Key Worksheet 17 Solubility and Complex Ion Equilibria: Selective Precipitation and Complex Ion Equilibria

Objectives
To be able to predict the order of precipitation of ions in a solution that contains a mixture of those ions. To be able to calculate the amount of an ion needed to just precipitate a counter ion. To be able to develop a reasonable qualitative analysis scheme. To calculate the effect of the formation of a complex ion on the concentration of an ion involved in the formation of that complex ion.

Selective Precipitation: The ionic compound with the lowest solubility will precipitate out first in a mixture of ions when a counter ion is added to the mixture. We can control which ion precipitates by controlling the amount of the counter ion in solution. When sulfide is the counter ion we can control this by adjusting the pH. The lower the pH the less sulfide there is in solution.

Complex Ions: When a compound that forms a complex with an ion is added to a solution we can add together the two relevant reactions and multiply the equilibrium constants to get the overall reaction and equilibrium constant.
1.) A solution is prepared by mixing together 75.00 mL of 0.150 M Pb(NO$_3$)$_2$ and 50.00 mL of 0.925 M NaCl. Calculate the concentration of Pb$^{2+}$ and Cl$^-$ at equilibrium. $K_{sp}$ for PbCl$_2$ = $1.6 \times 10^{-5}$.

$$\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{PbCl}_2(s)$$

*First find the limiting reactant, and thus the concentration of the excess reactant:*

$$0.07500 \text{ L} \times \frac{0.150 \text{ mol Pb}^{2+}}{\text{L}} = 0.01125 \text{ mol Pb}^{2+}$$

$$0.05000 \text{ L} \times \frac{0.925 \text{ mol Cl}^-}{\text{L}} = 0.04625 \text{ mol Cl}^-$$

$$0.01125 \text{ mol Pb}^{2+} \times \frac{2 \text{ moles Cl}^-}{1 \text{ mol Pb}^{2+}} = 0.02250 \text{ mol Cl}^- \text{ needed}$$

*We see that Pb$^{2+}$ is the limiting reactant, the moles of Cl$^-$ left in solution is:*

$$(0.04625 \text{ mol initial}) - (0.02250 \text{ mol used}) = 0.02375 \text{ mol left}$$

$$\Rightarrow [\text{Cl}^-] = \frac{0.02375 \text{ mol}}{0.1250 \text{ L}} = 0.190 \text{ M}$$

*Now we look at the solubility of the compound. Note that we have some chloride ion in solution which will affect the solubility.*

$$\text{PbCl}_2(s) \leftrightharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$$

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = s(0.190 + 2s)^2 \approx s(0.190)^2 = 1.6 \times 10^{-5} \Rightarrow s = 4.43 \times 10^{-4}$$

$$[\text{Pb}^{2+}]_{eq} = s = 4.43 \times 10^{-4} \text{ M} \quad [\text{Cl}^-]_{eq} = 0.190 \text{ M} + 2s = 0.1908 \text{ M}$$

$$[\text{Pb}^{2+}] = 0.00044 \text{ M}$$

$$[\text{Cl}^-] = 0.191 \text{ M}$$
2.) Hard water contains Ca\(^{2+}\) and Mg\(^{2+}\) ions. It is possible to remove the calcium ion by adding Na\(_2\)CO\(_3\). The \(K_{sp}\) of CaCO\(_3\) is 3.36 x 10\(^{-9}\). The \(K_{sp}\) of MgCO\(_3\) is 6.82 x 10\(^{-6}\).

Calculate the concentration of calcium ions in a 0.0750 \(M\) solution of Na\(_2\)CO\(_3\). The magnesium ions can be removed by adding enough slaked lime, Ca(OH)\(_2\), to make a saturated solution. The \(K_{sp}\) of Ca(OH)\(_2\) is 5.02 x 10\(^{-6}\). Calculate the pH in a saturated solution of slaked lime. The \(K_{sp}\) of Mg(OH)\(_2\) is 5.61 x 10\(^{-12}\). What is the [Mg\(^{2+}\)] at this pH?

**First the calcium ions in the sodium carbonate solution.**

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

\[
K_{sp} = s(0.0750 + s) \approx s(0.0750) = 3.36 \times 10^{-9} \Rightarrow s = 4.48 \times 10^{-8} \ M = [\text{Ca}^{2+}] 
\]

**Next the pH of the calcium hydroxide solution.**

\[
\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)
\]

\[
K_{sp} = s(2s)^2 = 4s^3 = 5.02 \times 10^{-6} \Rightarrow s = 0.01078
\]

\[
[\text{OH}^-] = 2s = 0.02157 \ M \Rightarrow \text{pOH} = -\log(0.02157) = 1.6660
\]

\[
\text{pH} = 14.00 - 1.6660 = 12.333
\]

**Now the concentration of magnesium at this pH.**

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

\[
K_{sp} = s(0.02157 + 2s)^2 \approx s(0.02157)^2 = 5.61 \times 10^{-12} \Rightarrow s = 1.205 \times 10^{-8} \ M = [\text{Mg}^{2+}] 
\]

\[
[\text{Ca}^{2+}] = 4.48 \times 10^{-8} \ M
\]

\[
\text{pH} = 12.33
\]

\[
[\text{Mg}^{2+}] = 1.21 \times 10^{-8} \ M
\]
3.) The Fe$^{3+}$ ion complexes with the cyanide ion to form the complex ion Fe(CN)$_6^{3-}$. In a 0.11 M solution of KCN the equilibrium concentration of Fe$^{3+}$ is 8.5 x 10$^{-40}$ M and that of Fe(CN)$_6^{3-}$ is 1.5 x 10$^{-5}$ M. Calculate the overall formation constant, $K_f$, for Fe(CN)$_6^{3-}$.

\[ K_f = \frac{[\text{Fe(CN)}_6^{3-}]}{[\text{Fe}^{3+}][\text{CN}^-]^6} = \frac{0.0015}{(8.5 \times 10^{-40})(0.11)^6} = 9.96 \times 10^{41} \]

$K_f = 1.0 \times 10^{42}$

4.) The following steps are performed to a solution of silver nitrate. Write a chemical equation for each of the steps a – e. What can you determine about the relative values of the $K_{sp}$'s for AgI, AgCl, and AgBr?

a.) A sodium chloride solution is added to the silver nitrate solution and a white precipitate forms.

\[ \text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl(s)} + \text{NaNO}_3(aq) \]

b.) Next a solution of ammonia is added and the precipitate dissolves.

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

c.) Then a solution of potassium bromide is added and a yellow precipitate forms.

\[ \text{Ag}^+(aq) + \text{Br}^- (aq) \rightarrow \text{AgBr(s)} \]

d.) Next, a solution of sodium thiosulfate is added and the yellow precipitate disappears.

\[ \text{AgBr(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^- (aq) \]
\[ \text{Ag}^+(aq) + 2\text{S}_2\text{O}_3^{2-} (aq) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-} (aq) \]

e.) Finally a solution of potassium iodide is added and another yellow precipitate forms.

\[ \text{Ag}^+(aq) + \text{I}^- (aq) \rightarrow \text{AgI(s)} \]

Relative $K_{sp}$’s? AgCl > AgBr > AgI
5.) The $K_{sp}$ for AgBr is $5.35 \times 10^{-13}$. Calculate the molar solubility of AgBr in water. Silver forms a complex with ammonia, Ag(NH$_3$)$_2^+$. $K_f$ for this complex ion is $1.69 \times 10^7$. Calculate the molar solubility of AgBr in 1.50 $M$ NH$_3$. What mass of AgBr will dissolve in 175 mL of 1.5 $M$ NH$_3$?

*First in water:*

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

$$K_{sp} = s^2 = 5.35 \times 10^{-13} \Rightarrow s = 7.314 \times 10^{-7} \text{ M}$$

*Now in the ammonia solution:*

$$\text{AgBr}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq) \quad K_{sp} = 5.35 \times 10^{-13}$$

$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) \quad K_f = 1.69 \times 10^7$$

$$\text{AgBr}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) + \text{Br}^-(aq) \quad K = 9.041 \times 10^{-6}$$

$$k = \frac{[\text{Ag(NH}_3)_2^+][\text{Br}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(1.50 - 2s)^2} \approx \frac{s^2}{(1.50)^2} = 9.041 \times 10^{-6}$$

$$\Rightarrow s = 0.00451_0 \text{ M}$$

*Now the mass of AgBr that will dissolve:*

$$\frac{0.00451_0 \text{ mol AgBr Dissolves}}{L} \times 0.175 \text{ L} = 7.89_3 \times 10^{-4} \text{ mol AgBr Dissolved}$$

$$7.89_3 \times 10^{-4} \text{ mol AgBr} \times \frac{187.772 \text{ g AgBr}}{1 \text{ mol AgBr}} = 0.148_2 \text{ g AgBr Dissolved}$$

Solubility in Water $7.31 \times 10^{-7} \text{ M}$

Solubility in 1.50 $M$ NH$_3$ = $0.00451 \text{ M}$

Mass of AgBr Dissolved = 0.148 g
6.) A mixture contains 0.00100 \(M\) Cu\(^{2+}\) and 0.00100 \(M\) Mn\(^{2+}\). This mixture also has 0.10 \(M\) H\(_2\)S in it. Calculate a pH where CuS precipitates but MnS does not. \(K_{sp}\) for CuS = 8.5 \(\times\) 10\(^{-45}\) and \(K_{sp}\) for MnS = 2.3 \(\times\) 10\(^{-13}\). \(K_{a1}\) for H\(_2\)S = 1.0 \(\times\) 10\(^{-7}\). \(K_{a2}\) for H\(_2\)S = 1.0 \(\times\) 10\(^{-19}\).

First find the maximum concentration of sulfide ion that will not cause manganese to precipitate:

\[\text{MnS}(s) \rightleftharpoons \text{Mn}^{2+}(aq) + \text{S}^2-(aq)\]

\[K_{sp} = [\text{Mn}^{2+}][\text{S}^2-] = (0.00100 + s)s \approx (0.00100)s = 2.3 \times 10^{-13} \Rightarrow s = 2.3 \times 10^{-10} = [\text{S}^2-]\]

We need less than this. Now let’s see the minimum amount of sulfide ion we need to cause copper to precipitate:

\[\text{CuS}(s) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{S}^2-(aq)\]

\[K_{sp} = [\text{Cu}^{2+}][\text{S}^2-] = (0.00100 + s)s \approx (0.00100)s = 8.5 \times 10^{-45} \Rightarrow s = 8.5 \times 10^{-42} = [\text{S}^2-]\]

Now find \(K\) for forming sulfide from H\(_2\)S by multiplying \(K_{a1}\) and \(K_{a2}\):

\[\text{H}_2\text{S}(aq) \rightleftharpoons \text{H}^+(aq) + \text{HS}^-(aq) \quad K_{a1} = 1.0 \times 10^{-7}\]

\[\text{HS}^-(aq) \rightleftharpoons \text{H}^+(aq) + \text{S}^2-(aq) \quad K_{a1} = 1.0 \times 10^{-19}\]

\[\text{H}_2\text{S}(aq) \rightleftharpoons 2\text{H}^+(aq) + \text{S}^2-(aq) \quad K = 1.0 \times 10^{-26}\]

\[K = \frac{[\text{H}^+]^2[\text{S}^2-]}{[\text{H}_2\text{S}]}\]

We need \([\text{S}^2-]\) to be less than 2.3 \(\times\) 10\(^{-10}\), so let’s find the \([\text{H}^+]\) at this value.

\[K = \frac{[\text{H}^+]^2[\text{S}^2-]}{[\text{H}_2\text{S}]} = \frac{(2s)^2(2.3 \times 10^{-10})}{0.10 - s} \approx \frac{(2s)^2(2.3 \times 10^{-10})}{0.10} = 1.0 \times 10^{-26}\]

\[\Rightarrow s = 1.04 \times 10^{-9}\]

\[[\text{H}^+] = 2s = 2.08 \times 10^{-9} \Rightarrow \text{pH} = -\log(2.08 \times 10^{-9}) = 8.680\]

Since we need \([\text{H}^+]\) to be > 2.08 \(\times\) 10\(^{-9}\), any pH less than 8.68 will work.

\[\text{pH} = < 8.68\]