

- **Homework 16-5:** Problems pg. 724-725 # 55, 56, 57, 59, 60, 61

55 Solid NaI is slowly added to a solution that is 0.010 M in Cu^+ and 0.010 M in Ag^+ .

(a) Which compound will begin to precipitate first?

The solubility product expressions for both substances have exactly the same mathematical form and are therefore directly comparable. The substance having the smaller K_{sp} (**AgI**) will precipitate first. (Think about why!)

(b) Calculate $[\text{Ag}^+]$ when **CuI just begins to precipitate.**

When CuI just begins to precipitate the solubility product expression will just equal K_{sp} (saturated solution). The concentration of Cu^+ at this point is 0.010 M (given in the problem), so the concentration of iodide ion must be:

$$K_{sp} = [\text{Cu}^+][\text{I}^-] = (0.010)[\text{I}^-] = 5.1 \times 10^{-12}; \quad [\text{I}^-] = \frac{5.1 \times 10^{-12}}{0.010} = 5.1 \times 10^{-10} \text{ M}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{I}^-]} = \frac{8.3 \times 10^{-17}}{5.1 \times 10^{-10}} = 1.6 \times 10^{-7} \text{ M}$$

(c) What percent of Ag^+ remains in solution at this point?

$$\% \text{Ag}^+(\text{aq}) = \frac{1.6 \times 10^{-7} \text{ M}}{0.010 \text{ M}} \times 100\% = 0.0016\% \text{ or } 1.6 \times 10^{-3}\%$$

56 Find the approximate pH range suitable for the separation of Fe^{3+} and Zn^{2+} ions by precipitation of $\text{Fe}(\text{OH})_3$ from a solution that is initially 0.010 M in both Fe^{3+} and Zn^{2+} .

$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 \text{ or } [\text{OH}^-] = \left(\frac{K_{sp}}{[\text{Fe}^{3+}]} \right)^{\frac{1}{3}} = \left(\frac{1.1 \times 10^{-36}}{0.010} \right)^{\frac{1}{3}} = 4.8 \times 10^{-12} \text{ M}$$

This $[\text{OH}^-]$ corresponds to a pH of 2.68. In other words, $\text{Fe}(\text{OH})_3$ will begin to precipitate from this solution at pH of 2.68. For $\text{Zn}(\text{OH})_2$, $K_{sp} = 1.8 \times 10^{-14}$. When $[\text{Zn}^{2+}] = 0.010 \text{ M}$, the $[\text{OH}^-]$ value is:

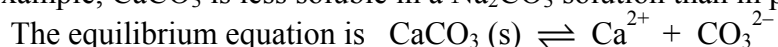
$$[\text{OH}^-] = \left(\frac{K_{sp}}{[\text{Zn}^{2+}]} \right)^{\frac{1}{2}} = \left(\frac{1.8 \times 10^{-14}}{0.010} \right)^{\frac{1}{2}} = 1.3 \times 10^{-6} \text{ M}$$

This corresponds to a pH of 8.11. So $\text{Zn}(\text{OH})_2$ will begin to precipitate from the solution at pH = 8.11. These results show that $\text{Fe}(\text{OH})_3$ will precipitate when the pH just exceeds 2.68 and that $\text{Zn}(\text{OH})_2$ will precipitate when the pH just exceeds 8.11. Therefore, to selectively remove iron as $\text{Fe}(\text{OH})_3$, the pH must be *greater than 2.68* but *less than 8.11*.

57 How does the common ion effect influence solubility equilibria? Use Le Châtelier's principle to explain the decrease in solubility of CaCO_3 in a Na_2CO_3 solution.

When a common ion is already present in solution, the solubility of a solid is decreased.

For example, CaCO_3 is less soluble in a Na_2CO_3 solution than in pure water.



Thus, the increased concentration of CO_3^{2-} ions in solution shifts the equilibrium to the left, precipitating some CaCO_3 solid.

59 How many grams of CaCO_3 will dissolve in 3.0×10^2 mL of $0.050 \text{ M Ca(NO}_3)_2$?

First let s be the molar solubility of CaCO_3 in this solution.

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

Initial (M):	0.050	0
Change (M):	-s	+s
Equilibrium (M):	(0.050 + s)	s

$$K_{\text{sp}} = 8.7 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (0.050 + s)s \approx 0.050s;$$

$$s = \frac{8.7 \times 10^{-9}}{0.050} = 1.7 \times 10^{-7} \text{ M}$$

$$\text{Mass CaCO}_3 = (3.0 \times 10^2 \text{ mL}) \times \frac{1.7 \times 10^{-7} \text{ mol}}{1000 \text{ mL soln}} \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol}} = 5.1 \times 10^{-6} \text{ g CaCO}_3$$

60 The solubility product of PbBr_2 is 8.9×10^{-6} .

(a) Determine the molar solubility in pure water.

$$\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq)$$

Initial (M)	0	0
Change (M)	-s	+2s
Equilibrium (M)	s	2s

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2 = 8.9 \times 10^{-6} = (s)(2s)^2; s = \text{molar solubility} = 0.013 \text{ M}$$

(b) Determine the molar solubility in 0.20 M KBr solution.

KBr is a soluble salt that ionizes completely giving an initial concentration of $\text{Br}^- = 0.20 \text{ M}$.

$$\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq)$$

Initial (M)	0	0.20
Change (M)	-s	+2s
Equilibrium (M)	s	0.20 + 2s

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2 = 8.9 \times 10^{-6} = (s)(0.20 + 2s)^2 \approx (s)(0.20)^2; s = 2.2 \times 10^{-4} \text{ M}$$

(c) Determine the molar solubility in $0.20 \text{ M Pb(NO}_3)_2$ solution.

$\text{Pb(NO}_3)_2$ is a soluble salt that dissociates completely giving an initial concentration of $[\text{Pb}^{2+}] = 0.20 \text{ M}$.

$$\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq)$$

Initial (M):	0.20	0
Change (M):	-s	+2s
Equilibrium (M):	0.20 + s	2s

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2 = 8.9 \times 10^{-6} = (0.20 + s)(2s)^2 \approx (0.20)(2s)^2; s = 3.3 \times 10^{-3} \text{ M}$$

Check: You should also be able to predict the decrease in solubility due to a common-ion using Le Châtelier's principle. Adding Br^- or Pb^{2+} ions shifts the system to the left, thus decreasing the solubility of PbBr_2 .

61 Calculate the molar solubility of AgCl in a 1.00-L solution containing 10.0 g of dissolved CaCl₂

We first calculate the concentration of chloride ion in the solution.

$$[\text{Cl}^-] = \frac{10.0 \text{ g CaCl}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol CaCl}_2}{111.0 \text{ g CaCl}_2} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol CaCl}_2} = 0.180 \text{ M}$$

	$\text{AgCl}(s)$	\rightleftharpoons	$\text{Ag}^+(aq)$	$+$	$\text{Cl}^-(aq)$
Initial (M):			0.000		0.180
Change (M):	-s		+s		+s
Equilibrium (M):			s		(0.180 + s)

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10} = (s)(0.180 + s) \approx 0.180s; \quad s = \frac{1.6 \times 10^{-10}}{0.180} = 8.9 \times 10^{-10} \text{ M}$$

The molar solubility of AgCl in 0.180 M Cl⁻ is **8.9 × 10⁻¹⁰ M**.