Chapter 18 Homework Answers

18.19  
(a) \text{AgI(s)} \rightleftharpoons \text{Ag}^+ + \text{I}^-  
\text{K}_{sp} = [\text{Ag}^+][\text{I}^-] 
(b) \text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3\text{Ag}^+ + \text{PO}_4^{3-} 
\text{K}_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] 
(c) \text{PbCrO}_4(s) \rightleftharpoons \text{Pb}^{2+} + \text{CrO}_4^{2-} 
\text{K}_{sp} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] 
(d) \text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^- 
\text{K}_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3 
(e) \text{ZnCO}_3(s) \rightleftharpoons \text{Zn}^{2+} + \text{CO}_3^{2-} 
\text{K}_{sp} = [\text{Zn}^{2+}][\text{CO}_3^{2-}] 
(f) \text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+} + 2\text{OH}^- 
\text{K}_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2 

18.25 To solve this problem we need to realize that the concentration of the solution is equal to the number of moles of solid recovered divided by the volume of the solution, i.e., 

\[ [\text{CaCrO}_4] = \left( \frac{0.649 \text{ g CaCrO}_4}{156 \text{ mL}} \right) \left( \frac{1 \text{ mole CaCrO}_4}{156.1 \text{ g CaCrO}_4} \right) \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) = 0.0267 \text{ M} \]

The equilibrium for this problem is CaCrO$_4$($s$) \rightleftharpoons Ca$^{2+}$ + CrO$_4^{2-}$ 
\text{K}_{sp} = [\text{Ca}^{2+}][\text{CrO}_4^{2-}] = (0.0267)^2 = 7.13 \times 10^{-4}$

18.31  
\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} 

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\text{K}_{sp} = (2x)^2(x) = 4x^3 = 1.2 \times 10^{-12}, x = \sqrt[3]{\frac{1.2 \times 10^{-12}}{4}} = 6.7 \times 10^{-5} \text{ M} 

18.37 First determine the molar solubility of the M$_2$X$_3$ salt. 
M$_2$X$_3$ ($s$) \rightleftharpoons 2\text{M}^{3+}(aq) + 3\text{X}^2-(aq) 
\text{K}_{sp} = [\text{M}^{3+}]^2[\text{X}^2^-]^3 

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\text{K}_{sp} = (2x)^3(3x)^3 = 2.2 \times 10^{-30} = 108x^5 
\text{x} = 4.6 \times 10^{-5} \text{ M} 

The molar solubility of this compound is 4.6 \times 10^{-5} \text{ moles/L}.

We want the molar solubility of the M$_2$X compound to be twice the value just calculated or 9.2 \times 10^{-5} \text{ moles/L}. We need to solve the equilibrium expression:

M$_2$X ($s$) \rightleftharpoons 2\text{M}^+(aq) + \text{X}^2-(aq) 
\text{K}_{sp} = [\text{M}^+]^2[\text{X}^2^-] 

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\text{K}_{sp} = (2x)^2(x) = 4x^3 
\text{where} \text{x} = 9.2 \times 10^{-5} \text{ M} 

\text{So,} \text{K}_{sp} = 4(9.2 \times 10^{-5})^3 = 3.1 \times 10^{-12}
18.43 \( \text{AuCl}_3(s) \ \rightleftharpoons \ \text{Au}^{3+} + 3\text{Cl}^- \quad \text{K}_{sp} = [\text{Au}^{3+}][\text{Cl}^-]^3 = 3.2 \times 10^{-25} \)

(a) \( \text{let } x = [\text{Au}^{3+}]; \text{ then } [\text{Cl}^-] = 3x \)
\[ K_{sp} = (x)(3x)^3 = 27x^4 \]
\[ x = \sqrt[4]{\frac{3.2 \times 10^{-25}}{27}} = 3.3 \times 10^{-7} M \]

The molar solubility of \( \text{AuCl}_3 \) is \( 3.3 \times 10^{-7} M \) in \( \text{H}_2\text{O} \).

(b) \( [\text{Au}^{3+}] = x; \ [\text{Cl}^-] = 0.010 + 3x \)
\[ K_{sp} = (x)(0.010 + 3x)^3 : \text{ Assume } 3x << 0.010 \]
\[ K_{sp} = (x)(0.010)^3 \]
\[ x = 3.2 \times 10^{-19} M \]

The molar solubility of \( \text{AuCl}_3 \) is \( 3.2 \times 10^{-19} M \) in \( 0.010 M \text{ HCl} \).

(c) \( [\text{Au}^{3+}] = x; \ [\text{Cl}^-] = 0.020 + 3x \)
\[ K_{sp} = (x)(0.020 + 3x)^3 : \text{ Assume } 3x << 0.020 \]
\[ K_{sp} = (x)(0.020)^3 \]
\[ x = 4.0 \times 10^{-20} M \]

The molar solubility of \( \text{AuCl}_3 \) is \( 4.0 \times 10^{-20} M \) in \( 0.010 M \text{ MgCl}_2 \).

(d) \( [\text{Au}^{3+}] = 0.010 + x; \ [\text{Cl}^-] = 3x \)
\[ K_{sp} = (0.010 + x)(3x)^3 : \text{ Assume } x << 0.010 \]
\[ K_{sp} = (0.010)(3x)^3 \]
\[ x = \sqrt[3]{\frac{3.2 \times 10^{-25}}{0.27}} = 1.1 \times 10^{-8} M \]

The molar solubility of \( \text{AuCl}_3 \) is \( 1.1 \times 10^{-8} M \) in \( 0.010 M \text{ Au(NO}_3\text{)}_3 \).

18.53 (a) \( \text{Ca(OH)}_2(s) \ \rightleftharpoons \ \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \quad \text{K}_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 5.0 \times 10^{-5} \)
\[ \text{let } 2x = [\text{OH}^-], \ [\text{Ca}^{2+}] = x + 0.10 \quad \text{K}_{sp} = (x)(2x)^2 = 5.0 \times 10^{-5} \]

By successive approximations, \( x = 0.0036 \)

The molar solubility of \( \text{Ca(OH)}_2 \) in \( 0.10 M \text{ CaCl}_2 \) is \( 0.0036 \text{ moles/L} \).

(b) \( \text{Ca(OH)}_2(s) \ \rightleftharpoons \ \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \quad \text{K}_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 5.0 \times 10^{-5} \)
\[ \text{let } x = [\text{Ca}^{2+}], \ [\text{OH}^-] = 2x + 0.10 \quad \text{K}_{sp} = (x)(2x + 0.10)^2 = 5.0 \times 10^{-5} \]

By successive approximations, \( x = 4.9 \times 10^{-4} \)

The molar solubility of \( \text{Ca(OH)}_2 \) in \( 0.10 M \text{ NaOH} \) is \( 4.9 \times 10^{-4} \text{ moles/L} \).

18.61 This problem is similar to 18.60 except that the \( \text{K}_{sp} \) constants are closer in value. We first determine the minimum amount of \( \text{SO}_4^{2-} \) that must be added to initiate the precipitation of \( \text{CaSO}_4 \). \( \text{CaSO}_4 \) will precipitate after \( \text{SrSO}_4 \) due to its larger value for \( \text{K}_{sp} \): \( \text{K}_{sp}(\text{CaSO}_4) = 4.9 \times 10^{-5} \) and \( \text{K}_{sp}(\text{SrSO}_4) = 3.4 \times 10^{-7} \) (see Table 18.1)

(a) \( \text{Let } x = [\text{Ca}^{2+}]; \quad \text{K}_p = [\text{Ca}^{2+}][\text{SO}_4^{2-}]^2 = (0.15)(x) = 4.9 \times 10^{-5} \)
\[ x = [\text{SO}_4^{2-} ] = 3.3 \times 10^{-4} M \]

When the \( [\text{SO}_4^{2-} ] = 3.3 \times 10^{-4} M \) the \( \text{CaSO}_4 \) will start to precipitate. Now we ask, what is the \( [\text{Sr}^{2+}] \) if \( [\text{SO}_4^{2-} ] = 3.3 \times 10^{-4} M \)?
\[
\text{SrSO}_4 (s) \rightleftharpoons \text{Sr}^{2+} (aq) + \text{SO}_4^{2-} (aq) \quad K_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}]
\]

### Table

|   | [Sr\(^{2+}\)] | [SO\(_4^{2-}\)] |
|---|---------------|----------------|---|---|
| I | -             | \(3.3 \times 10^{-4}\) | C | + x | \(3.3 \times 10^{-4} + x\) |
| E | + x           | \(3.3 \times 10^{-4} + x\) |

\[
K_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = (x)(1.6 \times 10^{-4} + x) = 3.2 \times 10^{-7}
\]

For this problem, we must solve the quadratic equation and we determine that \(x = 4.4 \times 10^{-4}\) M. Thus, the \([\text{Sr}^{2+}] = 4.4 \times 10^{-4}\) M when the CaSO\(_4\) starts to precipitate.

(b) Initially the solution had a concentration of 0.15 M. The solution now has a \([\text{Sr}^{2+}] = 4.4 \times 10^{-4}\) M.

So, the percentage of \(\text{Sr}^{2+}\) precipitated is:

\[
\left(\frac{0.15 - 4.4 \times 10^{-4}}{0.15}\right) \times 100\% = 99.7\%
\]

18.69 (a) \(\text{Ag}^+ (aq) + 2\text{S}_2\text{O}_3^{2-} (aq) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-} (aq)\)

\[
K_{form} = \frac{[\text{Ag(S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2}
\]

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

\[
K_{form} = \frac{[\text{Zn(NH}_3)_4^{2+}]}{[\text{Zn}^{2+}][\text{NH}_3]^4}
\]

(c) \(\text{Sn}^{4+} (aq) + 3\text{S}^{2-} (aq) \rightleftharpoons \text{SnS}_3^{2-} (aq)\)

\[
K_{form} = \frac{[\text{SnS}_3^{2-}]}{[\text{Sn}^{4+}][\text{S}^{2-}]^3}
\]

18.79 The applicable equilibria are as follows:

\(\text{AgI(s)} \rightleftharpoons \text{Ag}^+ (aq) + \Gamma (aq)\)

\[
K_{sp} = [\text{Ag}^+][\Gamma] = 8.5 \times 10^{-17}
\]

\(\text{Ag}^+ (aq) + 2\Gamma (aq) \rightleftharpoons \text{AgI}_2^- (aq)\)

\[
K_{form} = \frac{[\text{AgI}_2^-]}{[\text{Ag}^+][\Gamma]^2} = 1 \times 10^{11}
\]

The two equations above may be combined and \(K_c\) found as follows:

\(\text{AgI(s)} + \Gamma (aq) \rightleftharpoons \text{AgI}_2^- (aq)\)

\[
K_c = \frac{[\text{AgI}_2^-]}{[\Gamma]} = K_{sp} \times K_{form} = 8.5 \times 10^{-6}
\]

If all of the AgI dissolves, it will be in the form of Ag(I)\(_2\), therefore the concentration of Ag(I)\(_2^-\) is:

\[
[\text{AgI}_2^-] = \frac{0.020 \text{ mol AgI}_2^-}{0.100 \text{ L solution}} = 0.200 \text{ M AgI}_2^-\]

\[
[\text{CN}^-] = \frac{0.200}{8.5 \times 10^{-6}} = 2.4 \times 10^4 \text{ M}
\]
The amount of KI that must be added is: \((2.4 \times 10^4 \text{M})(0.100 \text{L}) = 2400 \text{ mol KI}
\]
\(\text{g KI} = (2400 \text{ mol KI})(166 \text{ g/mol}) = 3.98 \times 10^5 \text{ g KI}
\]

18.85 The student would not collect PbCl\(_2\) by adding HCl to the final solution. The Pb\(^{2+}\) would be precipitated in step (1) when H\(_2\)S was added to the acidified solution. This precipitate was separated from the remaining solution.

The first precipitate would consist of PbS and CdS while the second precipitate consists of NiS.

18.99 Initially, both Ag\(^+\) and HC\(_2\)H\(_3\)O\(_2\) are at 1.0 \text{M} concentrations. These values will be used to determine if the AgC\(_2\)H\(_3\)O\(_2\) will precipitate.

First, determine the concentration of the acetate ion from the equilibrium:

\[
\text{HC}_2\text{H}_3\text{O}_2^- \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \\
K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2^-]} = 1.8 \times 10^{-5}
\]

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<th>[HC(_2)H(_3)O(_2)]</th>
<th>[H(<em>3)O(</em>+)]</th>
<th>[C(_2)H(_3)O(_2)^-]</th>
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<tr>
<td>I</td>
<td>1.0</td>
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<tr>
<td>C</td>
<td>– x</td>
<td>+ x</td>
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<td>E</td>
<td>1.0 – x</td>
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Assume \(x \ll 1.0\)

\[
K_a = \frac{[x][x]}{[1.0]} = 1.8 \times 10^{-5} \\
x = 4.2 \times 10^{-3} = [\text{C}_2\text{H}_3\text{O}_2^-]
\]

Next, using the concentration of the acetate ion, determine whether or not a precipitate will form.

\[
\text{AgC}_2\text{H}_3\text{O}_2(s) \rightleftharpoons \text{Ag}^+ + \text{C}_2\text{H}_3\text{O}_2^- \\
K_{sp} = [\text{Ag}^+][\text{C}_2\text{H}_3\text{O}_2^-]
\]

\[
Q = [\text{Ag}^+][\text{C}_2\text{H}_3\text{O}_2^-] \text{ before equilibrium is established} \\
Q = (1.0 \text{M})(4.2 \times 10^{-3} \text{M}) = 4.2 \times 10^{-3}
\]

\(Q > K_{sp}\) therefore a precipitate will form.

18.107 To answer this question we can use cation groupings from qualitative analysis. Ag\(^+\) and Pb\(^{2+}\) are group I ions. These ions can be separated from the others by adding Cl\(^-\) to the solution. AgCl and PbCl\(_2\) will precipitate and can be filtered off from the solution. AgCl can be separated from PbCl\(_2\) by adding 6 M NH\(_3\). AgCl will react forming Ag(NH\(_3\))\(^{2+}\) while PbCl\(_2\) will remain a solid.

Cu\(^{2+}\) and Bi\(^{3+}\) can be separated by adding 0.1 M H\(_2\)S and 6M HCl. This will precipitate CuS and Bi\(_2\)S\(_3\) which can be filtered. The solids can be converted to soluble species by adding HNO\(_3\). Then, base can be added to precipitate hydroxides: Cu(OH)\(_2\) and Bi(OH)\(_3\). The addition of 6M NH\(_3\) will convert the Cu(OH)\(_2\) to Cu(NH\(_3\))\(^{2+}\) leaving the solid Bi(OH)\(_3\).

Then add base to the remaining solution along with H\(_2\)S to precipitate CoS and MnS. Filter the solution and dissolve the solid by adding acid. Cobalt can be separated by adding KNO\(_3\) which forms a yellow precipitate while Mn\(^{2+}\) remains in solution.

Finally, Ba\(^{2+}\) and Ca\(^+\) can be separated by adding acid to make a weakly acidic solution and then adding Na\(_2\)CrO\(_4\). BaCrO\(_4\) will precipitate while Ca\(^{2+}\) will remain in solution.
The volume of a cone is given by $V = \frac{1}{3} \pi r^2 h$

$$V = \frac{1}{3} \times 3.1415 \times (5 \text{ ft})^2 \times 16 \text{ ft} \times \left(\frac{12 \text{ in}}{\text{ ft}}\right)^3 \times \left(\frac{2.54 \text{ cm}}{\text{ in}}\right)^3$$

$$V = 1.19 \times 10^7 \text{ cm}^3$$

The mass of the cone is:

$$1.19 \times 10^7 \text{ cm}^3 \times 2.71 \text{ g cm}^{-3} = 3.22 \times 10^7 \text{ g CaCO}_3$$

Saturated CaCO$_3$ has a molar concentration of Ca$^{2+}$ equal to:

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = K_{sp}^{1/2} = (3.4 \times 10^{-9})^{1/2} = 5.8 \times 10^{-5} \text{ M}$$

Mass of CaCO$_3$ dissolved in a liter of saturated solution is:

$$5.8 \times 10^{-5} \text{ mol L}^{-1} \times (100.09 \text{ g mol CaCO}_3) = 5.8 \times 10^{-3} \text{ g L}^{-1}$$

The volume of solution required to build the cone would be equal to:

$$3.22 \times 10^7 \text{ g CaCO}_3 \times (1 \text{ L} / 5.8 \times 10^{-3} \text{ g}) = 5.6 \times 10^9 \text{ L}$$

10 drops have a volume of 1 mL.

$$(10 \text{ drops/L} \times 1000 \text{ mL/L}) = 10000 \text{ drops/L}$$

The number of drops required to deposit enough CaCO$_3$ is given by:

$$(10000 \text{ drops/L}) \times 5.6 \times 10^9 \text{ L} = 5.6 \times 10^{13} \text{ drops}$$

The age of the stalagmite equals:

$$5.6 \times 10^{13} \text{ drops} \times (1 \text{ s/drop}) \times (1 \text{ hr/3600 s}) \times (1 \text{ day/24 hrs}) \times (1 \text{ yr/365 days}) = 1.8 \times 10^6 \text{ yrs}$$