g $Ca(NO_3)_2$ has been added.

88.

	$Mn(OH)_2(s)$	$\rightleftharpoons$	$Mn^{2+}(aq)$	+	$2\ OH^-(aq)$	$K_{sp} = [Mn^{2+}][OH^-]^2$
Initial	s = solubility (mol/L)		0		1.0×10^{-7} *M* (from water)	
Equil.			s		$1.0 \times 10^{-7} + 2s$	

$K_{sp} = 2.0 \times 10^{-13} = s(1.0 \times 10^{-7} + 2s) \approx s(2s)^2 = 4s^3$, $s = 3.7 \times 10^{-5}$ mol/L; assumption good.

$$1.3\ \text{L} \times \frac{3.7 \times 10^{-5}\ \text{mol Mn(OH)}_2}{\text{L}} \times \frac{88.96\ \text{g Mn(OH)}_2}{\text{mol}} = 4.3 \times 10^{-3}\ \text{g Mn(OH)}_2$$

89. $$s = \text{solubility} = \frac{0.24\ \text{g PbI}_2 \times \dfrac{1\ \text{mol PbI}_2}{461.0\ \text{g}}}{0.2000\ \text{L}} = 2.6 \times 10^{-3}\ M$$

	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2\ I^-(aq)$	$K_{sp} = [Pb^{2+}][I^-]^2$
Initial	s = solubility (mol/L)		0		0	
Equil.			s		$2s$	

$K_{sp} = s(2s)^2 = 4s^3$, $K_{sp} = 4(2.6 \times 10^{-3})^3 = 7.0 \times 10^{-8}$

90. $$1.0\ \text{mL} \times \frac{1.0\ \text{mmol}}{\text{mL}} = 1.0\ \text{mmol Cd}^{2+}\ \text{added to the ammonia solution}$$

Thus $[Cd^{2+}]_0 = 1.0 \times 10^{-3}$ mol/L. We will first calculate the equilibrium Cd^{2+} concentration using the complex ion equilibrium and then determine if this Cd^{2+} concentration is large enough to cause precipitation of $Cd(OH)_2(s)$.

	Cd^{2+}	+ $4\ NH_3$	$\rightleftharpoons$	$Cd(NH_3)_4^{2+}$	$K_f = 1.0 \times 10^7$
Before	1.0×10^{-3} *M*	5.0 *M*		0	
Change	-1.0×10^{-3}	-4.0×10^{-3}	$\rightarrow$	$+1.0 \times 10^{-3}$	Reacts completely
After	0	$4.996 \approx 5.0$		1.0×10^{-3}	New initial
	x mol/L $Cd(NH_3)_4^{2+}$ dissociates to reach equilibrium				
Change	$+x$	$+4x$	$\leftarrow$	$-x$	
Equil.	x	$5.0 + 4x$		$0.0010 - x$	

$$K_f = 1.0 \times 10^7 = \frac{(0.010 - x)}{(x)(5.0 + 4x)^4} \approx \frac{(0.010)}{(x)(5.0)^4}$$

$x = [Cd^{2+}] = 1.6 \times 10^{-13}$ *M*; assumptions good. This is the maximum $[Cd^{2+}]$ possible. Now we will determine if $Cd(OH)_2(s)$ forms at this concentration of Cd^{2+}. In 5.0 *M* NH_3 we can calculate the pH:

	NH_3 + H_2O	$\rightleftharpoons$	NH_4^+	+ OH^-	$K_b = 1.8 \times 10^{-5}$
Initial	5.0 *M*		0	~0	
Equil.	$5.0 - y$		y	y	

$K_b = 1.8 \times 10^{-5} = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{y^2}{5.0 - y} \approx \dfrac{y^2}{5.0}$, $y = [OH^-] = 9.5 \times 10^{-3}\ M$; assumptions good.

We now calculate the value of the solubility quotient, Q:

$$Q = [Cd^{2+}][OH^-]^2 = (1.6 \times 10^{-13})(9.5 \times 10^{-3})^2$$

$Q = 1.4 \times 10^{-17} < K_{sp}\ (5.9 \times 10^{-15})$; therefore, no precipitate forms.

91. a.

$$\begin{array}{rcll} Cu(OH)_2 & \rightleftharpoons & Cu^{2+} + 2\ OH^- & K_{sp} = 1.6 \times 10^{-19} \\ Cu^{2+} + 4\ NH_3 & \rightleftharpoons & Cu(NH_3)_4^{2+} & K_f = 1.0 \times 10^{13} \\ \hline Cu(OH)_2(s) + 4\ NH_3(aq) & \rightleftharpoons & Cu(NH_3)_4^{2+}(aq) + 2\ OH^-(aq) & K = K_{sp}K_f = 1.6 \times 10^{-6} \end{array}$$

b.

$$Cu(OH)_2(s) + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} + 2\ OH^- \qquad K = 1.6 \times 10^{-6}$$

	NH_3	$Cu(NH_3)_4^{2+}$	OH^-
Initial	5.0 *M*	0	0.0095 *M*
s mol/L $Cu(OH)_2$ dissolves to reach equilibrium			
Equil.	$5.0 - 4s$	s	$0.0095 + 2s$

$$K = 1.6 \times 10^{-6} = \frac{[Cu(NH_3)_4^{2+}][OH^-]^2}{[NH_3]^4} = \frac{s(0.0095 + 2s)^2}{(5.0 - 4s)^4}$$

If s is small: $1.6 \times 10^{-6} = \dfrac{s(0.0095)^2}{(5.0)^4}$, $s = 11.$ mol/L

Assumptions are horrible. We will solve the problem by successive approximations.

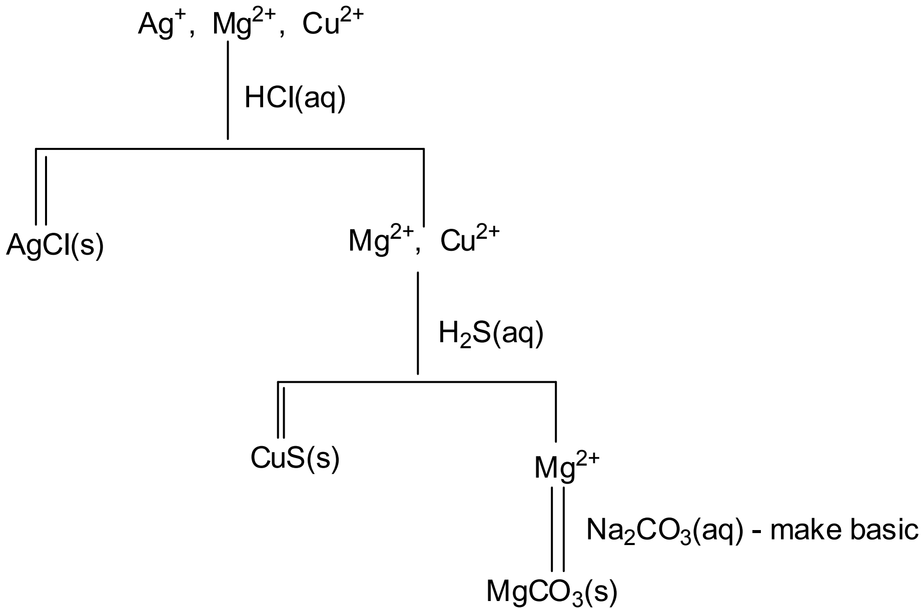
$s_{calc} = \dfrac{1.6 \times 10^{-6}\ (5.0 - 4s_{guess})^4}{(0.0095 + 2s_{guess})^2}$; the results from six trials are:

s_{guess}: 0.10, 0.050, 0.060, 0.055, 0.056

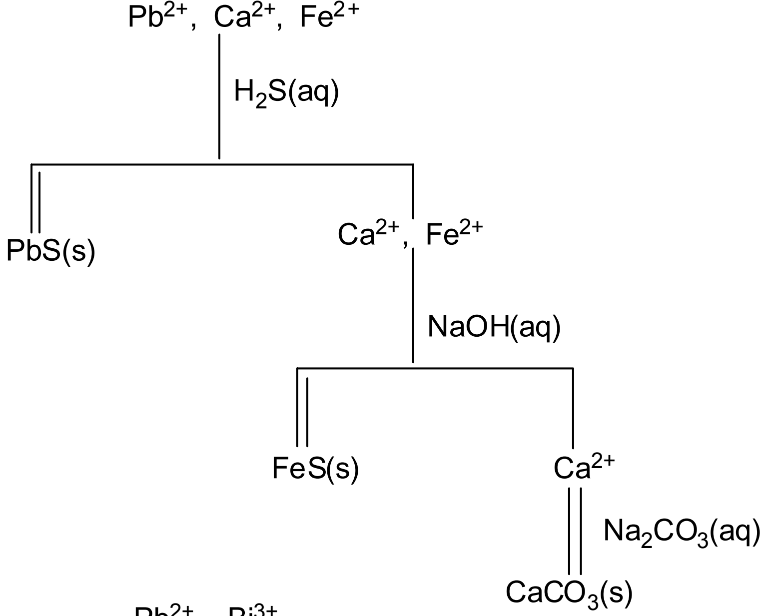
s_{calc}: 1.6×10^{-2}, 0.071, 0.049, 0.058, 0.056

Thus the solubility of $Cu(OH)_2$ is 0.056 mol/L in 5.0 *M* NH_3.

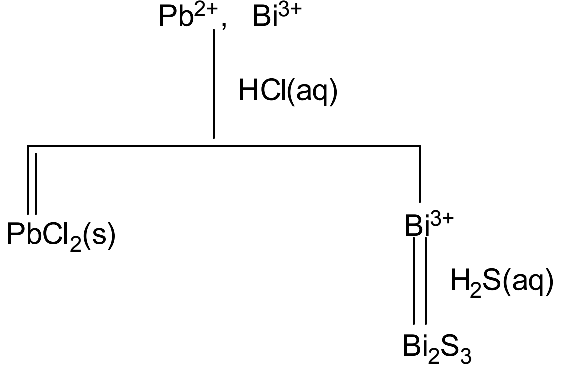
92. a.


Ag+, Mg2+, Cu2+
HCl(aq)
AgCl(s)
Mg2+, Cu2+
H2S(aq)
CuS(s)
Mg2+
Na2CO3(aq) - make basic
MgCO3(s)

b.


Pb2+, Ca2+, Fe2+
H2S(aq)
PbS(s)
Ca2+, Fe2+
NaOH(aq)
FeS(s)
Ca2+
Na2CO3(aq)
CaCO3(s)

c.


Pb2+, Bi3+
HCl(aq)
PbCl2(s)
Bi3+
H2S(aq)
Bi2S3

93. $Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = [Ba^{2+}][OH^-]^2 = 5.0 \times 10^{-3}$

Initial	s = solubility (mol/L)	0	~0
Equil.		s	$2s$

$K_{sp} = 5.0 \times 10^{-3} = s(2s)^2 = 4s^3$, $s = 0.11$ mol/L; assumption good.

$[OH^-] = 2s = 2(0.11) = 0.22$ mol/L; pOH = 0.66, pH = 13.34

$Sr(OH)_2(s) \rightleftharpoons Sr^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = [Sr^{2+}][OH^-]^2 = 3.2 \times 10^{-4}$

Equil. s $2s$

$K_{sp} = 3.2 \times 10^{-4} = 4s^3$, $s = 0.043$ mol/L; asssumption good.

$[OH^-] = 2(0.043) = 0.086\ M$; pOH = 1.07, pH = 12.93

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = [Ca^{2+}][OH^-]^2 = 1.3 \times 10^{-6}$

Equil. s $2s$

$K_{sp} = 1.3 \times 10^{-6} = 4s^3$, $s = 6.9 \times 10^{-3}$ mol/L; assumption good.

$[OH^-] = 2(6.9 \times 10^{-3}) = 1.4 \times 10^{-2}$ mol/L; pOH = 1.85, pH = 12.15

94. $K_{sp} = 6.4 \times 10^{-9} = [Mg^{2+}][F^-]^2$, $6.4 \times 10^{-9} = (0.00375 - y)(0.0625 - 2y)^2$

This is a cubic equation. No simplifying assumptions can be made since y is relatively large. Solving cubic equations is difficult unless you have a graphing calculator. However, if you don't have a graphing calculator, one way to solve this problem is to make the simplifying assumption to run the precipitation reaction to completion. This assumption is made because of the very small value for K, indicating that the ion concentrations are very small. Once this assumption is made, the problem becomes much easier to solve.

Challenge Problems

95. a.

$$\begin{array}{ll} CuBr(s) \rightleftharpoons Cu^+ + Br^- & K_{sp} = 1.0 \times 10^{-5} \\ Cu+\ +\ 3\ CN^- \rightleftharpoons Cu(CN)_3^{2-} & K_f = 1.0 \times 10^{11} \\ \hline CuBr(s) + 3\ CN^- \rightleftharpoons Cu(CN)_3^{2-} + Br^- & K = 1.0 \times 10^6 \end{array}$$

Because K is large, assume that enough CuBr(s) dissolves to completely use up the 1.0 M CN^-; then solve the back equilibrium problem to determine the equilibrium concentrations.

	$CuBr(s)$	$+\ 3\,CN^-$	$\rightleftharpoons$	$Cu(CN)_3^{2-}$	$+\ Br^-$
Before	x	1.0 M		0	0
	x mol/L of CuBr(s) dissolves to react completely with 1.0 M CN^-				
Change	$-x$	$-3x$	$\rightarrow$	$+x$	$+x$
After	0	$1.0 - 3x$		x	x

For reaction to go to completion, $1.0 - 3x = 0$ and $x = 0.33$ mol/L. Now solve the back-equilibrium problem.

	$CuBr(s)$	$+\ 3\,CN^-$	$\rightleftharpoons$	$Cu(CN)_3^{2-}$	$+\ Br^-$
Initial		0		0.33 M	0.33 M
	Let y mol/L of $Cu(CN)_3^{2-}$ react to reach equilibrium.				
Change		$+3y$	$\leftarrow$	$-y$	$-y$
Equil.		3y		$0.33 - y$	$0.33 - y$

$$K = 1.0\times 10^{6} = \frac{(0.33-y)^2}{(3y)^3} \approx \frac{(0.33)^2}{27y^3},\ y = 1.6\times 10^{-3}\ M;\ \text{assumptions good.}$$

Of the initial 1.0 M CN^-, only $3(1.6\times 10^{-3}) = 4.8\times 10^{-3}$ M is present at equilibrium. Indeed, enough CuBr(s) did dissolve to essentially remove the initial 1.0 M CN^-. This amount, 0.33 mol/L, is the solubility of CuBr(s) in 1.0 M NaCN.

b. $[Br^-] = 0.33 - y = 0.33 - 1.6\times 10^{-3} = 0.33\ M$

c. $[CN^-] = 3y = 3(1.6\times 10^{-3}) = 4.8\times 10^{-3}\ M$

96.

$$\begin{array}{ll} Ag^+ + NH_3 \rightleftharpoons AgNH_3^+ & K_1 = 2.1\times 10^3 \\ AgNH_3^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ & K_2 = 8.2\times 10^3 \\ \hline Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+ & K = K_1K_2 = 1.7\times 10^7 \end{array}$$

The initial concentrations are halved because equal volumes of the two solutions are mixed. Let the reaction go to completion since K is large; then solve an equilibrium problem.

	Ag^+	$+\ 2\,NH_3$	$\rightleftharpoons$	$Ag(NH_3)_2^+$
Before	0.20 M	2.0 M		0
After	0	1.6		0.20
Equil.	x	$1.6 + 2x$		$0.20 - x$

$$K = 1.7\times 10^{7} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{0.20 - x}{x(1.6+2x)^2} \approx \frac{0.20}{x(1.6)^2},\ x = 4.6\times 10^{-9}\ M;$$

assumptions good.

$[Ag^+] = x = 4.6\times 10^{-9}\ M$; $[NH_3] = 1.6\ M$; $[Ag(NH_3)_2^+] = 0.20\ M$

Use either the K_1 or K_2 equilibrium expression to calculate $[AgNH_3^+]$.

$AgNH_3^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $\quad K_2 = 8.2 \times 10^3$

$$8.2 \times 10^3 = \frac{[Ag(NH_3)_2^+]}{[AgNH_3^+][NH_3]} = \frac{0.20}{[AgNH_3^+](1.6)},\ [AgNH_3^+] = 1.5 \times 10^{-5}\ M$$

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

	$AgBr(s)$	$Ag^+(aq)$	$Br^-(aq)$
Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = 5.0 \times 10^{-13} = s^2$, $s = 7.1 \times 10^{-7}$ mol/L

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

$Ag^+ + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $\quad K_f = 1.7 \times 10^7$

$AgBr(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Br^-(aq)$ $\quad K = K_{sp} \times K_f = 8.5 \times 10^{-6}$

	$AgBr(s)$ +	$2\ NH_3$ $\rightleftharpoons$	$Ag(NH_3)_2^+$ +	Br^-
Initial		$3.0\ M$	0	0
	s mol/L of AgBr(s) dissolves to reach equilibrium = molar solubility			
Equil.		$3.0 - 2s$	s	s

$$K = \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2} = \frac{s^2}{(3.0 - 2s)^2} = 8.5 \times 10^{-6} \approx \frac{s^2}{(3.0)^2},\ s = 8.7 \times 10^{-3}\ \text{mol/L}$$

Assumption good.

c. The presence of NH_3 increases the solubility of AgBr. Added NH_3 removes Ag^+ from solution by forming the complex ion, $Ag(NH_3)_2^+$. As Ag^+ is removed, more AgBr(s) will dissolve to replenish the Ag^+ concentration.

d. $$\text{Mass AgBr} = 0.2500\ \text{L} \times \frac{8.7 \times 10^{-3}\ \text{mol AgBr}}{\text{L}} \times \frac{187.8\ \text{g AgBr}}{\text{mol AgBr}} = 0.41\ \text{g AgBr}$$

e. Added HNO_3 will have no effect on the AgBr(s) solubility in pure water. Neither H^+ nor NO_3^- react with Ag^+ or Br^- ions. Br^- is the conjugate base of the strong acid HBr, so it is a terrible base. However, added HNO_3 will reduce the solubility of AgBr(s) in the ammonia solution. NH_3 is a weak base ($K_b = 1.8 \times 10^{-5}$). Added H^+ will react with NH_3 to form NH_4^+. As NH_3 is removed, a smaller amount of the $Ag(NH_3)_2^+$ complex ion will form, resulting in a smaller amount of AgBr(s) that will dissolve.

98. $$[NH_3]_0 = \frac{3.00\ M}{2} = 1.50\ M;\ [Cu^{2+}]_0 = \frac{2.00 \times 10^{-3}\ M}{2} = 1.00 \times 10^{-3}\ M$$

Because $[NH_3]_0 >> [Cu^{2+}]_0$, and because K_1, K_2, K_3 and K_4 are all large, $Cu(NH_3)_4^{2+}$ will be the dominant copper-containing species. The net reaction will be $Cu^{2+} + 4\ NH_3 \rightarrow Cu(NH_3)_4^{2+}$. Here, 1.00×10^{-3} *M* Cu^{2+} plus $4(1.00 \times 10^{-3}\ M)$ NH_3 will produce 1.00×10^{-3} *M* $Cu(NH_3)_4^{2+}$. At equilibrium:

$$[Cu(NH_3)_4^{2+}] \approx 1.00 \times 10^{-3}\ M$$

$$[NH_3] = [NH_3]_0 - [NH_3]_{\text{reacted}} = 1.50\ M - 4(1.00 \times 10^{-3}\ M) = 1.50\ M$$

Calculate $[Cu(NH_3)_3^{2+}]$ from the K_4 reaction:

$$1.55 \times 10^2 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu(NH_3)_3^{2+}][NH_3]} = \frac{1.00 \times 10^{-3}}{[Cu(NH_3)_3^{2+}](1.50)},\ [Cu(NH_3)_3^{2+}] = 4.30 \times 10^{-6}\ M$$

Calculate $[Cu(NH_3)_2^{2+}]$ from K_3 reaction:

$$1.00 \times 10^3 = \frac{[Cu(NH_3)_3^{2+}]}{[Cu(NH_3)_2^{2+}][NH_3]} = \frac{4.30 \times 10^{-6}}{[Cu(NH_3)_2^{2+}](1.50)},\ [Cu(NH_3)_2^{2+}] = 2.87 \times 10^{-9}\ M$$

Calculate $[Cu(NH_3)_3^{2+}]$ from the K_2 reaction:

$$3.88 \times 10^3 = \frac{[Cu(NH_3)_2^{2+}]}{[CuNH_3^{2+}][NH_3]} = \frac{2.87 \times 10^{-9}}{[CuNH_3^{2+}](1.50)},\ [CuNH_3^{2+}] = 4.93 \times 10^{-13}\ M$$

Calculate $[Cu^{2+}]$ from the K_1 reaction:

$$1.86 \times 10^4 = \frac{[CuNH_3^{2+}]}{[Cu^{2+}][NH_3]} = \frac{4.93 \times 10^{-13}}{[Cu^{2+}](1.50)},\ [Cu^{2+}] = 1.77 \times 10^{-17}\ M$$

The assumptions are valid. $Cu(NH_3)_4^{2+}$ is clearly the dominant copper-containing component.

99.

$$\begin{array}{ll} AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq) & K_{sp} = 2.2 \times 10^{-12} \\ H^+(aq) + CN^-(aq) \rightleftharpoons HCN(aq) & K = 1/K_{a,\,HCN} = 1.6 \times 10^9 \\ \hline AgCN(s) + H^+(aq) \rightleftharpoons Ag^+(aq) + HCN(aq) & K = 2.2 \times 10^{-12}(1.6 \times 10^9) = 3.5 \times 10^{-3} \end{array}$$

	$AgCN(s)$ +	$H^+(aq)$	$\rightleftharpoons Ag^+(aq)$ +	$HCN(aq)$
Initial		1.0 *M*	0	0
	s mol/L AgCN(s) dissolves to reach equilibrium			
Equil.		1.0 – *s*	*s*	*s*

$$3.5 \times 10^{-3} = \frac{[\mathrm{Ag^+}][\mathrm{HCN}]}{[\mathrm{H^+}]} = \frac{s(s)}{1.0 - s} \approx \frac{s^2}{1.0},\ \ s = 5.9 \times 10^{-2}$$

Assumption fails the 5% rule (s is 5.9% of 1.0 M). Using the method of successive approximations:

$$3.5 \times 10^{-3} = \frac{s^2}{1.0 - 0.059},\ s = 5.7 \times 10^{-2}$$

$$3.5 \times 10^{-3} = \frac{s^2}{1.0 - 0.057},\ s = 5.7 \times 10^{-2}\ \text{(consistent answer)}$$

The molar solubility of AgCN(s) in 1.0 M H^+ is 5.7×10^{-2} mol/L.

100. Solubility in pure water:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \qquad K_{sp} = 2 \times 10^{-9}$$

		Ca^{2+}	$C_2O_4^{2-}$
Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = s^2 = 2 \times 10^{-9}$, s = solubility = $4.47 \times 10^{-5} = 4 \times 10^{-5}$ mol/L

Solubility in 1.0 M H^+:

$$\begin{array}{rcll} CaC_2O_4(s) & \rightleftharpoons & Ca^{2+} + C_2O_4^{2-} & K_{sp} = 2 \times 10^{-9} \\ C_2O_4^{2-} + H^+ & \rightleftharpoons & HC_2O_4^- & K = 1/K_{a_2} = 1.6 \times 10^4 \\ HC_2O_4^- + H^+ & \rightleftharpoons & H_2C_2O_4 & K = 1/K_{a_1} = 15 \\ \hline CaC_2O_4(s) + 2\,H^+ & \rightleftharpoons & Ca^{2+} + H_2C_2O_4 & K_{overall} = 5 \times 10^{-4} \end{array}$$

	H^+	Ca^{2+}	$H_2C_2O_4$
Initial	0.10 M	0	0
	s mol/L of $CaC_2O_4(s)$ dissolves to reach equilibrium		
Equil.	$0.10 - 2s$	s	s

$$5 \times 10^{-4} = \frac{s^2}{(0.10 - 2s)^2},\ \ \frac{s}{0.10 - 2s} = (5 \times 10^{-4})^{1/2},\ \ s = 2 \times 10^{-3}\ \text{mol/L}$$

$$\frac{\text{Solubility in 0.10 } M\ \mathrm{H^+}}{\text{Solubility in pure water}} = \frac{2 \times 10^{-3}}{4 \times 10^{-5}} = 50$$

$CaC_2O_4(s)$ is 50 times more soluble in 0.10 M H^+ than in pure water. This increase in solubility is due to the weak base properties of $C_2O_4^{2-}$.

101. $K_{sp} = [Ni^{2+}][S^{2-}] = 3 \times 10^{-21}$

$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \qquad K_{a_1} = 1.0 \times 10^{-7}$

$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \qquad K_{a_2} = 1 \times 10^{-19}$

$$H_2S(aq) \rightleftharpoons 2\,H^+(aq) + S^{2-}(aq) \qquad K = K_{a_1} \times K_{a_2} = 1 \times 10^{-26} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Because K is very small, only a tiny fraction of the H_2S will react. At equilibrium, $[H_2S] = 0.10\,M$ and $[H^+] = 1 \times 10^{-3}$.

$$[S^{2-}] = \frac{K[H_2S]}{[H^+]^2} = \frac{(1 \times 10^{-26})(0.10)}{(1 \times 10^{-3})^2} = 1 \times 10^{-21}\,M$$

$NiS(s) \rightleftharpoons Ni^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = 3.0 \times 10^{-21}$

Precipitation of NiS will occur when $Q > K_{sp}$. We will calculate $[Ni^{2+}]$ for $Q = K_{sp}$.

$$Q = K_{sp} = [Ni^{2+}][S^{2-}] = 3.0 \times 10^{-21}, \quad [Ni^{2+}] = \frac{3.0 \times 10^{-21}}{1 \times 10^{-21}} = 3\,M$$

102. We need to determine $[S^{2-}]_0$ that will cause precipitation of CuS(s) but not MnS(s).
For CuS(s):

$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq) \quad K_{sp} = [Cu^{2+}][S^{2-}] = 8.5 \times 10^{-45}$

$$[Cu^{2+}]_0 = 1.0 \times 10^{-3}\,M, \quad \frac{K_{sp}}{[Cu^{2+}]_0} = \frac{8.5 \times 10^{-45}}{1.0 \times 10^{-3}} = 8.5 \times 10^{-42}\,M = [S^{2-}]$$

This $[S^{2-}]$ represents the concentration that we must exceed to cause precipitation of CuS because if $[S^{2-}]_0 > 8.5 \times 10^{-42}\,M$, $Q > K_{sp}$.

For MnS(s):

$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = [Mn^{2+}][S^{2-}] = 2.3 \times 10^{-13}$

$$[Mn^{2+}]_0 = 1.0 \times 10^{-3}\,M, \quad \frac{K_{sp}}{[Mn^{2+}]} = \frac{2.3 \times 10^{-13}}{1.0 \times 10^{-3}} = 2.3 \times 10^{-10}\,M = [S^{2-}]$$

This value of $[S^{2-}]$ represents the largest concentration of sulfide that can be present without causing precipitation of MnS. That is, for this value of $[S^{2-}]$, $Q = K_{sp}$, and no precipitatation of MnS occurs. However, for any $[S^{2-}]_0 > 2.3 \times 10^{-10}\,M$, MnS(s) will form.

We must have $[S^{2-}]_0 > 8.5 \times 10^{-45}\,M$ to precipitate CuS but $[S^{2-}]_0 < 2.3 \times 10^{-10}\,M$ to prevent precipitation of MnS.

The question asks for a pH that will precipitate CuS(s) but not MnS(s). We need to first choose an initial concentration of S^{2-} that will do this. Let's choose $[S^{2-}]_0 = 1.0 \times 10^{-10}\,M$

because this will clearly cause CuS(s) to precipitate but is still less than the $[S^{2-}]_0$ required for MnS(s) to precipitate. The problem now is to determine the pH necessary for a 0.1 *M* H_2S solution to have $[S^{2-}] = 1.0 \times 10^{-10}$ *M*. Let's combine the K_{a_1} and K_{a_2} equations for H_2S to determine the required $[H^+]$.

$$\begin{array}{ll} H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) & K_{a_1} = 1.0 \times 10^{-7} \\ HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) & K_{a_2} = 1 \times 10^{-19} \\ \hline HS^-(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq) & K = K_{a_1} \times K_{a_2} = 1.0 \times 10^{-26} \end{array}$$

$$1 \times 10^{-26} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[H^+]^2(1 \times 10^{-10})}{0.10},\ [H^+] = 3 \times 10^{-9}\ M$$

$pH = -\log(3 \times 10^{-9}) = 8.5$. So, if pH = 8.5, $[S^{2-}] = 1 \times 10^{-10}$ *M,* which will cause precipitation of CuS(s) but not MnS(s).

Note: Any pH less than 8.7 would be a correct answer to this problem.

103. $Mg^{2+} + P_3O_{10}^{5-} \rightleftharpoons MgP_3O_{10}^{3-}$ $K = 4.0 \times 10^8$

$$[Mg^{2+}]_0 = \frac{50. \times 10^{-3}\ g}{L} \times \frac{1\ mol}{24.31\ g} = 2.1 \times 10^{-3}\ M$$

$$[P_3O_{10}^{5-}]_0 = \frac{40.\ g\ Na_5P_3O_{10}}{L} \times \frac{1\ mol}{367.86\ g} = 0.11\ M$$

Assume the reaction goes to completion because K is large. Then solve the back-equilibrium problem to determine the small amount of Mg^{2+} present.

	Mg^{2+}	+	$P_3O_{10}^{5-}$	$\rightleftharpoons$	$MgP_3O_{10}^{3-}$	
Before	$2.1 \times 10^{-3}\ M$		$0.11\ M$		0	
Change	-2.1×10^{-3}		-2.1×10^{-3}	$\rightarrow$	$+2.1 \times 10^{-3}$	React completely
After	0		0.11		2.1×10^{-3}	New initial condition
	x mol/L $MgP_3O_{10}^{3-}$ dissociates to reach equilibrium					
Change	$+x$		$+x$	$\leftarrow$	$-x$	
Equil.	x		$0.11 + x$		$2.1 \times 10^{-3} - x$	

$$K = 4.0 \times 10^8 = \frac{[MgP_3O_{10}^{3-}]}{[Mg^{2+}][P_3O_{10}^{5-}]} = \frac{2.1 \times 10^{-3} - x}{x(0.11 + x)}\ (\text{assume } x << 2.1 \times 10^{-3})$$

$$4.0 \times 10^8 \approx \frac{2.1 \times 10^{-3}}{x(0.11)},\ x = [Mg^{2+}] = 4.8 \times 10^{-11}\ M;\ \text{assumptions good.}$$

104. $MX \rightleftharpoons M^+ + X^-$; $\Delta T = K_f m,\ m = \dfrac{\Delta T}{K_f} = \dfrac{0.028^\circ C}{1.86^\circ C/\text{molal}} = 0.015\ \text{mol/kg}$

$\dfrac{0.015\ \text{mol}}{\text{kg}} \times \dfrac{1\ \text{kg}}{1000\ \text{g}} \times 250\ \text{g} = 0.00375$ mol total solute particles (carrying extra sig. fig.)

$0.0375\ \text{mol} = \text{mol } M^+ + \text{mol } X^-,\ \text{mol } M^+ = \text{mol } X^- = 0.0375/2$

Because the density of the solution is 1.0 g/mL, 250 g = 250 mL of solution.

$[M^+] = \dfrac{(0.00375/2)\ \text{mol } M^+}{0.25\ \text{L}} = 7.5 \times 10^{-3}\ M,\ [X^-] = \dfrac{(0.00375/2)\ \text{mol } X^-}{0.25\ \text{L}} = 7.5 \times 10^{-3}\ M$

$K_{sp} = [M^+][X^-] = (7.5 \times 10^{-3})^2 = 5.6 \times 10^{-5}$

105. a.

	$SrF_2(s)$	$\rightleftharpoons$	$Sr^{2+}(aq)$	+	$2\ F^-(aq)$
Initial			0		0
	s mol/L SrF_2 dissolves to reach equilibrium				
Equil.			s		$2s$

$[Sr^{2+}][F^-]^2 = K_{sp} = 7.9 \times 10^{-10} = 4s^3,\ s = 5.8 \times 10^{-4}$ mol/L in pure water

b. Greater, because some of the F^- would react with water:

$$F^- + H_2O \rightleftharpoons HF + OH^- \quad K_b = \frac{K_w}{K_{a,\,HF}} = 1.4 \times 10^{-11}$$

This lowers the concentration of F^-, forcing more SrF_2 to dissolve.

c. $SrF_2(s) \rightleftharpoons Sr^{2+} + 2\ F^- \quad K_{sp} = 7.9 \times 10^{-10} = [Sr^{2+}][F^-]^2$

Let s = solubility = $[Sr^{2+}]$; then $2s$ = total F^- concentration.

Since F^- is a weak base, some of the F^- is converted into HF. Therefore:

total F^- concentration = $2s = [F^-] + [HF]$

$HF \rightleftharpoons H^+ + F^-\ \ K_a = 7.2 \times 10^{-4} = \dfrac{[H^+][F^-]}{[HF]} = \dfrac{1.0 \times 10^{-2}[F^-]}{[HF]}$ (since pH = 2.00 buffer)

$7.2 \times 10^{-2} = \dfrac{[F^-]}{[HF]}$, $[HF] = 14[F^-]$; solving:

$[Sr^{2+}] = s;\ 2s = [F^-] + [HF] = [F^-] + 14[F^-],\ 2s = 15[F^-],\ [F^-] = 2s/15$

$K_{sp} = 7.9 \times 10^{-10} = [Sr^{2+}][F^-]^2 = (s)\left(\dfrac{2s}{15}\right)^2$, $s = 3.5 \times 10^{-3}$ mol/L in pH = 2.00 solution

Integrative Problems

106. $M_3X_2(s) \longrightarrow 3\,M^{2+}(aq) + 2\,X^{3-}(aq) \qquad K_{sp} = [M^{2+}]^3[X^{3-}]^2$

		M^{2+}	X^{3-}
Initial	s = solubility (mol/L)	0	0
Equil.		$3s$	$2s$

$K_{sp} = (3s)^3(2s)^2 = 108\,s^5$; total ion concentration = $3s + 2s = 5s$

$$\pi = iMRT,\ iM = \text{total ion concentration} = \frac{\pi}{RT} = \frac{2.64 \times 10^{-2}\ \text{atm}}{0.08206\ \text{L atm/K}\bullet\text{mol} \times 298\ \text{K}}$$

$$= 1.08 \times 10^{-3}\ \text{mol/L}$$

$5s = 1.08 \times 10^{-3}$ mol/L, $s = 2.16 \times 10^{-4}$ mol/L; $K_{sp} = 108s^5 = 108(2.16 \times 10^{-4})^5$

$K_{sp} = 5.08 \times 10^{-17}$

107. Major species: H^+, HSO_4^-, Ba^{2+}, NO_3^-, and H_2O; Ba^{2+} will react with the SO_4^{2-} produced from the K_a reaction for HSO_4^-.

$$\begin{array}{ll}
HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} & K_{a_2} = 1.2 \times 10^{-2} \\
Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4(s) & K = 1/K_{sp} = 1/(1.5 \times 10^{-9}) = 6.7 \times 10^{8} \\
\hline
Ba^{2+} + HSO_4^- \rightleftharpoons H^+ + BaSO_4(s) & K_{overall} = (1.2 \times 10^{-2}) \times (6.7 \times 10^{8}) = 8.0 \times 10^{6}
\end{array}$$

Because $K_{overall}$ is so large, the reaction essentially goes to completion. Because H_2SO_4 is a strong acid, $[HSO_4^-]_0 = [H^+]_0 = 0.10\ M$.

	Ba^{2+}	+ HSO_4^-	$\rightleftharpoons$	H^+	+ $BaSO_4(s)$	
Before	0.30 M	0.10 M		0.10 M		
Change	–0.10	–0.10	→	+0.10		
After	0.20	0		0.20 M		New initial
Change	$+x$	$+x$		$-x$		
Equil.	$0.20 + x$	x		$0.20 - x$		

$$K = 8.0 \times 10^{6} = \frac{0.20 - x}{(0.20 + x)x} \approx \frac{0.20}{0.20(x)},\quad x = 1.3 \times 10^{-7}\ M;\ \text{assumptions good.}$$

$[H^+] = 0.20 - 1.3 \times 10^{-7} = 0.20\ M$; pH $= -\log(0.20) = 0.70$

$[Ba^{2+}] = 0.20 + 1.3 \times 10^{-7} = 0.20\ M$

From the initial reaction essentially going to completion, 1.0 L(0.10 mol HSO_4^-/L) = 0.10 mol HSO_4^- reacted; this will produce 0.10 mol $BaSO_4(s)$. Only 1.3×10^{-7} mol of this dissolves to reach equilibrium, so 0.10 mol $BaSO_4(s)$ is produced.

$$0.10 \text{ mol BaSO}_4 \times \frac{233.4 \text{ g BaSO}_4}{\text{mol}} = 23 \text{ g BaSO}_4 \text{ produced}$$

108. M: $[Xe]6s^2 4f^{14} 5d^{10}$; this is mercury, Hg. Because X^- has 54 electrons, X has 53 protons and is iodine, I. The identity of Q = Hg_2I_2.

$$[I^-]_0 = \frac{1.98 \text{ g NaI} \times \frac{1 \text{ mol NaI}}{149.9 \text{ g}} \times \frac{1 \text{ mol I}^-}{\text{mol NaI}}}{0.150 \text{ L}} = 0.0881 \text{ mol/L}$$

$$Hg_2I_2(s) \rightleftharpoons Hg_2^{2+} + 2\, I^- \qquad K_{sp} = 4.5 \times 10^{-29}$$

Initial s = solubility (mol/L) 0 0.0881 *M*
Equil. *s* 0.0881 + 2*s*

$$K_{sp} = 4.5 \times 10^{-29} = [Hg_2^{2+}][I^-]^2 = s(0.0881 + 2s)^2 \approx s(0.0881)^2$$

$s = 5.8 \times 10^{-27}$ mol/L; assumption good.

Marathon Problem

109. a. In very acidic solutions, the reaction that occurs to increase the solubility is $Al(OH)_3(s) + 3H^+ \rightarrow Al^{3+}(aq) + 3H_2O(l)$. In very basic solutions, the reaction that occurs to increase solubility is $Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$.

b. $Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3\, OH^-$; $Al(OH)_3(s) + OH^- \rightleftharpoons Al(OH)_4^-$

S = solubility = total Al^{3+} concentration = $[Al^{3+}] + [Al(OH)_4^-]$

$$[Al^{3+}] = \frac{K_{sp}}{[OH^-]^3} = K_{sp} \times \frac{[H^+]^3}{K_w{}^3}, \text{ because } [OH^-]^3 = (K_w/[H^+])^3$$

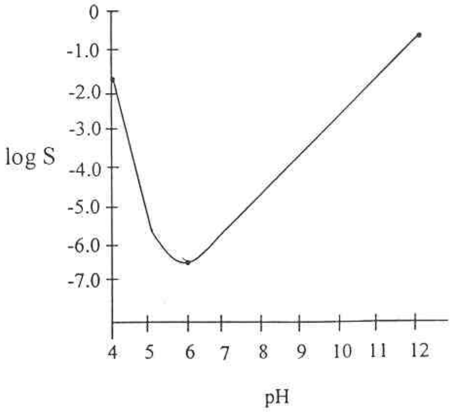
$$\frac{[Al(OH)_4^-]}{[OH^-]} = K;\ [OH^-] = \frac{K_w}{[H^+]};\ [Al(OH)_4^-] = K[OH^-] = \frac{KK_w}{[H^+]}$$

$$S = [Al^{3+}] + [Al(OH)_4^-] = [H^+]^3K_{sp}/K_w{}^3 + KK_w/[H^+]$$

c. $K_{sp} = 2 \times 10^{-32}$; $K_w = 1.0 \times 10^{-14}$; $K = 40.0$

$$S = \frac{[H^+]^3(2 \times 10^{-32})}{(1.0 \times 10^{-14})^3} + \frac{40.0(1.0 \times 10^{-14})}{[H^+]} = [H^+]^3(2 \times 10^{10}) + \frac{4.0 \times 10^{-13}}{[H^+]}$$

pH	solubility (S, mol/L)	log S
4.0	2×10^{-2}	−1.7
5.0	2×10^{-5}	−4.7
6.0	4.2×10^{-7}	−6.38
7.0	4.0×10^{-6}	−5.40
8.0	4.0×10^{-5}	−4.40
9.0	4.0×10^{-4}	−3.40
10.0	4.0×10^{-3}	−2.40
11.0	4.0×10^{-2}	−1.40
12.0	4.0×10^{-1}	−0.40



As expected, the solubility of $Al(OH)_3(s)$ is increased by very acidic solutions and by very basic solutions.