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

c. \( \text{BaF}_2(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2 \text{F}^- (\text{aq}) \) \( K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2 \)

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 \( K_{\text{sp}} \) expression, we do not need to worry about their initial and equilibrium amounts.

a. \( \text{CaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>0</th>
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<tbody>
<tr>
<td>Change</td>
<td>(-s)</td>
<td>(+s)</td>
</tr>
<tr>
<td>Equil.</td>
<td>(s)</td>
<td>(s)</td>
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</tbody>
</table>

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

\( K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (s)(s) = s^2, \ K_{\text{sp}} = (4.8 \times 10^{-5})^2 = 2.3 \times 10^{-9} \)

b. \( \text{BiI}_3(\text{s}) \rightleftharpoons \text{Bi}^{3+}(\text{aq}) + 3 \text{I}^- (\text{aq}) \)

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<tbody>
<tr>
<td>Change</td>
<td>(-s)</td>
<td>(+s)</td>
</tr>
<tr>
<td>Equil.</td>
<td>(s)</td>
<td>(3s)</td>
</tr>
</tbody>
</table>

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

22. a. \( \text{Pb}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3 \text{Pb}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq}) \)

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<tbody>
<tr>
<td>Change</td>
<td>(-s)</td>
<td>(+3s)</td>
</tr>
<tr>
<td>Equil.</td>
<td>(3s)</td>
<td>(2s)</td>
</tr>
</tbody>
</table>

\( K_{\text{sp}} = [\text{Pb}^{2+}][\text{PO}_4^{3-}]^2 = (3s)^2(2s)^2 = 108s^5, \ K_{\text{sp}} = 108(6.2 \times 10^{-12})^5 = 9.9 \times 10^{-55} \)

b. \( \text{Li}_2\text{CO}_3(\text{s}) \rightleftharpoons 2 \text{Li}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>(s) = solubility (mol/L)</th>
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<tbody>
<tr>
<td>Equil.</td>
<td>(2s)</td>
<td>(s)</td>
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</table>

\( K_{\text{sp}} = [\text{Li}^+][\text{CO}_3^{2-}]^2 = (2s)^2(s) = 4s^3, \ K_{\text{sp}} = 4(7.4 \times 10^{-2})^3 = 1.6 \times 10^{-3} \)

23. 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) ⇌ Ni²⁺(aq) + 2OH⁻(aq)

Initial: 0 1.0 × 10⁻⁷ M (from water)

Change: −s → +s +2s

Equil. s 1.0 × 10⁻⁷ + 2s

From the calculated molar solubility, 1.0 × 10⁻⁷ + 2s ≈ 2s.

K_{sp} = [Ni²⁺][OH⁻]² = s(2s)² = 4s³,  K_{sp} = 4(1.5 × 10⁻³)³ = 1.4 × 10⁻⁸

M₂X₃(s) ⇌ 2 M³⁺(aq) + 3 X²⁻(aq)  \quad K_{sp} = [M³⁺]^2[X²⁻]^3

Initial: 0 0

Change: −s +2s +3s

Equil. 2s 3s

K_{sp} = (2s)²(3s)³ = 108s⁵;  s = \frac{3.60 × 10⁻⁷ g}{L} × \frac{1 \text{ mol M}_2X_3}{288 \text{ g}} = 1.25 × 10⁻⁹ mol/L

K_{sp} = 108(1.25 × 10⁻⁹)⁵ = 3.30 × 10⁻⁴³

PbBr₂(s) ⇌ Pb²⁺(aq) + 2 Br⁻(aq)

Initial: 0 0

Change: −s → +s +2s

Equil. s 2s

From the problem, s = [Pb²⁺] = 2.14 × 10⁻² M. So:

K_{sp} = [Pb²⁺][Br⁻]² = s(2s)² = 4s³,  K_{sp} = 4(2.14 × 10⁻²)³ = 3.92 × 10⁻⁵

Ag₂C₂O₄(s) ⇌ 2 Ag⁺(aq) + C₂O₄²⁻(aq)

Initial: s = solubility (mol/L) 0 0

Equil. 2s s

From problem, [Ag⁺] = 2s = 2.2 × 10⁻⁴ M,  s = 1.1 × 10⁻⁴ M

K_{sp} = [Ag⁺]²[C₂O₄²⁻] = (2s)²(s) = 4s³ = 4(1.1 × 10⁻⁴)³ = 5.3 × 10⁻¹²

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. \[ \text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3 \text{Ag}^+(aq) + \text{PO}_4^{3-}(aq) \]

Initial

\[ s \text{ mol/L of Ag}_3\text{PO}_4(s) \text{ dissolves to reach equilibrium} \]

Change

\[ -s \rightarrow +3s +s \]

Equil.

\[ 3s \]

\[ s \]

\[ K_{sp} = 1.8 \times 10^{-18} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (3s)^3(s) = 27s^4 \]

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

b. \[ \text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \]

Initial

\[ s = \text{solubility (mol/L)} \]

Equil.

\[ s \]

\[ s \]

\[ K_{sp} = 8.7 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = s^2, \quad s = 9.3 \times 10^{-5} \text{ mol/L} \]

c. \[ \text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2 \text{Cl}^-(aq) \]

Initial

\[ s = \text{solubility (mol/L)} \]

Equil.

\[ s \]

\[ 2s \]

\[ K_{sp} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (2s)^2 = 4s^3, \quad s = 6.5 \times 10^{-7} \text{ mol/L} \]

28. a. \[ \text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{I}^-(aq) \]

Initial

\[ s = \text{solubility (mol/L)} \]

Equil.

\[ s \]

\[ 2s \]

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

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

b. \[ \text{CdCO}_3(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{CO}_3^{2-}(aq) \]

Initial

\[ s = \text{solubility (mol/L)} \]

Equil.

\[ s \]

\[ s \]

\[ K_{sp} = 5.2 \times 10^{-12} = [\text{Cd}^{2+}][\text{CO}_3^{2-}] = s^2, \quad s = 2.3 \times 10^{-6} \text{ mol/L} \]

c. \[ \text{Sr}_3(\text{PO}_4)_2(s) \rightleftharpoons 3 \text{Sr}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq) \]

Initial

\[ s = \text{solubility (mol/L)} \]

Equil.

\[ 3s \]

\[ 2s \]

\[ K_{sp} = 1 \times 10^{-31} = [\text{Sr}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5, \quad s = 2 \times 10^{-7} \text{ mol/L} \]
29. \[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \]

Initial \[ s = \text{solubility (mol/L)} \quad 0 \quad 1.0 \times 10^{-7} M \text{ (from water)} \]

Equil. \[ s \quad 1.0 \times 10^{-7} + 2s \]

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

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

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

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

Initial \[ s = \text{solubility (mol/L)} \quad 0 \quad 1.0 \times 10^{-7} M \]

Equil. \[ s \quad 1.0 \times 10^{-7} + 2s \]

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

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

Assumption is good (1.0 \times 10^{-7} is 0.4\% of 2s). Molar solubility = 1.1 \times 10^{-5} \text{ 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.

\[ \text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \]

Initial \[ s = \text{mol/L of Al(OH)}_3(s) \text{ dissolves to reach equilibrium} = \text{molar solubility} \quad 0 \quad 1.0 \times 10^{-7} M \text{ (from water)} \]

Change \[ -s \rightarrow +s +3s \quad +3s \]

Equil. \[ s \quad 1.0 \times 10^{-7} + 3s \]

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

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

32. Let \( s \) = solubility of Co(OH)₃ in mol/L.

\[ \text{Co(OH)}_3(s) \rightleftharpoons \text{Co}^{3+}(aq) + 3\text{OH}^-(aq) \]

Initial \[ s = \text{mol/L of Co(OH)}_3(s) \text{ dissolves to reach equilibrium} = \text{molar solubility} \quad 0 \quad 1.0 \times 10^{-7} M \text{ (from water)} \]

Change \[ -s \rightarrow +s +3s \quad +3s \]

Equil. \[ s \quad 1.0 \times 10^{-7} + 3s \]

\[ K_{sp} = 2.5 \times 10^{-43} = [\text{Co}^{3+}][\text{OH}^-]^3 = (s)(1.0 \times 10^{-7} + 3s)^3 \approx s(1.0 \times 10^{-7})^3 \]
\[ s = \frac{2.5 \times 10^{-43}}{1.0 \times 10^{-21}} = 2.5 \times 10^{-22} \text{ mol/L}; \text{ assumption good (}1.0 \times 10^{-7} + 3s \approx 1.0 \times 10^{-7}) \]

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{align*}
\text{Ca}_3(\text{PO}_4)_2(s) & \rightleftharpoons 3 \text{Ca}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq) \quad \text{\( K_{sp} = 1.3 \times 10^{-32} \)} \\
\text{FePO}_4(s) & \rightleftharpoons \text{Fe}^{3+}(aq) + \text{PO}_4^{3-}(aq) \quad \text{\( K_{sp} = 1.0 \times 10^{-22} \)}
\end{align*}
\]

\[
\begin{align*}
\text{Initial} & \quad s = \text{solubility (mol/L)} \quad 0 \quad 0 \\
\text{Equil.} & \quad 3s \quad 2s \\
\text{\( K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5 \),} \quad s = (1.3 \times 10^{-32}/108)^{1/5} = 1.6 \times 10^{-7} \text{ mol/L} \\
\text{FePO}_4 & \rightleftharpoons \text{Fe}^{3+}(aq) + \text{PO}_4^{3-}(aq) \quad \text{\( K_{sp} = 1.0 \times 10^{-22} \)}
\end{align*}
\]

FePO\(_4\) has the smallest molar solubility.

34. a. \( \text{FeC}_2\text{O}_4(s) \rightleftharpoons \text{Fe}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \)

\[
\begin{align*}
\text{Equil.} & \quad s = \text{solubility (mol/L)} \quad s \quad s \\
\text{\( K_{sp} = 2.1 \times 10^{-7} = [\text{Fe}^{2+}][\text{C}_2\text{O}_4^{2-}] = s^2 \),} \quad s = 4.6 \times 10^{-4} \text{ mol/L} \\
\text{Cu(IO}_4)_2(s) & \rightleftharpoons \text{Cu}^{2+}(aq) + 2 \text{IO}_4^-(aq)
\end{align*}
\]

\[
\begin{align*}
\text{Equil.} & \quad s \quad 2s \quad (1.4 \times 10^{-7}/4)^{1/3} \\
\text{\( K_{sp} = 1.4 \times 10^{-7} = [\text{Cu}^{2+}][\text{IO}_4^-]^2 = s(2s)^2 = 4s^3 \),} \quad s = (1.4 \times 10^{-7}/4)^{1/3} = 3.3 \times 10^{-3} \text{ mol/L} \\
\text{By comparing calculated molar solubilities, FeC}_2\text{O}_4(s) \text{ is less soluble (in mol/L).}
\end{align*}
\]

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. \( \text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3 \text{OH}^-(aq) \)

\[
\begin{align*}
\text{Initial} & \quad 0 \quad 1 \times 10^{-7} \text{ M (from water)} \\
\text{\( s \text{ mol/L of Fe(OH)}_3(s) \) dissolves to reach equilibrium = molar solubility} \\
\text{Change} & \quad -s \quad \rightarrow \quad +s \quad +3s \\
\text{Equil.} & \quad s \quad 1 \times 10^{-7} + 3s
\end{align*}
\]
\[ K_{sp} = 4 \times 10^{-38} = [\text{Fe}^{3+}][\text{OH}^-]^3 = (s)(1 \times 10^{-7} + 3s)^3 \approx s(1 \times 10^{-7})^3 \]

\[ s = 4 \times 10^{-17} \text{ mol/L}; \text{ assumption good (3s} \ll 1 \times 10^{-7}) \]

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

\[
\begin{array}{c|c|c}
\text{Initial} & 0 & 1 \times 10^{-9} M \\
\text{mol/L} & \text{(buffered)} \\
\text{Change} & -s & +s \\
\text{mol/L} & \text{ Equil.} & s & 1 \times 10^{-9} \\
\end{array}
\]

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

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

\[
\begin{array}{c|c|c}
\text{Initial} & 0 & 0.001 M \\
\text{mol/L} & \text{(buffered)} \\
\text{Change} & -s & +s \\
\text{mol/L} & \text{ Equil.} & s & 0.001 \\
\end{array}
\]

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

Note: As \([\text{OH}^-] \) increases, solubility decreases. This is the common ion effect.

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

\[
\begin{array}{c|c|c}
\text{Initial} & s = \text{solubility (mol/L)} & 0 & 1.0 \times 10^{-3} \text{ (buffered)} \\
\text{mol/L} & \text{ Equil.} & s & 1.0 \times 10^{-3} \text{ (assume no pH change)} \\
\end{array}
\]

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

37. a. \( \text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{SO}_4^{2-}(aq) \)

\[
\begin{array}{c|c|c}
\text{Initial} & s = \text{solubility (mol/L)} & 0 & 0 \\
\text{mol/L} & \text{ Equil.} & 2s & s \\
\end{array}
\]

\[ K_{sp} = 1.2 \times 10^{-5} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2s = 4s^3, \ s = 1.4 \times 10^{-2} \text{ mol/L} \]

b. \( \text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{SO}_4^{2-}(aq) \)

\[
\begin{array}{c|c|c}
\text{Initial} & s = \text{solubility (mol/L)} & 0.10 M & 0 \\
\text{mol/L} & \text{ Equil.} & 0.10 + 2s & s \\
\end{array}
\]

\[ K_{sp} = 1.2 \times 10^{-5} = (0.10 + 2s)^2(s) \approx (0.10)^2(s), \ s = 1.2 \times 10^{-3} \text{ mol/L}; \text{ assumption good.} \]
c. \[ \text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{SO}_4^{2-}(aq) \]

Initial \[ s = \text{solubility (mol/L)} \]

Equil \[ 2s \]

Initial \[ 0 \]

Equil \[ 0.20 + s \]

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

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. \[ \text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{I}^-(aq) \]

Initial \[ s = \text{solubility (mol/L)} \]

Equil \[ s \]

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

b. \[ \text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{I}^-(aq) \]

Initial \[ s = \text{solubility (mol/L)} \]

Equil \[ 0.10 + s \]

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

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

39. \[ \text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3 \text{Ca}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq) \]

Initial \[ s = \text{mol/L of Ca}_3(\text{PO}_4)_2(s) \]

Change \[ -s \]

Equil \[ 3s \]

\[ K_{sp} = 1.3 \times 10^{-32} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3s)^3(0.20 + 2s)^2 \]

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

\[ s = \text{molar solubility} = 2.3 \times 10^{-11} \text{ mol/L}; \ \text{assumption good.} \]

40. \[ \text{Pb}_3(\text{PO}_4)_2(s) \rightleftharpoons 3 \text{Pb}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq) \]

Initial \[ s = \text{solubility (mol/L)} \]

Equil \[ 0.10 + 3s \]

\[ 1 \times 10^{-54} = (0.10 + 3s)^3(2s)^2 \approx (0.10)^3(2s)^2, \ s = 2 \times 10^{-26} \text{ mol/L}; \ \text{assumptions good.} \]
41. \[ \text{Ce}(\text{IO}_3)_3(s) \rightleftharpoons \text{Ce}^{3+}(\text{aq}) + 3 \text{IO}_3^-(\text{aq}) \]

Initial \( s = \text{solubility (mol/L)} \) 
0 
0.20 M

Equil. 
\( s \) 
0.20 + 3s

\[ K_{sp} = [\text{Ce}^{3+}][\text{IO}_3^-]^3 = s(0.20 + 3s)^3 \]

From the problem, \( s = 4.4 \times 10^{-8} \text{ mol/L} \); 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. \[ \text{Pb}(\text{IO}_3)_2(s) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{IO}_3^-(\text{aq}) \]

Initial \( s = \text{solubility (mol/L)} \) 
0 
0.10 M

Equil. 
\( s \) 
0.10 + 2s

\[ K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = (s)(0.10 + 2s)^2 \]

From the problem, \( s = 2.6 \times 10^{-11} \text{ mol/L} \); 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 \( \text{H}^+ \) 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 \( \text{Ag}_3\text{PO}_4, \text{CaCO}_3, \text{CdCO}_3, \) and \( \text{Sr}_3(\text{PO}_4)_2 \). \( \text{Hg}_2\text{Cl}_2 \) and \( \text{PbI}_2 \) do not have any pH dependence since \( \text{Cl}^- \) and \( \Gamma \) are terrible bases (the conjugate bases of strong acids).

\[ \text{Ag}_3\text{PO}_4(s) + \text{H}^+(aq) \rightarrow 3 \text{Ag}^+(aq) + \text{HPO}_4^{2-}(aq) \]

\[ \text{CaCO}_3(s) + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \]

\[ \text{CdCO}_3(s) + \text{H}^+ \rightarrow \text{Cd}^{2+} + \text{HCO}_3^- \]

\[ \text{Sr}_3(\text{PO}_4)_2(s) + 2 \text{H}^+ \rightarrow 3 \text{Sr}^{2+} + 2 \text{HPO}_4^{2-} \]

44. a. \( \text{AgF} \)  b. \( \text{Pb(OH)}_2 \)  c. \( \text{Sr(NO}_2)_2 \)  d. \( \text{Ni(CN)}_2 \)

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. \[ \text{ZnS(s)} \rightleftharpoons \text{Zn}^{2+} + \text{S}^{2-} \quad \text{K}_{sp} = [\text{Zn}^{2+}][\text{S}^{2-}] \]

Initial \( s = \text{solubility (mol/L)} \) \( 0.050 \text{ M} \) \( 0 \)

Equil. \( 0.050 + s \) \( s \)

\[ \text{K}_{sp} = 2.5 \times 10^{-22} = (0.050 + s)(s) \approx (0.050)s, \quad s = 5.0 \times 10^{-21} \text{ mol/L;} \quad \text{assumption good.} \]

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, \([\text{Mg}^{2+}] = 0.01(0.052 \text{ M})\). Using the \( \text{K}_{sp} \) equilibrium constant, calculate the \([\text{OH}^-]\) required to reach this reduced \([\text{Mg}^{2+}]\).

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad \text{K}_{sp} = 8.9 \times 10^{-12} \]

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

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

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

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad \text{K}_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 8.9 \times 10^{-12} \]

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

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

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

Because \( Q < \text{K}_{sp} \), Mg(OH\(_2\))(s) will not precipitate, so no precipitate forms.

48. AgCN(s) ⇌ Ag\(^+\)(aq) + CN\(^-\)(aq) \quad \text{K}_{sp} = 2.2 \times 10^{-12} \]

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

Because \( Q > \text{K}_{sp} \), AgCN(s) will form as a precipitate.

49. PbF\(_2\)(s) ⇌ Pb\(^{2+}\)(aq) + 2 F\(^-\)(aq) \quad \text{K}_{sp} = 4 \times 10^{-8} \]

\[ [\text{Pb}^{2+}]_0 = \frac{\text{mmol Pb}^{2+}(\text{aq})}{\text{total mL solution}} = \frac{100.0 \text{ mL} \times 1.0 \times 10^{-2} \text{ mmol Pb}^{2+}}{100.0 \text{ mL} + 100.0 \text{ mL}} = 5.0 \times 10^{-3} \text{ M} \]
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\[ [F^-]_0 = \frac{\text{mmol F}^-}{\text{total mL solution}} = \frac{100.0 \text{ mL} \times 1.0 \times 10^{-3} \text{ mmol F}^-}{200.0 \text{ mL}} = 5.0 \times 10^{-4} \text{ M} \]

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

Because \( Q < K_{sp} \), PbF\(_2\) will not form as a precipitate.

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

\[ Q = [\text{Ce}^{3+}]_0 [\text{IO}_3^-]_0^3 = (2.0 \times 10^{-3})(1.0 \times 10^{-2})^3 = 2.0 \times 10^{-9} \]

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\(_2\)O\(_4\)(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.

\[
100. \text{ mL} \times \frac{0.200 \text{ mmol K}_2\text{C}_2\text{O}_4}{\text{mL}} = 20.0 \text{ mmol K}_2\text{C}_2\text{O}_4
\]

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

\[
\text{Ba}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightarrow \text{BaC}_2\text{O}_4(s) \quad K = 1/K_{sp} >> 1
\]

Before: 37.5 mmol \quad 20.0 mmol \quad 0

Change: -20.0 \quad -20.0 \quad \rightarrow \quad +20.0

Reacts completely (\( K \) is large).

After: 17.5 \quad 0 \quad 20.0

New initial concentrations (after complete precipitation) are:

\[
[\text{Ba}^{2+}] = \frac{17.5 \text{ mmol}}{250. \text{ mL}} = 7.00 \times 10^{-2} \text{ M}; \quad [\text{C}_2\text{O}_4^{2-}] = 0 \text{ M}
\]

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

For \( K^+ \) and \( \text{Br}^- \), these are also the final concentrations. We can’t have \( 0 \text{ M} \) \( \text{C}_2\text{O}_4^{2-} \). For \( \text{Ba}^{2+} \) and \( \text{C}_2\text{O}_4^{2-} \), we need to perform an equilibrium calculation.

\[
\text{BaC}_2\text{O}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \quad K_{sp} = 2.3 \times 10^{-8}
\]

Initial \quad 0.0700 \text{ M} \quad 0

\( s \) mol/L of BaC\(_2\)O\(_4\)(s) dissolves to reach equilibrium

Equil. \quad 0.0700 + s \quad s
\[ K_{sp} = 2.3 \times 10^{-8} = [\text{Ba}^{2+}][\text{C}_2\text{O}_4^{2-}] = (0.0700 + s)(s) \approx (0.0700)s \]

\[ s = [\text{C}_2\text{O}_4^{2-}] = 3.3 \times 10^{-7} \text{ mol/L}; \ [\text{Ba}^{2+}] = 0.0700 \text{ M}; \text{ assumption good (}s \ll 0.0700). \]

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

\[ [\text{SO}_4^{2-}]_0 = \frac{125 \text{ mL} \times 0.040 \text{ mmol}}{200. \text{ mL}} = 2.5 \times 10^{-2} \text{ M} \]

\[ Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]_0 = (7.5 \times 10^{-3})(2.5 \times 10^{-2}) = 1.9 \times 10^{-4} > K_{sp} (1.5 \times 10^{-9}) \]

A precipitate of BaSO_4(s) will form.

\[
\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}
\]

Before

\[ \text{Let } 0.0075 \text{ mol/L Ba}^{2+} \text{ react with SO}_4^{2-} \text{ to completion because } K_{sp} \ll 1. \]

Change

\[ \text{Reacts completely} \]

After

\[ 0 \quad 0.0175 \]

\[ s \text{ mol/L BaSO}_4 \text{ dissolves to reach equilibrium} \]

\[ \text{Equil. } s \quad 0.0175 + s \]

\[ K_{sp} = 1.5 \times 10^{-9} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (s)(0.0175 + s) \approx s(0.0175) \]

\[ s = 8.6 \times 10^{-8} \text{ mol/L}; \ [\text{Ba}^{2+}] = 8.6 \times 10^{-8} \text{ M}; \ [\text{SO}_4^{2-}] = 0.018 \text{ M}; \text{ assumption good.} \]

53.  
\[ 50.0 \text{ mL} \times 0.00200 \text{ M} = 0.100 \text{ mmol Ag}^+; \ 50.0 \text{ mL} \times 0.0100 \text{ M} = 0.500 \text{ mmol IO}_3^- \]

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.

\[
\text{AgIO}_3(s) \rightleftharpoons \text{Ag}^+ (aq) + \text{IO}_3^- (aq)
\]

Initial

\[ 0 \quad \frac{0.400 \text{ mmol}}{100.0 \text{ mL}} = 4.00 \times 10^{-3} \text{ M} \]

\[ s \text{ mol/L AgIO}_3(s) \text{ dissolves to reach equilibrium} \]

\[ \text{Equil. } s \quad 4.00 \times 10^{-3} + s \]

\[ K_{sp} = [\text{Ag}^+][\text{IO}_3^-] = 3.0 \times 10^{-8} = s(4.00 \times 10^{-3} + s) \approx s(4.00 \times 10^{-3}) \]

\[ s = 7.5 \times 10^{-6} \text{ mol/L} = [\text{Ag}^+]; \text{ assumptions good.} \]
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 10.0 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) ⇌ Pb$^{2+}$(aq) + 2 Cl$^{-}$(aq)

Initial

<table>
<thead>
<tr>
<th></th>
<th>PbCl$_2$(s)</th>
<th>Pb$^{2+}$(aq)</th>
<th>2 Cl$^{-}$(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/L</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$s$ mol/L of PbCl$_2$(s) dissolves to reach equilibrium

$$s = 0.40 + 2s$$

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

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

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

55. Ag$_3$PO$_4$(s) ⇌ 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$_3$PO$_4$(s). In this problem, [PO$_4^{3-}$]$_0$ = [Na$_3$PO$_4$]$_0$ = 1.0 × 10$^{-5}$ M.

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

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

When [Ag$^+$]$_0$ = [AgNO$_3$]$_0$ is greater than 5.6 × 10$^{-5}$ M, precipitation of Ag$_3$PO$_4$(s) will occur.

56. Al(OH)$_3$(s) ⇌ Al$^{3+}$(aq) + 3 OH$^-$(aq)  

$$K_{sp} = 2 \times 10^{-32}$$

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

pOH = −log(4.6 × 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 × 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) ⇌ Pb$^{2+}$(aq) + 2 F$^-$(aq)  

$$K_{sp} = 4 \times 10^{-8}; Q = 4 \times 10^{-8} = [Pb^{2+}]_0[F^-]^2$$

$$[Pb^{2+}]_0 = \frac{4 \times 10^{-8}}{(1 \times 10^{-4})^2} = 4 M$$
\[
PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq) \quad K_{sp} = 7 \times 10^{-29}; \quad Q = 7 \times 10^{-29} = [Pb^{2+}]_0[S^{2-}]_0
\]

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

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

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

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

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. \[ \text{Ni}^{2+} + \text{CN}^- \rightleftharpoons \text{NiCN}^+ \quad K_1 \]
   \[ \text{NiCN}^+ + \text{CN}^- \rightleftharpoons \text{Ni(CN)}_2^- \quad K_2 \]
   \[ \text{Ni(CN)}_2^- + \text{CN}^- \rightleftharpoons \text{Ni(CN)}_3^{2-} \quad K_3 \]
   \[ \text{Ni(CN)}_3^{2-} + \text{CN}^- \rightleftharpoons \text{Ni(CN)}_4^{2-} \quad K_4 \]

   \[ \text{Ni}^{2+} + 4 \text{CN}^- \rightleftharpoons \text{Ni(CN)}_4^{2-} \quad K_f = K_1 K_2 K_3 K_4 \]

   \text{Note:} \text{ The various } K \text{ constants are included for your information. Each } \text{NH}_3 \text{ adds with a corresponding } K \text{ value associated with that reaction. The overall formation constant } K_f \text{ for the overall reaction is equal to the product of all the stepwise } K \text{ values.} \]

b. \[ \text{V}^{3+} + 2 \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{VC}_2\text{O}_4^{+} \quad K_1 \]
   \[ \text{VC}_2\text{O}_4^{+} + 2 \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{V(C}_2\text{O}_4)_2^{-} \quad K_2 \]
   \[ \text{V(C}_2\text{O}_4)_2^{-} + 2 \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{V(C}_2\text{O}_4)_3^{3-} \quad K_3 \]

   \[ \text{V}^{3+} + 3 \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{V(C}_2\text{O}_4)_3^{3-} \quad K_f = K_1 K_2 K_3 \]

60. a. \[ \text{Co}^{3+} + \text{F}^- \rightleftharpoons \text{CoF}^{2+} \quad K_1 \]
   \[ \text{CoF}^{2+} + \text{F}^- \rightleftharpoons \text{CoF}_2^+ \quad K_2 \]
   \[ \text{CoF}_2^+ + \text{F}^- \rightleftharpoons \text{CoF}_3^- \quad K_3 \]
   \[ \text{CoF}_3^- + \text{F}^- \rightleftharpoons \text{CoF}_4^{2-} \quad K_4 \]
   \[ \text{CoF}_4^{2-} + \text{F}^- \rightleftharpoons \text{CoF}_5^{3-} \quad K_5 \]
   \[ \text{CoF}_5^{3-} + \text{F}^- \rightleftharpoons \text{CoF}_6^{4-} \quad K_6 \]

   \[ \text{Co}^{3+} + 6 \text{F}^- \rightleftharpoons \text{CoF}_6^{4-} \quad K_f = K_1 K_2 K_3 K_4 K_5 K_6 \]

b. \[ \text{Zn}^{2+} + \text{NH}_3 \rightleftharpoons \text{ZnNH}_3^{2+} \quad K_1 \]
   \[ \text{ZnNH}_3^{2+} + \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_2^{2+} \quad K_2 \]
   \[ \text{Zn(NH}_3)_2^{2+} + \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_3^{2+} \quad K_3 \]
   \[ \text{Zn(NH}_3)_3^{2+} + \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_4^{2+} \quad K_4 \]

   \[ \text{Zn}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_4^{2+} \quad K_f = K_1 K_2 K_3 K_4 \]

61. \[ \text{Fe}^{3+}(\text{aq}) + 6 \text{CN}^- (\text{aq}) \rightleftharpoons \text{Fe(CN)}_6^{3-} \quad K = \frac{[\text{Fe(CN)}_6^{3-}]}{[\text{Fe}^{3+}][\text{CN}^-]^6} \]
   \[ K = \frac{1.5 \times 10^{-3}}{(8.5 \times 10^{-40})(0.11)^6} = 1.0 \times 10^{42} \]

62. \[ \text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(\text{aq}) \quad K = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} \]
   \[ K = \frac{1.0 \times 10^{-3}}{(1.8 \times 10^{-17})(1.5)^4} = 1.1 \times 10^{13} \]
63. \[ \text{Hg}^2+ (aq) + 2 \Gamma (aq) \rightarrow \text{Hgl}_2(s); \] orange ppt
\[ \text{Hgl}_2(s) + 2 \Gamma (aq) \rightarrow \text{Hgl}_4^{2-} (aq) \] soluble complex ion

64. \[ \text{Ag}^+ (aq) + \text{Cl}^− (aq) \rightleftharpoons \text{AgCl}(s), \text{ white ppt.}; \] AgCl(s) + 2 NH₃(aq) \rightleftharpoons Ag(NH₃)₂⁺(aq) + Cl⁻(aq)
\[ \text{Ag(NH₃)₂⁺}(aq) + \text{Br}^−(aq) \rightleftharpoons \text{AgBr}(s) + 2 \text{NH}_3(aq), \text{ pale yellow ppt.} \]
\[ \text{AgBr}(s) + 2 \text{S}_2\text{O}_3^{2−}(aq) \rightleftharpoons \text{Ag(S}_2\text{O}_3^{2−})(aq) + \text{Br}^−(aq) \]
Ag(S₂O₃)²⁻(aq) + I⁻(aq) \rightleftharpoons AgI(s) + 2 S₂O₃²⁻(aq), yellow ppt.

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

65. The formation constant for HgI₄²⁻ is an extremely large number. Because of this, we will let the Hg²⁺ and I⁻ ions present initially react to completion and then solve an equilibrium problem to determine the Hg²⁺ concentration.

\[ \text{Hg}^2+ (aq) + 4 \Gamma (aq) \rightleftharpoons \text{Hgl}_4^{2−} (aq) \quad \text{K} = 1.0 \times 10^{30} \]

Before
\[ 0.010 \quad 0.78 \]
Change
\[ -0.010 \quad -0.040 \rightarrow +0.010 \]
Reacts completely (K is large).

After
\[ 0 \quad 0.74 \]
\[ 0.010 \]

x mol/L Hgl₄²⁻ dissociates to reach equilibrium

Change
\[ +x \quad +4x \quad \leftarrow \quad -x \]

Equil.
\[ x \quad 0.74 + 4x \]
\[ 0.010 - x \]

\[ K = 1.0 \times 10^{30} = \frac{[\text{Hgl}_4^{2−}]}{[\text{Hg}^2+][\Gamma]^{4}} = \frac{(0.010 - x)}{(x)(0.74 + 4x)^4}; \text{ making normal assumptions:} \]

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

Note: 3.3 × 10⁻³² mol/L corresponds to one Hg²⁺ ion per 5 × 10⁷ L. It is very reasonable to approach this problem in two steps. The reaction does essentially go to completion.

66. \[ \text{Ni}^2+ (aq) + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3)_6^{2+} (aq) \quad \text{K} = 5.5 \times 10^8 \]

Initial
\[ 3.0 \quad 0.10 \text{ mol}/0.50 \text{ L} = 0.20 \text{ M} \]
Change
\[ +x \quad +6x \quad \leftarrow \quad -x \]

Equil.
\[ x \quad 3.0 + 6x \]
\[ 0.20 - x \]

\[ K = 5.5 \times 10^8 = \frac{[\text{Ni(NH}_3)_6^{2+}]}{[\text{Ni}^2+][\text{NH}_3]^6} = \frac{(0.20 - x)}{(x)(3.0 + 6x)^6}, \quad 5.5 \times 10^8 \approx \frac{(0.20)}{(x)(3.0)^6} \]

\[ x = [\text{Ni}^2+] = 5.0 \times 10^{-13} M; \quad [\text{Ni(NH}_3)_6^{2+}] = 0.20 M - x = 0.20 M; \text{ assumptions good.} \]
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.

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

Before \(1.0 \times 10^{-3} \, M\) 5.00 \(M\) 0
After \(0\) 5.00 \(-3(10^{-3}) \approx 5.00\) 1.0 \times 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.

\[
Be^{2+}(aq) + 4 F^-(aq) \rightleftharpoons BeF_4^{2-}(aq) \quad K = K_1K_2K_3K_4 = 7.5 \times 10^{12}
\]

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 concentrations.
K₁ = 7.9 × 10⁴ = \frac{[\text{BeF}^+]}{[\text{Be}^{2+}][\text{F}^-]} = \frac{[\text{BeF}^+]}{(2.6 \times 10^{-20})(4.0)}$, \[\text{[BeF}^+] = 8.2 \times 10^{-15} \text{ M} \]

K₂ = 5.8 × 10³ = \frac{[\text{BeF}_2^-]}{[\text{BeF}^+][\text{F}^-]} = \frac{[\text{BeF}_2^-]}{(8.2 \times 10^{-15})(4.0)}$, \[\text{[BeF}_2^-] = 1.9 \times 10^{-10} \text{ M} \]

K₃ = 6.1 × 10² = \frac{[\text{BeF}_3^-]}{[\text{BeF}_2^-][\text{F}^-]} = \frac{[\text{BeF}_3^-]}{(1.9 \times 10^{-10})(4.0)}$, \[\text{[BeF}_3^-] = 4.6 \times 10^{-7} \text{ M} \]

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

Initial \(s = \text{solubility (mol/L)}\) \quad 0 \quad 0

Equil. \(s \quad s\)

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

b. \(\text{AgI(s)} \rightleftharpoons \text{Ag}^+ + \Gamma\quad K_{sp} = 1.5 \times 10^{-16}\)

\(\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+\quad K_f = 1.7 \times 10^7\)

\(\text{AgI(s)} + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) + \Gamma(aq) \quad K = K_{sp} \times K_f = 2.6 \times 10^{-9}\)

\(\text{AgI(s)} + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ + \Gamma\)

Initial \(3.0 \text{ M} \quad 0 \quad 0\)

Equil. \(3.0 - 2s \quad s \quad s\)

\(K = \frac{[\text{Ag(NH}_3)_2^+][\Gamma]}{[\text{NH}_3]^2} = \frac{s^2}{(3.0 - 2s)^2} = 2.6 \times 10^{-9} \approx \frac{s^2}{(3.0)^2}, \quad s = 1.5 \times 10^{-4} \text{ mol/L}\)

Assumption good.

c. The presence of \(\text{NH}_3\) increases the solubility of \(\text{AgI}\). Added \(\text{NH}_3\) removes \(\text{Ag}^+\) from solution by forming the complex ion, \(\text{Ag(NH}_3)_2^+\). As \(\text{Ag}^+\) is removed, more \(\text{AgI(s)}\) will dissolve to replenish the \(\text{Ag}^+\) concentration.

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

\(\text{Ag}^+ + 2 \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-}\quad K_f = 2.9 \times 10^{13}\)

\(\text{AgBr(s)} + 2 \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-} + \text{Br}^-\quad K = K_{sp} \times K_f = 14.5 \quad \text{(Carry extra sig. figs.)}\)
\[
\text{AgBr(s)} + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-}(\text{aq}) + \text{Br}^-\text{aq})
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.500 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-s)</td>
<td>(-2s)</td>
<td>(+s)</td>
</tr>
<tr>
<td>Equil.</td>
<td>(0.500 - 2s)</td>
<td>(s)</td>
<td>(s)</td>
</tr>
</tbody>
</table>

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

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

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

71. \(\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-\) \(K_{sp} = 1.6 \times 10^{-10}\)

\(\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+\) \(K_f = 1.7 \times 10^7\)

\[
\text{AgCl(s)} + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag(NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad K = K_{sp} \times K_f = 2.7 \times 10^{-3}
\]

\[
\text{AgCl(s)} + 2\text{NH}_3 \quad \rightleftharpoons \quad \text{Ag(NH}_3)_2^+ + \text{Cl}^-
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>1.0 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equil.</td>
<td>1.0 - 2s</td>
<td>s</td>
<td>s</td>
</tr>
</tbody>
</table>

\(K = 2.7 \times 10^{-3} = \frac{[\text{Ag(NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(1.0 - 2s)^2}\); taking the square root:

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

In pure water, the solubility of AgCl(s) is \((1.6 \times 10^{-10})^{1/2} = 1.3 \times 10^{-5} \text{ mol/L.}\) Notice how the presence of \(\text{NH}_3\) increases the solubility of AgCl(s) by over a factor of 3500.

72. a. \(\text{CuCl(s)} \rightleftharpoons \text{Cu}^+(\text{aq}) + \text{Cl}^-(\text{aq})\)

<table>
<thead>
<tr>
<th>Initial</th>
<th>(s = \text{ solubility (mol/L)})</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equil.</td>
<td>(s)</td>
<td>(s)</td>
<td>(s)</td>
</tr>
</tbody>
</table>

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

b. \(\text{Cu}^+\) forms the complex ion \(\text{CuCl}_2^+\) in the presence of \(\text{Cl}^-.\) We will consider both the \(K_{sp}\) reaction and the complex ion reaction at the same time.
CuCl(s) ⇌ Cu⁺(aq) + Cl⁻(aq) \[ K_{sp} = 1.2 \times 10^{-6} \]
Cu⁺(aq) + 2 Cl⁻(aq) ⇌ CuCl₂⁻(aq) \[ K_f = 8.7 \times 10^4 \]

\[
\text{CuCl(s) + Cl}^- \rightarrow \text{CuCl}_2^-; \quad K = K_{sp} \times K_f = 0.10
\]

Initial: 0.10 M \quad Equil: 0.10 - s \quad s where s = solubility of CuCl(s) in mol/L

\[
K = 0.10 = \frac{[\text{CuCl}_2^-]}{[\text{Cl}^-]} = \frac{s}{0.10 - s}, \quad 1.0 \times 10^{-2} - 0.10 \approx s, \quad s = 9.1 \times 10^{-3} \text{ mol/L}
\]

73. Test tube 1: Added Cl⁻ reacts with Ag⁺ to form a silver chloride precipitate. The net ionic equation is Ag⁺(aq) + Cl⁻(aq) → AgCl(s). Test tube 2: Added NH₃ reacts with Ag⁺ ions to form a soluble complex ion, Ag(NH₃)₂⁺. As this complex ion forms, Ag⁺ is removed from the solution, which causes the AgCl(s) to dissolve. When enough NH₃ is added, all the silver chloride precipitate will dissolve. The equation is AgCl(s) + 2 NH₃(aq) → Ag(NH₃)₂⁺(aq) + Cl⁻(aq). Test tube 3: Added H⁺ reacts with the weak base, NH₃, to form NH₄⁺. As NH₃ is removed from the Ag(NH₃)₂⁺ complex ion, Ag⁺ ions are released to solution and can then react with Cl⁻ to re-form AgCl(s). The equations are Ag(NH₃)₂⁺(aq) + 2 H⁺(aq) → Ag⁺(aq) + 2 NH₄⁺(aq) and Ag⁺(aq) + Cl⁻(aq) → AgCl(s).

74. In NH₃, Cu²⁺ forms the soluble complex ion Cu(NH₃)₄²⁺. This increases the solubility of Cu(OH)₂(s) because added NH₃ removes Cu²⁺ from the equilibrium causing more Cu(OH)₂(s) to dissolve. In HNO₃, H⁺ removes OH⁻ from the Ksp equilibrium causing more Cu(OH)₂(s) to dissolve. Any salt with basic anions will be more soluble in an acid solution. AgC₂H₃O₂(s) will be more soluble in either NH₃ or HNO₃. This is because Ag⁺ forms the complex ion Ag(NH₃)₂⁺, and C₂H₃O₂⁻ is a weak base, so it will react with added H⁺. AgCl(s) will be more soluble only in NH₃ due to Ag(NH₃)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 HNO₃.

 Connecting to Biochemistry

75. \[
\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{OH}^-
\]

Initial: \( s \) = solubility (mol/L) \quad 0 \quad 0 \quad 1.0 \times 10^{-7} \text{ from water}

Equil. \quad 5s \quad 3s \quad s + 1.0 \times 10^{-7} \approx s

\[
K_{sp} = 6.8 \times 10^{-37} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-] = (5s)^5(3s)^3(s)
\]

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

The solubility of hydroxyapatite will increase as the solution gets more acidic because both phosphate and hydroxide can react with H⁺.
\[
\text{Ca}_5(\text{PO}_4)_3\text{F(s)} \rightleftharpoons 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{F}^-
\]

Initial \( s = \text{solubility (mol/L)} \) 0 0 0
Equil. 5s 3s s

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

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. \[
\frac{1 \text{ mg F}^-}{\text{L}} \times \frac{1 \text{ g F}^-}{1000 \text{ mg}} \times \frac{1 \text{ mol F}^-}{19.00 \text{ g F}^-} = 5.3 \times 10^{-4} \text{ M F}^- = 5 \times 10^{-5} \text{ M F}^-
\]

\[
\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{F}^-(\text{aq}) \quad K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = 4.0 \times 10^{-11}; \quad \text{precipitation will occur when } Q > K_{sp}. \text{ Let’s calculate } [\text{Ca}^{2+}] \text{ so that } Q = K_{sp}.
\]

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

\[
\text{CaF}_2(s) \text{ will precipitate when } [\text{Ca}^{2+}]_0 > 2 \times 10^{-2} \text{ M}. \text{ Therefore, hard water should have a calcium ion concentration of less than } 2 \times 10^{-2} \text{ M in order to avoid } \text{CaF}_2(s) \text{ formation.}
\]

77. KBT dissolves to form the potassium ion (K') and the bitartrate ion (abbreviated as BT⁻).

\[
\text{KBT(s)} \rightleftharpoons \text{K}^+(\text{aq}) + \text{BT}^-(\text{aq}) \quad K_{sp} = 3.8 \times 10^{-4}
\]

Initial \( s = \text{solubility (mol/L)} \) 0 0
Equil. \( s \)

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

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

78. \[
\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \quad K_{sp} = 1.5 \times 10^{-9}
\]

Initial \( s = \text{solubility (mol/L)} \) 0 0
Equil. \( s \)

\[ 1.5 \times 10^{-9} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = s^2, \quad s = 3.9 \times 10^{-5} \text{ mol/L} \]

\[ 0.1000 \text{ L} \times \frac{3.9 \times 10^{-5} \text{ mol BaSO}_4}{L} \times \frac{233.4 \text{ g BaSO}_4}{\text{mol}} = 9.1 \times 10^{-4} \text{ g BaSO}_4 \]
79. Molar solubility of ZnSO₄ = \[ \frac{54.0 \text{ g ZnSO}_4}{0.1000 \text{ L}} \times \frac{1 \text{ mol ZnSO}_4}{161.45 \text{ g}} = 3.34 \text{ mol/L} \]

ZnSO₄(s) ⇌ Zn²⁺(aq) + SO₄²⁻(aq)  \[ K_{sp} = [\text{Zn}^{2+}][\text{SO}_4^{2-}] \]

Initial  \[ s = \text{solubility (mol/L)} \]
Equil.  \[ s \]

\[ K_{sp} = s(s) = s^2 = (3.34)^2, \quad K_{sp} = 11.2 \]

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.

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

Initial  \[ s = \text{solubility (mol/L)} \]
\[ 1.0 \times 10^{-7} \text{ M (from water)} \]
Equil.  \[ s \]

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

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

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

\[ \text{Mol OH}^- = 0.5000 \text{ L} \times \frac{2.6 \times 10^{-4} \text{ mol OH}^-}{\text{L}} = 1.3 \times 10^{-4} \text{ mol OH}^- \]

\( \text{OH}^- \) reacts with the acid in the stomach. As \( \text{OH}^- \) 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 \( \text{OH}^- \) to react with.

81. \[ \text{Mn}^{2+} + C_2O_4^{2-} \rightleftharpoons \text{MnC}_2\text{O}_4 \quad K_1 = 7.9 \times 10^3 \]
\[ \text{MnC}_2\text{O}_4 + C_2O_4^{2-} \rightleftharpoons \text{Mn(C}_2\text{O}_4)_2^{2-} \quad K_2 = 7.9 \times 10^1 \]

\[ \text{Mn}^{2+}(aq) + 2 \text{C}_2\text{O}_4^{2-}(aq) \rightleftharpoons \text{Mn(C}_2\text{O}_4)_2^{2-}(aq) \quad K_f = K_1K_2 = 6.2 \times 10^5 \]

82. \[ \text{Cr}^{3+} + \text{H}_2\text{EDTA}^{2-} \rightleftharpoons \text{CrEDTA}^- + 2 \text{H}^+ \]

Before  \[ 0.0010 \text{ M} \quad 0.050 \text{ M} \quad 0 \quad 1.0 \times 10^{-6} \text{ M (Buffer)} \]
Change  \[ -0.0010 \quad -0.0010 \quad +0.0010 \quad \text{No change} \quad \text{Reacted completely} \]
After  \[ 0 \quad 0.049 \quad 0.0010 \quad 1.0 \times 10^{-6} \text{ New initial} \]

\( x \text{ mol/L CrEDTA}^- \) dissociates to reach equilibrium

Change  \[ +x \quad +x \quad \leftrightarrow \quad -x \]
Equil.  \[ x \quad 0.049 + x \quad 0.0010 - x \quad 1.0 \times 10^{-6} \text{ (Buffer)} \]
83. a. $\text{Pb(OH)}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+} + 2\text{OH}^-$

Initial $s =$ solubility (mol/L) 0 $1.0 \times 10^{-7} \text{ M}$ from water

Equil. $s$ $1.0 \times 10^{-7} + 2s$

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

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

b. $\text{Pb(OH)}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+} + 2\text{OH}^-$

Initial 0 0.10 M pH = 13.00, $[\text{OH}^-] = 0.10 \text{ M}$

$s \text{ mol/L Pb(OH)}_2(\text{s})$ dissolves to reach equilibrium

Equil. $s$ 0.10 (Buffered solution)

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

c. We need to calculate the $\text{Pb}^{2+}$ 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 $\text{Pb}^{2+}$ concentration.

$\text{Pb}^{2+} + \text{EDTA}^{4-} \rightleftharpoons \text{PbEDTA}^{2-} \quad K = 1.1 \times 10^{18}$

Before 0.010 M 0.050 M 0

0.010 mol/L $\text{Pb}^{2+}$ reacts completely (large $K$)

Change $-0.010$ $-0.010$ $+0.010$ Reacts completely

After 0 0.040 0.010 New initial

$x \text{ mol/L PbEDTA}^{2-}$ dissociates to reach equilibrium

Equil. $x$ 0.040 + $x$ 0.010 $-x$

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

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

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

$\text{Pb(OH)}_2(\text{s})$ will not form since $Q$ is less than $K_{sp}$.
K = [C₇H₄O₃²⁻][Bi³⁺][OH⁻] = s(s)(1.0 × 10⁻⁷ + s); from the problem, s = 3.2 × 10⁻¹⁹ mol/L:

K = (3.2 × 10⁻¹⁹)²(1.0 × 10⁻⁷ + 3.2 × 10⁻¹⁹) = 1.0 × 10⁻⁴⁴

**Additional Exercises**

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

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.

\[
\begin{align*}
\text{Ag}^+(aq) + \text{I}^-(aq) & \rightarrow \text{AgI(s)} & K = 1/K_{sp} >> 1 \\
\text{Before} & \quad 0.048 \text{ mol} & 0.018 \text{ mol} & 0 \\
\text{Change} & \quad -0.018 & -0.018 & +0.018 \\
\text{After} & \quad 0.030 \text{ mol} & 0 & 0.018 \text{ mol} \\
\end{align*}
\]

Γ⁻ is limiting.

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

\[
\begin{align*}
\text{Ag}^+(aq) + \text{Br}^-(aq) & \rightarrow \text{AgBr(s)} & K = 1/K_{sp} >> 1 \\
\text{Before} & \quad 0.030 \text{ mol} & 0.018 \text{ mol} & 0 \\
\text{Change} & \quad -0.018 & -0.018 & +0.018 \\
\text{After} & \quad 0.012 \text{ mol} & 0 & 0.018 \text{ mol} \\
\end{align*}
\]

Br⁻ is limiting.

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

\[
\begin{align*}
\text{Ag}^+(aq) + \text{Cl}^-(aq) & \rightarrow \text{AgCl(s)} & K = 1/K_{sp} >> 1 \\
\text{Before} & \quad 0.012 \text{ mol} & 0.018 \text{ mol} & 0 \\
\text{Change} & \quad -0.012 & -0.012 & +0.012 \\
\text{After} & \quad 0 & 0.006 \text{ mol} & 0.012 \text{ mol} \\
\end{align*}
\]

Ag⁺ is limiting.

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

\[
\begin{align*}
\text{AgCl(s)} & \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq) & K_{sp} = 1.6 \times 10^{-10} \\
\text{Initial} & \quad s = \text{solubility (mol/L)} & 0 & 0.006 \text{ mol}/0.200 \text{ L} = 0.03 \text{ M} \\
\text{Change} & \quad -s & +s & +s \\
\text{Equil.} & \quad s & 0.03 + s \\
\end{align*}
\]
K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-] = s(0.03 + s) \approx (0.03)s

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

\text{Mol AgCl present} = 0.012 \text{ mol} - 5 \times 10^{-9} \text{ mol} = 0.012 \text{ mol}

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

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

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

\text{AgY(s) } \rightleftharpoons \text{ Ag}^+(aq) + \text{ 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,
$\text{AgY(s)}$ will be more soluble in acidic solution because more $Y^-$ will be removed
through reaction with $H^+$, which will cause more $\text{AgY(s)}$ to dissolve.

87. \quad \text{CaF}_2(s) \rightleftharpoons \text{ Ca}^{2+}(aq) + 2 \text{ F}^-(aq) \quad K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2

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

\[
\begin{align*}
\text{HF(aq)} & \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq) \quad K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} \\
\text{Initial} & \quad 1.0 \text{ M} \quad \sim 0 \quad 0 \\
\text{Equil.} & \quad 1.0 - x \quad x \quad x
\end{align*}
\]

\[ K_a = 7.2 \times 10^{-4} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}, \quad x = [F^-] = 2.7 \times 10^{-2} \text{ M; assumption good.} \]

Next, calculate the Ca$^{2+}$ concentration necessary for $Q = K_{sp, \text{CaF}_2}$.

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

\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}}
\]
\[ = 9.0 \times 10^{-6} \text{ g Ca(NO}_3)_2 \]

\text{For precipitation of CaF}_2(s) \text{ to occur, we need } Q > K_{sp}. \text{ When } 9.0 \times 10^{-6} \text{ g Ca(NO}_3)_2 \text{ has been added to 1.0 L of solution, } Q = K_{sp}. \text{ So precipitation of CaF}_2(s) \text{ will begin to occur when just over } 9.0 \times 10^{-6} \text{ g Ca(NO}_3)_2 \text{ has been added.}
88. \[ \text{Mn(OH)}_2(s) \rightleftharpoons \text{Mn}^{2+}(aq) + 2 \text{OH}^-(aq) \quad K_{sp} = [\text{Mn}^{2+}][\text{OH}^-]^2 \]

Initial \[ s = \text{solubility (mol/L)} \quad 0 \quad 1.0 \times 10^{-7} \text{ M (from water)} \]
Equil. \[ s \quad 1.0 \times 10^{-7} + 2s \]

\[ K_{sp} = 2.0 \times 10^{-13} = s(1.0 \times 10^{-7} + 2s) \approx s(2s)^2 = 4s^3, \quad s = 3.7 \times 10^{-5} \text{ mol/L}; \] 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. \[ s = \text{solubility} = \frac{0.24 \text{ g PbI}_2 \times \frac{1 \text{ mol PbI}_2}{461.0 \text{ g}}}{0.2000 \text{ L}} = 2.6 \times 10^{-3} \text{ M} \]

\[ \text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{I}^-(aq) \quad K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 \]

Initial \[ s = \text{solubility (mol/L)} \quad 0 \quad 0 \]
Equil. \[ s \quad 2s \]

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

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

\[ \text{Cd}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Cd(NH}_3)_4^{2+} \quad K_f = 1.0 \times 10^7 \]

Before \[ 1.0 \times 10^{-3} \text{ M} \quad 5.0 \text{ M} \quad 0 \]
Change \[ -1.0 \times 10^{-3} \quad -4.0 \times 10^{-3} \quad +1.0 \times 10^{-3} \quad \text{Reacts completely} \]
After \[ 0 \quad 4.996 \approx 5.0 \quad 1.0 \times 10^{-3} \quad \text{New initial} \]

\(x \text{ mol/L Cd(NH}_3)_4^{2+}\) dissociates to reach equilibrium

\[ x \quad +x \quad 4x \quad \leftarrow \quad -x \]

Equil. \[ 5.0 + 4x \quad 0.0010 - x \]

\[ K_f = 1.0 \times 10^7 = \frac{(0.010 - x)}{(x)(5.0 + 4x)} \approx \frac{(0.010)}{(x)(5.0)^3} \]

\[ x = [\text{Cd}^{2+}] = 1.6 \times 10^{-13} \text{ M}; \] assumptions good. This is the maximum \([\text{Cd}^{2+}]\) possible. Now we will determine if \(\text{Cd(OH)}_2(s)\) forms at this concentration of \(\text{Cd}^{2+}\). In \(5.0 \text{ M NH}_3\) we can calculate the pH:

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad K_b = 1.8 \times 10^{-5} \]

Initial \[ 5.0 \text{ M} \quad 0 \quad \sim 0 \]
Equil. \[ 5.0 - y \quad y \quad y \]
\[ K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{y^2}{5.0 - y} \approx \frac{y^2}{5.0}, \quad y = [\text{OH}^-] = 9.5 \times 10^{-3} \text{ M}; \quad \text{assumptions good.} \]

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

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

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

91. a. \[ \text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+} + 2 \text{OH}^- \quad K_{sp} = 1.6 \times 10^{-19} \]
\[ \text{Cu}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Cu(NH}_3)_4^{2+} \quad K_f = 1.0 \times 10^{13} \]

Cu(OH)$_2$(s) + 4 NH$_3$(aq) \rightleftharpoons Cu(NH$_3$)$_4^{2+}$(aq) + 2 OH$^-$(aq) \quad K = K_{sp}K_f = 1.6 \times 10^{-6}

b. \[ \text{Cu(OH)}_2(s) + 4 \text{NH}_3 \rightleftharpoons \text{Cu(NH}_3)_4^{2+} + 2 \text{OH}^- \quad K = 1.6 \times 10^{-6} \]

Initial \quad 5.0 M \quad 0 \quad 0.0095 M
Equil. \quad 5.0 - 4s \quad s \quad 0.0095 + 2s

K = 1.6 \times 10^{-6} = \frac{[\text{Cu(NH}_3)_4^{2+}][\text{OH}^-]^2}{[\text{NH}_3]^4} = \frac{s(0.0095 + 2s)^2}{(5.0 - 4s)^4}

If s is small: \[ 1.6 \times 10^{-6} = \frac{s(0.0095)^2}{(5.0)^4}, \quad s = 11. \text{ mol/L} \]

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

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

\[ s_{\text{guess}}: \quad 0.10, 0.050, 0.060, 0.055, 0.056 \]
\[ s_{\text{calc}}: \quad 1.6 \times 10^{-2}, 0.071, 0.049, 0.058, 0.056 \]

Thus the solubility of Cu(OH)$_2$ is 0.056 mol/L in 5.0 M NH$_3$. 
92. a. 

\[
\text{Ag}^+, \text{Mg}^{2+}, \text{Cu}^{2+} \\
\text{AgCl(s)} \\
\downarrow \\
\text{Mg}^{2+}, \text{Cu}^{2+} \\
\downarrow \\
\text{H}_2\text{S(aq)} \\
\downarrow \\
\text{CuS(s)} \\
\downarrow \\
\text{Mg}^{2+} \\
\downarrow \\
\text{Na}_2\text{CO}_3\text{(aq)} - \text{make basic}
\]

b. 

\[
\text{Pb}^{2+}, \text{Ca}^{2+}, \text{Fe}^{2+} \\
\text{H}_2\text{S(aq)} \\
\downarrow \\
\text{PbS(s)} \\
\downarrow \\
\text{Ca}^{2+}, \text{Fe}^{2+} \\
\downarrow \\
\text{NaOH(aq)} \\
\downarrow \\
\text{FeS(s)} \\
\downarrow \\
\text{Ca}^{2+} \\
\downarrow \\
\text{Na}_2\text{CO}_3\text{(aq)}
\]

c. 

\[
\text{Pb}^{2+}, \text{Bi}^{3+} \\
\text{HCl(aq)} \\
\downarrow \\
\text{PbCl}_2\text{(s)} \\
\downarrow \\
\text{Bi}^{3+} \\
\downarrow \\
\text{H}_2\text{S(aq)} \\
\downarrow \\
\text{Bi}_2\text{S}_3
\]
93. \[ \text{Ba(OH)}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \text{OH}^- (aq) \quad K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2 = 5.0 \times 10^{-3} \]

Initial \quad s = \text{solubility (mol/L)} \quad 0 \quad \sim 0

Equil. \quad s \quad 2s

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

\[ [\text{OH}^-] = 2s = 2(0.11) = 0.22 \, \text{mol/L}; \quad \text{pOH} = 0.66, \quad \text{pH} = 13.34 \]

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

Equil. \quad s \quad 2s

\[ K_{sp} = 3.2 \times 10^{-4} = 4s^3, \quad s = 0.043 \, \text{mol/L}; \quad \text{assumption good.} \]

\[ [\text{OH}^-] = 2(0.043) = 0.086 \, M; \quad \text{pOH} = 1.07, \quad \text{pH} = 12.93 \]

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

Equil. \quad s \quad 2s

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

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

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

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. \[ \text{CuBr(s)} \rightleftharpoons \text{Cu}^+ + \text{Br}^- \quad K_{sp} = 1.0 \times 10^{-5} \]

\[ \text{Cu}^+ + 3 \text{CN}^- \rightleftharpoons \text{Cu(CN)}_3^{2-} \quad K_f = 1.0 \times 10^{11} \]

\[ \frac{\text{CuBr(s)} + 3 \text{CN}^- \rightleftharpoons \text{Cu(CN)}_3^{2-} + \text{Br}^- \quad K = 1.0 \times 10^6} \]

Because \( K \) is large, assume that enough \( \text{CuBr(s)} \) dissolves to completely use up the 1.0 \( M \) \( \text{CN}^- \); then solve the back equilibrium problem to determine the equilibrium concentrations.
CuBr(s) + 3 CN\(^-\) ⇌ Cu(CN)\(_3\)\(^{2-}\) + Br\(^-\)

Before

<table>
<thead>
<tr>
<th>x</th>
<th>1.0 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
</table>

\(x\) mol/L of CuBr(s) dissolves to react completely with 1.0 \(M\) CN\(^-\)

Change

| -x | -3x | +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\(^-\) ⇌ 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 | -y | -y |

Equil.

| 3y | 0.33 - y | 0.33 - y |

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

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. \([\text{Br}^-] = 0.33 - y = 0.33 - 1.6 \times 10^{-3} = 0.33 \text{ M}\)

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

\[\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+\]

\[K_1 = 2.1 \times 10^3\]

\[\text{AgNH}_3^+ + \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+\]

\[K_2 = 8.2 \times 10^3\]

\[\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+\]

\[K = K_1K_2 = 1.7 \times 10^7\]

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.

\[\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+\]

Before

| 0.20 \(M\) | 2.0 \(M\) | 0 |

After

| 0 | 1.6 | 0.20 |

Equil.

| \(x\) | 1.6 + 2x | 0.20 - \(x\) |

\[K = 1.7 \times 10^7 = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{0.20 - x}{x(1.6 + 2x)^2} \approx \frac{0.20}{x(1.6)^2}, \quad x = 4.6 \times 10^{-9} \text{ M}; \quad \text{assumptions good.}\]

\([\text{Ag}^+] = 4.6 \times 10^{-9} \text{ M}; \quad [\text{NH}_3] = 1.6 \text{ M}; \quad [\text{Ag(NH}_3)_2^+] = 0.20 \text{ M}\]
Use either the $K_1$ or $K_2$ equilibrium expression to calculate $[\text{AgNH}_3^+]$.

$$\text{AgNH}_3^+ + \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad K_2 = 8.2 \times 10^3$$

$$8.2 \times 10^3 = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{AgNH}_3^+][\text{NH}_3]} \quad \Rightarrow \quad [\text{AgNH}_3^+] = \frac{0.20}{[\text{Ag(NH}_3)_2^+][1.6]}, \quad [\text{AgNH}_3^+] = 1.5 \times 10^{-5} \text{ M}$$

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

<table>
<thead>
<tr>
<th>Initial</th>
<th>$s$ = solubility (mol/L)</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equil.</td>
<td>$s$</td>
<td>$s$</td>
<td></td>
</tr>
</tbody>
</table>

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

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

$\text{Ag}^+ + 2 \text{ NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad K_f = 1.7 \times 10^7$

$$\text{AgBr(s)} + 2 \text{ NH}_3(\text{aq}) \rightleftharpoons \text{Ag(NH}_3)_2^+(\text{aq}) + \text{Br}^-(\text{aq}) \quad K = K_{sp} \times K_f = 8.5 \times 10^{-6}$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>3.0 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equil.</td>
<td>$3.0 - 2s$</td>
<td>$s$</td>
<td>$s$</td>
</tr>
</tbody>
</table>

$$K = \frac{[\text{Ag(NH}_3)_2^+][\text{Br}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(3.0 - 2s)^2} = 8.5 \times 10^{-6} \approx \frac{s^2}{(3.0)^2}, \quad s = 8.7 \times 10^{-3} \text{ mol/L}$$

Assumption good.

c. The presence of $\text{NH}_3$ increases the solubility of $\text{AgBr}$. Added $\text{NH}_3$ removes $\text{Ag}^+$ from solution by forming the complex ion, $\text{Ag(NH}_3)_2^+$. As $\text{Ag}^+$ is removed, more $\text{AgBr(s)}$ will dissolve to replenish the $\text{Ag}^+$ concentration.

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

e. Added $\text{HNO}_3$ will have no effect on the $\text{AgBr(s)}$ solubility in pure water. Neither $\text{H}^+$ nor $\text{NO}_3^-$ react with $\text{Ag}^+$ or $\text{Br}^-$ ions. $\text{Br}^-$ is the conjugate base of the strong acid $\text{HBr}$, so it is a terrible base. However, added $\text{HNO}_3$ will reduce the solubility of $\text{AgBr(s)}$ in the ammonia solution. $\text{NH}_3$ is a weak base ($K_b = 1.8 \times 10^{-5}$). Added $\text{H}^+$ will react with $\text{NH}_3$ to form $\text{NH}_4^+$. As $\text{NH}_3$ is removed, a smaller amount of the $\text{Ag(NH}_3)_2^+$ complex ion will form, resulting in a smaller amount of $\text{AgBr(s)}$ that will dissolve.

98. $[\text{NH}_3]_0 = \frac{3.00 M}{2} = 1.50 M; \quad [\text{Cu}^{2+}]_0 = \frac{2.00 \times 10^{-3} M}{2} = 1.00 \times 10^{-3} M$
Because \([\text{NH}_3]_0 \gg [\text{Cu}^{2+}]_0\), and because \(K_1, K_2, K_3\) and \(K_4\) are all large, \(\text{Cu(NH}_3)_4^{2+}\) will be the dominant copper-containing species. The net reaction will be \(\text{Cu}^{2+} + 4 \text{ NH}_3 \rightarrow \text{Cu(NH}_3)_4^{2+}\). Here, \(1.00 \times 10^{-3} \text{ M} \text{ Cu}^{2+}\) plus \(4(1.00 \times 10^{-3} \text{ M}) \text{ NH}_3\) will produce \(1.00 \times 10^{-3} \text{ M} \text{ Cu(NH}_3)_4^{2+}\). At equilibrium:

\[
[\text{Cu(NH}_3)_4^{2+}] \approx 1.00 \times 10^{-3} \text{ M}
\]

\([\text{NH}_3] = [\text{NH}_3]_0 - [\text{NH}_3]_{\text{reacted}} = 1.50 \text{ M} - 4(1.00 \times 10^{-3} \text{ M}) = 1.50 \text{ M}
\]

Calculate \([\text{Cu(NH}_3)_3^{2+}]\) from the \(K_4\) reaction:

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

Calculate \([\text{Cu(NH}_3)_2^{2+}]\) from \(K_3\) reaction:

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

Calculate \([\text{Cu(NH}_3)_3^{2+}]\) from the \(K_2\) reaction:

\[
3.88 \times 10^3 = \frac{[\text{Cu(NH}_3)_2^{2+}]}{[\text{Cu(NH}_3)_3^{2+}][\text{NH}_3]} = \frac{2.87 \times 10^{-9}}{[\text{CuNH}_3^{2+}](1.50)} \Rightarrow [\text{CuNH}_3^{2+}] = 4.93 \times 10^{-13} \text{ M}
\]

Calculate \([\text{Cu}^{2+}]\) from the \(K_1\) reaction:

\[
1.86 \times 10^4 = \frac{[\text{CuNH}_3^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]} = \frac{4.93 \times 10^{-13}}{[\text{Cu}^{2+}](1.50)} \Rightarrow [\text{Cu}^{2+}] = 1.77 \times 10^{-17} \text{ M}
\]

The assumptions are valid. \(\text{Cu(NH}_3)_4^{2+}\) is clearly the dominant copper-containing component.

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
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\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]

\[
\begin{array}{ccc}
\text{AgCN(s)} & \rightleftharpoons & \text{Ag}^+(aq) + \text{CN}^-(aq) \\
\text{H}^+(aq) + \text{CN}^-(aq) & \rightleftharpoons & \text{HCN(aq)} \\
\text{AgCN(s)} + \text{H}^+(aq) & \rightleftharpoons & \text{Ag}^+(aq) + \text{HCN(aq)}
\end{array}
\]
\[ 3.5 \times 10^{-3} = \frac{[\text{Ag}^+][\text{HCN}]}{[\text{H}^+]} = \frac{s(s)}{1.0 - s} \approx \frac{s^2}{1.0}, \quad s = 5.9 \times 10^{-2} \]

Assumption fails the 5% rule \((s = 5.9\% \text{ of } 1.0 \text{ M})\). Using the method of successive approximations:

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

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

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

100. Solubility in pure water:

\[
\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} \quad \text{K}_{sp} = 2 \times 10^{-9}
\]

Initial \(s\) = solubility (mol/L) 0 0

Equil. \(s\)  

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

Solubility in 1.0 M H\(^+\):

\[
\begin{align*}
\text{CaC}_2\text{O}_4(s) & \rightleftharpoons \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} \quad \text{K}_{sp} = 2 \times 10^{-9} \\
\text{C}_2\text{O}_4^{2-} + \text{H}^+ & \rightleftharpoons \text{HC}_2\text{O}_4^- \quad \text{K} = 1/K_{a_2} = 1.6 \times 10^4 \\
\text{HC}_2\text{O}_4^- + \text{H}^+ & \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 \quad \text{K} = 1/K_{a_1} = 15 \\
\text{CaC}_2\text{O}_4(s) + 2 \text{H}^+ & \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{C}_2\text{O}_4 \quad \text{K}_{overall} = 5 \times 10^{-4}
\end{align*}
\]

Initial \(0.10 \text{ M}\) 0 0

\(s\) mol/L of CaC\(_2\)O\(_4\)(s) dissolves to reach equilibrium

Equil. \(0.10 - 2s\)  

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

Solubility in 0.10 M H\(^+\) \(= 2 \times 10^{-3}\)

Solubility in pure water \(= 4 \times 10^{-5} = 50\)

CaC\(_2\)O\(_4\)(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\(_2\)O\(_4\)^{2-}.  

\[
\text{CaC}_2\text{O}_4(s) \text{ is } 50 \text{ times more soluble in } 0.10 \text{ M H}^+ \text{ than in pure water. This increase in solubility is due to the weak base properties of C}_2\text{O}_4^{2-}. 
\]
101. \( K_{sp} = [\text{Ni}^{2+}][\text{S}^{2-}] = 3 \times 10^{-21} \)

\[
\begin{align*}
\text{H}_2\text{S}(aq) & \rightleftharpoons \text{H}^+(aq) + \text{HS}^-(aq) \quad K_a_1 = 1.0 \times 10^{-7} \\
\text{HS}^-(aq) & \rightleftharpoons \text{H}^+(aq) + \text{S}^{2-}(aq) \quad K_a_2 = 1 \times 10^{-19} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{S}(aq) & \rightleftharpoons 2 \text{H}^+(aq) + \text{S}^{2-}(aq) \quad K = K_{a_1} \times K_{a_2} = 1 \times 10^{-26} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \\
\end{align*}
\]

Because \( K \) is very small, only a tiny fraction of the \( \text{H}_2\text{S} \) will react. At equilibrium, \( [\text{H}_2\text{S}] = 0.10 \) M and \( [\text{H}^+] = 1 \times 10^{-3} \) M.

\[
[\text{S}^{2-}] = \frac{K[\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{(1 \times 10^{-26})(0.10)}{(1 \times 10^{-3})^2} = 1 \times 10^{-21} \text{ M}
\]

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

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

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

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

For CuS(s):

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

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

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

For MnS(s):

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

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

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

We must have \( [\text{S}^{2-}]_0 > 8.5 \times 10^{-45} \text{ M} \) to precipitate CuS but \( [\text{S}^{2-}]_0 < 2.3 \times 10^{-10} \text{ M} \) 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 \( \text{S}^{2-} \) that will do this. Let’s choose \( [\text{S}^{2-}]_0 = 1.0 \times 10^{-10} \text{ M} \).
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 \([S^{2−}] = 1.0 × 10^{−10}\) M. Let’s combine the \(K_{a1}\) and \(K_{a2}\) equations for \(H_2S\) to determine the required \([H^+]\).

\[
H_2S(aq) \rightleftharpoons H^+(aq) + HS^−(aq) \quad K_{a1} = 1.0 \times 10^{−7}
\]

\[
HS^−(aq) \rightleftharpoons H^+(aq) + S^{2−}(aq) \quad K_{a2} = 1 \times 10^{−19}
\]

\[
HS^−(aq) \rightleftharpoons 2H^+(aq) + S^{2−}(aq) \quad K = K_{a1} \times K_{a2} = 1.0 \times 10^{−26}
\]

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

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

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

103. \(Mg^{2+} + P_{3}O_{10}^{5−} \rightleftharpoons MgP_{3}O_{10}^{3−}; \quad K = 4.0 \times 10^{8}\)

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

\[
[P_{3}O_{10}^{5−}]_0 = \frac{40. \text{ g Na}_3P_{3}O_{10}}{L} \times \frac{1 \text{ mol}}{367.86 \text{ g}} = 0.11 \text{ M}
\]

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.

\[
\begin{align*}
\text{Before} & \quad 2.1 \times 10^{−3} \text{ M} & 0.11 \text{ M} & \quad 0 \\
\text{Change} & \quad -2.1 \times 10^{−3} & -2.1 \times 10^{−3} & \quad +2.1 \times 10^{−3} & \quad \text{React completely} \\
\text{After} & \quad 0 & 0.11 & \quad 2.1 \times 10^{−3} & \quad \text{New initial condition} \\
\text{x mol/L } MgP_{3}O_{10}^{3−} \quad \text{dissociates to reach equilibrium} & \quad +x & \quad +x & \quad -x \\
\text{Change} & \quad +x & \quad -x \\
\text{Equil.} & \quad x & 0.11 + x & 2.1 \times 10^{−3} - x
\end{align*}
\]

\[
K = 4.0 \times 10^{8} = \frac{[MgP_{3}O_{10}^{3−}]}{[Mg^{2+}][P_{3}O_{10}^{5−}]} = \frac{2.1 \times 10^{−3} - x}{x(0.11 + x)} \quad \text{(assume } x \ll 2.1 \times 10^{−3})
\]

\[
4.0 \times 10^{8} \approx \frac{2.1 \times 10^{−3}}{x(0.11)}, \quad x = [Mg^{2+}] = 4.8 \times 10^{−11} \text{ M}; \quad \text{assumptions good.}
\]
104. \( MX \rightleftharpoons M^+ + X^- \); \( \Delta T = K_c m, \ m = \frac{\Delta T}{K_c} = \frac{0.028^\circ C}{1.86^\circ C / \text{molal}} = 0.015 \text{ mol/kg} \)

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

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

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

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

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

105. a. \( \text{SrF}_2(s) \rightleftharpoons \text{Sr}^{2+}(aq) + 2 \text{F}^-(aq) \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>s mol/L SrF(_2) dissolves to reach equilibrium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Equil.</th>
<th>s</th>
<th>2s</th>
</tr>
</thead>
</table>

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

b. Greater, because some of the \( \text{F}^- \) would react with water:

\( \text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^- \quad K_b = \frac{K_w}{K_{a, \text{HF}}} = 1.4 \times 10^{-11} \)

This lowers the concentration of \( \text{F}^- \), forcing more \( \text{SrF}_2 \) to dissolve.

c. \( \text{SrF}_2(s) \rightleftharpoons \text{Sr}^{2+} + 2 \text{F}^- \quad K_{sp} = 7.9 \times 10^{-10} = [\text{Sr}^{2+}][\text{F}^-]^2 \)

Let \( s = \text{solubility} = [\text{Sr}^{2+}] \); then \( 2s = \text{total F}^- \) concentration.

Since \( \text{F}^- \) is a weak base, some of the \( \text{F}^- \) is converted into \( \text{HF} \). Therefore:

\[
\text{total F}^- \text{ concentration} = 2s = [\text{F}^-] + [\text{HF}]
\]

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

\[
7.2 \times 10^{-2} = \frac{[\text{F}^-]}{[\text{HF}]}, \quad [\text{HF}] = 14[\text{F}^-] \quad \text{solving:}
\]

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

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

106.  \[ \text{M}_3\text{X}_2(s) \rightarrow 3 \text{M}^{2+}(aq) + 2 \text{X}^3^-(aq) \quad K_{sp} = [\text{M}^{2+}]^3[\text{X}^3^-]^2 \]

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Equil.</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>3s</td>
</tr>
<tr>
<td>E q u i l .</td>
<td>2s</td>
<td></td>
</tr>
</tbody>
</table>

\[ K_{sp} = (3s)^3(2s)^2 = 108s^5; \text{ total ion concentration} = 3s + 2s = 5s \]

\[ \pi = iMRT, \quad iM = \text{total ion concentration} = \frac{\pi}{RT} = \frac{2.64 \times 10^{-2} \text{ atm}}{0.08206 \text{ L atm/K mol} \times 298 \text{ K}} = 1.08 \times 10^{-3} \text{ mol/L} \]

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

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

107. Major species: \( \text{H}^+, \text{HSO}_4^-, \text{Ba}^{2+}, \text{NO}_3^-, \) and \( \text{H}_2\text{O} \); \( \text{Ba}^{2+} \) will react with the \( \text{SO}_4^{2-} \) produced from the \( k_a \) reaction for \( \text{HSO}_4^- \).

\[ \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \quad K_a = 1.2 \times 10^{-2} \]

\[ \text{Ba}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{BaSO}_4(s) \quad K = 1/K_{sp} = 1/(1.5 \times 10^{-9}) = 6.7 \times 10^8 \]

\[ \text{Ba}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{BaSO}_4(s) \quad K_{overall} = (1.2 \times 10^{-2}) \times (6.7 \times 10^8) = 8.0 \times 10^6 \]

Because \( K_{overall} \) is so large, the reaction essentially goes to completion. Because \( \text{H}_2\text{SO}_4 \) is a strong acid, \( [\text{HSO}_4^-]_0 = [\text{H}^+]_0 = 0.10 \text{ M} \).

\[ \text{Ba}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{BaSO}_4(s) \]

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>Change</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ba}^{2+} )</td>
<td>0.30 M</td>
<td>-0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{HSO}_4^- )</td>
<td>0.10 M</td>
<td>-0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{H}^+ )</td>
<td>0.10 M</td>
<td>+0.10</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{New initial} \]

\[ \text{Change} \]

\[ \text{Equil.} \]

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

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

\[ [\text{Ba}^{2+}] = 0.20 + 1.3 \times 10^{-7} = 0.20 \text{ M} \]
From the initial reaction essentially going to completion, 1.0 L(0.10 mol HSO₄⁻/L) = 0.10 mol HSO₄⁻ reacted; this will produce 0.10 mol BaSO₄(s). Only 1.3 × 10⁻⁷ mol of this dissolves to reach equilibrium, so 0.10 mol BaSO₄(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]6s²4f¹⁴5d¹⁰; this is mercury, Hg. Because X⁻ has 54 electrons, X has 53 protons and is iodine, I. The identity of Q = Hg₂I₂.

\[
\begin{align*}
\text{[I⁻]}_0 &= \frac{1.98 \text{ g NaI} \times \frac{1 \text{ mol NaI}}{149.9 \text{ g} \text{ mol NaI}} \times \frac{1 \text{ mol I⁻}}{0.150 \text{ L}}} \\
&= 0.0881 \text{ mol/L}
\end{align*}
\]

\[
\text{Hg}_2\text{I}_2(\text{s}) \rightleftharpoons \text{Hg}^{2⁺} + 2 \text{I⁻} \quad \text{K}_\text{sp} = 4.5 \times 10^{-29}
\]

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

\[
\text{K}_\text{sp} = 4.5 \times 10^{-29} = [\text{Hg}^{2⁺}][\text{I⁻}]^2 = s(0.0881 + 2s)^2 \approx s(0.0881)^2
\]

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

**Marathon Problem**

109. a. In very acidic solutions, the reaction that occurs to increase the solubility is Al(OH)₃(s) + 3H⁺ → Al³⁺(aq) + 3H₂O(l). In very basic solutions, the reaction that occurs to increase solubility is Al(OH)₃(s) + OH⁻(aq) → Al(OH)₄⁻(aq).

b. Al(OH)₃(s) ⇌ Al³⁺ + 3 OH⁻; Al(OH)₃(s) + OH⁻ ⇌ Al(OH)₄⁻

\[
S = \text{solubility} = \text{total Al}^{3⁺} \text{ concentration} = [\text{Al}^{3⁺}] + [\text{Al(OH)}₄⁻]
\]

\[
[\text{Al}^{3⁺}] = \frac{\text{K}_\text{sp}}{[\text{OH}⁻]^3} = \text{K}_\text{sp} \times \frac{[\text{H}⁺]^3}{\text{K}_\text{w}^3}, \text{ because } [\text{OH}⁻]^3 = (\text{K}_\text{w}/[\text{H}⁺])^3
\]

\[
\frac{[\text{Al(OH)}₄⁻]}{[\text{OH}⁻]} = \text{K}; \quad [\text{OH}⁻] = \frac{\text{K}_\text{w}}{[\text{H}⁺]}; \quad [\text{Al(OH)}₄⁻] = \text{K}[\text{OH}⁻] = \frac{\text{KK}_\text{w}}{[\text{H}⁺]}
\]

\[
S = [\text{Al}^{3⁺}] + [\text{Al(OH)}₄⁻] = [\text{H}⁺]^3\text{K}_\text{sp}/\text{K}_\text{w}^3 + \text{KK}_\text{w}/[\text{H}⁺]
\]
c.  \( K_{sp} = 2 \times 10^{-32} \),  \( K_w = 1.0 \times 10^{-14} \),  \( K = 40.0 \)

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

<table>
<thead>
<tr>
<th>pH</th>
<th>solubility (S, mol/L)</th>
<th>log S</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>2 \times 10^{-2}</td>
<td>-1.7</td>
</tr>
<tr>
<td>5.0</td>
<td>2 \times 10^{-5}</td>
<td>-4.7</td>
</tr>
<tr>
<td>6.0</td>
<td>4.2 \times 10^{-7}</td>
<td>-6.38</td>
</tr>
<tr>
<td>7.0</td>
<td>4.0 \times 10^{-6}</td>
<td>-5.40</td>
</tr>
<tr>
<td>8.0</td>
<td>4.0 \times 10^{-5}</td>
<td>-4.40</td>
</tr>
<tr>
<td>9.0</td>
<td>4.0 \times 10^{-4}</td>
<td>-3.40</td>
</tr>
<tr>
<td>10.0</td>
<td>4.0 \times 10^{-3}</td>
<td>-2.40</td>
</tr>
<tr>
<td>11.0</td>
<td>4.0 \times 10^{-2}</td>
<td>-1.40</td>
</tr>
<tr>
<td>12.0</td>
<td>4.0 \times 10^{-1}</td>
<td>-0.40</td>
</tr>
</tbody>
</table>

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