4. (E) Let \( s \) = solubility of each compound in moles of compound per liter of solution.

(a) \( K_{sp} = [\text{Ba}^{2+}] [\text{CrO}_4^{2-}] = 12.0 s^2 = 1.2 \times 10^{-10} \quad s = 1.1 \times 10^{-5} \text{ M} \)

(b) \( K_{sp} = [\text{Pb}^{2+}] [\text{Br}^-] = 0.0221 s = 4.0 \times 10^{-5} \quad s = 2.2 \times 10^{-2} \text{ M} \)

(c) \( K_{sp} = [\text{Ce}^{3+}] [\text{F}^-] = 27 s^4 = 8 \times 10^{-16} \quad s = 7 \times 10^{-5} \text{ M} \)

(d) \( K_{sp} = [\text{Mg}^{2+}] [\text{AsO}_4^{3-}] = 108 s^5 = 2.1 \times 10^{-20} \quad s = 4.5 \times 10^{-5} \text{ M} \)

14. (M) The titration reaction is \( \text{Ca(OH)}_2 (aq) + 2 \text{HCl}(aq) \rightarrow \text{CaCl}_2 (aq) + 2 \text{H}_2 \text{O}(l) \)

\[
\begin{align*}
10.7 \text{ mL HCl} &\times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1032 \text{ mol HCl}}{1 \text{ L}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol HCl}} = 0.0221 \text{ M} \\
50.00 \text{ mL Ca(OH)}_2 \text{ soln} &\times \frac{1 \text{ L}}{1000 \text{ mL}} \\
\end{align*}
\]

In a saturated solution of \( \text{Ca(OH)}_2, \quad [\text{Ca}^{2+}] = [\text{OH}^-]^2 + 2 \text{M} \)

\( K_{sp} = [\text{Ca}^{2+}] [\text{OH}^-]^2 = (0.0221 + 2)(0.0221)^2 = 5.40 \times 10^{-6} \quad (5.5 \times 10^{-6} \text{ in Appendix D}). \)

15. (E) We let \( s \) = molar solubility of \( \text{Mg(OH)}_2 \) in moles solute per liter of solution.

(a) \( K_{sp} = [\text{Mg}^{2+}] [\text{OH}^-]^2 = (s)(2s)^2 = 4s^3 = 1.8 \times 10^{-11} \quad s = 1.7 \times 10^{-4} \text{ M} \)

(b) Equation:\n
\[
\text{Mg(OH)}_2 (s) \underset{\text{aq}}{\rightleftharpoons} \text{Mg}^{2+} (aq) + 2\text{OH}^- (aq)
\]

Initial: \(-\quad 0.0862 \text{ M} \quad \approx 0 \text{ M} \)

Changes: \(- \quad +s \text{ M} \quad +2s \text{ M} \)

Equil: \(- \quad (0.0862 + s) \text{ M} \quad 2s \text{ M} \)

\( K_{sp} = (0.0862 + s)(2s)^2 = 1.8 \times 10^{-11} \approx (0.0862)(2s)^2 = 0.34 s^2 \quad s = 7.3 \times 10^{-6} \text{ M} \)

\( s << 0.0802 \text{ M}, \text{ thus, the approximation was valid.} \)

(c) \( [\text{OH}^-] = [\text{KOH}] = 0.0355 \text{ M} \)

Equation:\n
\[
\text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+} (aq) + 2\text{OH}^- (aq)
\]

Initial: \(-\quad 0 \text{ M} \quad 0.0355 \text{ M} \)

Changes: \(- \quad +s \text{ M} \quad +2s \text{ M} \)

Equil: \(- \quad s \text{ M} \quad (0.0355 + 2s) \text{ M} \)

\( K_{sp} = (s)(0.0355 + 2s)^2 = 1.8 \times 10^{-11} \approx (s)(0.0355)^2 = 0.0013 s \quad s = 1.4 \times 10^{-8} \text{ M} \)

20. (M) Equation: \( \text{CaSO}_4 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{SO}_4^{2-} (aq) \).

Soln: \(-\quad 0 \text{ M} \quad 0.0025 \text{ M} \)
Chapter 18: Solubility and Complex-Ion Equilibria

Add \( \text{CaSO}_4 \) (s) — +\( x \) M +\( x \) M

Equil: — \( x \) M \( (0.0025 + x) \) M

If we use the approximation that \( x \ll 0.0025 \), we find \( x = 0.0036 \). Clearly, \( x \) is larger than 0.0025 and thus the approximation is not valid. The quadratic equation must be solved.

\[
K_{sp} = \left[ \text{Ca}^{2+} \right] \left[ \text{SO}_4^{2-} \right] = 9.1 \times 10^{-6} = x(0.0025 + x) = 0.0025x + x^2
\]

\[
x^2 + 0.0025x - 9.1 \times 10^{-6} = 0
\]

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0025 \pm \sqrt{6.3 \times 10^{-6} + 3.6 \times 10^{-5}}}{2} = 2.0 \times 10^{-3} \text{M} = \left[ \text{CaSO}_4 \right]
\]

mass \( \text{CaSO}_4 \) = \( 0.1000 \text{L} \times \frac{2.0 \times 10^{-3} \text{mol} \text{CaSO}_4}{1 \text{L soln}} \times \frac{136.1 \text{g} \text{CaSO}_4}{1 \text{mol} \text{CaSO}_4} = 0.027 \text{g} \text{CaSO}_4
\]

28. (E) The solutions mutually dilute each other.

\[
\left[ \text{Cl}^- \right] = 0.016 \text{M} \times \frac{155 \text{mL}}{155 \text{mL} + 245 \text{mL}} = 6.2 \times 10^{-3} \text{M}
\]

\[
\left[ \text{Pb}^{2+} \right] = 0.175 \text{M} \times \frac{245 \text{mL}}{245 \text{mL} + 155 \text{mL}} = 0.107 \text{M}
\]

Then we compute the value of the ion product and compare it to the solubility product constant value.

\[
Q_{sp} = \left[ \text{Pb}^{2+} \right] \left[ \text{Cl}^- \right]^2 = (0.107)(6.2 \times 10^{-3})^2 = 4.1 \times 10^{-6} < 1.6 \times 10^{-5} = K_{sp}
\]

Thus, precipitation of \( \text{PbCl}_2 \) (s) will not occur from these mixed solutions.

36. (M) \( [\text{Ag}^+] \text{diluted} = 0.0208 \text{M} \times \frac{175 \text{mL}}{425 \text{mL}} = 0.008565 \text{M} \)

\( [\text{CrO}_4^{2-}] \text{diluted} = 0.0380 \text{M} \times \frac{250 \text{mL}}{425 \text{mL}} = 0.02235 \text{M} \)

\[
Q_{sp} = [\text{Ag}^+]^2 \left[ \text{CrO}_4^{2-} \right] = 1.6 \times 10^{-6} > K_{sp}
\]

Because \( Q_{sp} > K_{sp} \), then more \( \text{Ag}_3\text{Cr}_2\text{O}_7 \) precipitates out. Assume that the limiting reagent is used up (100% reaction in the reverse direction) and re-establish the equilibrium in the reverse direction. Here \( \text{Ag}^+ \) is the limiting reagent.

\[
\text{Ag}_3\text{Cr}_2\text{O}_7(s) + \frac{K_{sp}}{[\text{Ag}^+]_{\text{CrO}_4^{2-}}} = 1.1 \times 10^{-12} \rightarrow 2 \text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq)
\]

Initial — 0.008565 M 0.02235 M

Change — \( x = 0.00428 \text{M} \) \( -2x \) \(-x\)

100% rxn — 0 0.0181

Change — re-establish equil \( +2y \) \(+y\)

Equil — (assume \( y \sim 0 \)) \( 2y \) 0.0181 + \( y\)

\[
1.1 \times 10^{-12} = (2y)^2(0.0181 + y) = (2y)^2(0.0181) \quad y = 3.9 \times 10^{-6} \text{M}
\]

891
Chapter 18: Solubility and Complex-Ion Equilibria

\[ y \ll 0.0181, \text{ so this assumption is valid.} \]
\[ 2y = [Ag^+] = 7.8 \times 10^{-6} \text{ M after precipitation is complete.} \]
\[ \% [Ag^+]_{\text{unprecipitated}} = \frac{7.8 \times 10^{-6}}{0.00856} \times 100\% = 0.091\% \text{ (precipitation is essentially quantitative)} \]

42. (D) Normally we would worry about the mutual dilution of the two solutions, but the values of the solubility product constants are so small that only a very small volume of 0.50 M Pb(NO_3)_2 solution needs to be added, as we shall see.

(a) Since the two anions are present at the same concentration and they have the same type of formula (one anion per cation), the one forming the compound with the smallest \( K_{sp} \) value will precipitate first. Thus, CrO_4^{2-} is the first anion to precipitate.

(b) At the point where SO_4^{2-} begins to precipitate, we have
\[ K_{sp} = [Pb^{2+}][SO_4^{2-}] = 1.6 \times 10^{-8} = [Pb^{2+}](0.010M) \]
\[ [Pb^{2+}] = \frac{1.6 \times 10^{-8}}{0.010} = 1.6 \times 10^{-6} \text{ M} \]
Now we can test our original assumption, that only a very small volume of 0.50 M Pb(NO_3)_2 solution has been added. We assume that we have 1.00 L of the original solution, the one with the two anions dissolved in it, and compute the volume of 0.50 M Pb(NO_3)_2 that has to be added to achieve \( [Pb^{2+}] = 1.6 \times 10^{-6} \text{ M} \).
\[ V_{\text{added}} = 1.00 \text{ L} \times \frac{1.6 \times 10^{-6} \text{ mol Pb}^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ mol Pb(NO}_3)_2}{1 \text{ mol Pb}^{2+}} \times \frac{1 \text{ L Pb}^{2+} \text{ soln}}{0.50 \text{ mol Pb(NO}_3)_2} \]
\[ V_{\text{added}} = 3.2 \times 10^{-5} \text{ L Pb}^{2+} \text{ soln} = 0.0032 \text{ mL Pb}^{2+} \text{ soln} \]
This is less than one drop (0.05 mL) of the Pb^{2+} solution, clearly a very small volume.

(b) The two anions are effectively separated if \( [Pb^{2+}] \) has not reached 1.6 \times 10^{-6} \text{ M when} \[ [CrO_4^{2-}] \text{ is reduced to 0.1\% of its original value, that is, to} \]
\[ 0.010 \times 10^{-5} \text{ M} = 1.0 \times 10^{-5} \text{ M} = [CrO_4^{2-}] \]
\[ K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 2.8 \times 10^{-13} = [Pb^{2+}] \times 0.0 \times 10^{-5} \]
\[ [Pb^{2+}] = \frac{2.8 \times 10^{-13}}{1.0 \times 10^{-5}} = 2.8 \times 10^{-8} \text{ M} \]
Thus, the two anions can be effectively separated by fractional precipitation.

46. (E) In each case we indicate whether the compound is more soluble in base than in water. We write the net ionic equation for the reaction in which the solid dissolves in base. Substances are
soluble in base if either (1) acid-base reaction occurs [as in (b)] or (2) a gas is produced, since escape of the gas from the reaction mixture causes the reaction to shift to the right.

Water:  BaSO\(_4\) is less soluble in base, hydrolysis of SO\(_4^{2-}\) will be repressed.  

Base:  H\(_2\)C\(_2\)O\(_4\) (s) + 2OH\(^-\) (aq) → C\(_2\)O\(_4^{2-}\) (aq) + 2H\(_2\)O(l)

Water:  Fe(OH)\(_3\) is less soluble in base because of the OH\(^-\) common ion.

Same:  NaNO\(_3\) (neither Na\(^+\) nor NO\(_3^-\) react with H\(_2\)O to a measurable extent).

Water:  MnS is less soluble in base because hydrolysis of S\(_2^-\) will be repressed.

57. (M) We first compute the free \([Ag^+]\) in the original solution. The size of the complex ion formation equilibrium constant indicates that the reaction lies far to the right, so we form as much complex ion as possible stoichiometrically.

Equation:  
\[ Ag^+ (aq) + 2NH_3 (aq) \rightarrow [Ag(NH_3)_2]^+ \]

In soln:  
- Ag\(^+\) = 0.10 M  
- NH\(_3\) = 1.00 M

Form complex:  
- Ag\(^+\) = -0.10 M  
- NH\(_3\) = -0.20 M  
- [Ag(NH\(_3\)_2])\(^+\) = +0.10 M  
- [NH\(_3\)] = 0.80 M

Changes:  
- +x M  
- +2x M  
- -x M

Equil:  
- x M  
- [Ag(NH\(_3\)_2])\(^+\) = 0.80 + 2x M  
- 0.10 M

\[ K_f = 1.6 \times 10^7 = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} = \frac{0.10-x}{x(0.80+2x)^2} = \frac{0.10}{x(0.80)^2} \]

Thus, \([Ag^+] = 9.8 \times 10^{-9} M.\] We next determine the \([I^-]\) that can coexist in this solution without precipitation.

\[ K_{sp} = \frac{[Ag^+][I^-]}{[I^-]} = 8.5 \times 10^{-17} = \left(9.8 \times 10^{-9}\right)[I^-]; \quad [I^-] = \frac{8.5 \times 10^{-17}}{9.8 \times 10^{-9}} = 8.7 \times 10^{-9} M\]

Finally, we determine the mass of KI needed to produce this \([I^-]\)

\[ \text{mass KI} = 1.00 \text{ L soln} \times \frac{8.7 \times 10^{-9} \text{ mol I}^-}{1 \text{ L soln}} \times \frac{1 \text{ mol KI}}{1 \text{ mol I}^-} \times \frac{166.0 \text{ g KI}}{1 \text{ mol KI}} = 1.4 \times 10^{-6} \text{ g KI} \]

60. (M) Since the cation concentrations are identical, the value of \(Q_{\text{spa}}\) is the same for each one. It is this value of \(Q_{\text{spa}}\) that we compare with \(K_{\text{spa}}\) to determine if precipitation occurs.

\[ Q_{\text{spa}} = \left[\frac{M^{2+}}{H_2S}\right]\left[\frac{H_3O^+}{H_3O^+}\right] = \frac{0.05 \text{ M} \times 0.10 \text{ M}}{(0.010 \text{ M})^2} = 5 \times 10^1 \]
If \( Q_{\text{spa}} > K_{\text{spa}} \), precipitation of the metal sulfide should occur. But, if \( Q_{\text{spa}} < K_{\text{spa}} \), precipitation will not occur.

For CuS, \( K_{\text{spa}} = 6 \times 10^{-16} < Q_{\text{spa}} = 5 \times 10^4 \) Precipitation of CuS(s) should occur.

For HgS, \( K_{\text{spa}} = 2 \times 10^{-32} < Q_{\text{spa}} = 5 \times 10^4 \) Precipitation of HgS(s) should occur.

For MnS, \( K_{\text{spa}} = 3 \times 10^7 > Q_{\text{spa}} = 5 \times 10^4 \) Precipitation of MnS(s) will not occur.