

11.12 The dissolution-precipitation equilibrium is $\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{Cl}^-(aq)$. From the chemical equation, one mole of mercury(I) ions forms in solution for every one mole of solid that dissolves. Let S equal the concentration of mercury(I) present at equilibrium. Then the concentration of chloride is $2S$. The solubility-product expression is $K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = S(2S)^2 = 4S^3$. Solving for S gives a concentration of 8×10^{-7} M for the mercury(I) ion and 2×10^{-6} M for the chloride ion.

11.20 The calcium chloride and sodium fluoride solutions dilute each other as they are mixed. The concentration of Ca^{2+} is $2/3$ of 0.0010 M immediately after mixing, and the concentration of F^- is $1/3$ of 6.0×10^{-5} M. Substituting these concentrations in the K_{sp} expression for CaF_2 gives a Q of about 2.7×10^{-13} . Because this is less than K_{sp} , no precipitate forms.

11.26 The common-ion effect greatly reduces the solubility of the AgCl , which is only very slightly soluble in pure water in the first place. Let S represent this solubility. Then, $[\text{Cl}^-] = (0.150 + S)$ M and $[\text{Ag}^+] = S$ M. Substituting in the K_{sp} expression gives

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = S(0.150 + S) = 1.6 \times 10^{-10}$$

Solving for S gives the molar solubility of AgCl under these circumstances: 1.07×10^{-9} *mol/L*. This means that 1.07×10^{-10} mol of AgCl dissolves in 100 mL of the 0.150 M NaCl . Taking M of AgCl as 143.3 g mol^{-1} gives the gram-solubility as 1.5×10^{-8} g per 100 mL.

11.32 (a) Assume that neither the Mg^{2+} ion nor the OH^- ion from the dissolution of the $\text{Mg}(\text{OH})_2$ interacts further in the solution. Then, if S is the solubility of the $\text{Mg}(\text{OH})_2$, the concentration of Mg^{2+} ion is S and the concentration of OH^- ion is $2S$. At equilibrium,

$$K_{\text{sp}} = 1.2 \times 10^{-11} = S(2S)^2 \quad \text{from which} \quad S = 1.4 \times 10^{-4} \text{ mol L}^{-1}$$

(b) If the pH is buffered at a value of 9, then the $[\text{OH}^-]$ is being held at 10^{-5} M. This concentration is *less* than what forms from the dissolution of the $\text{Mg}(\text{OH})_2$ in pure water. After the dissolution of $\text{Mg}(\text{OH})_2$ comes to equilibrium, the concentration of OH^- ion remains at 10^{-5} M because of the action of the buffer. Let S again represent the solubility of the salt. Then:

$$K_{\text{sp}} = 1.2 \times 10^{-11} = S(10^{-5})^2$$

and the solubility is 0.12 mol L^{-1} .

11.36 (a) If the F^- ion concentration exceeds 8.8×10^{-6} M, then CaF_2 precipitates. If it exceeds 4.1×10^{-3} M, BaF_2 precipitates. These two concentrations are calculated by substitution into the two K_{sp} expressions. If we maintain the $[\text{F}^-]$ below 4.1×10^{-3} M, only the CaF_2 precipitates.

(b) If the $[\text{F}^-]$ is held at 4.1×10^{-3} M then the concentration of Ca^{2+} in equilibrium with it and the $\text{CaF}_2(s)$ is only 2.3×10^{-6} M. This is a fraction 4.6×10^{-6} of the 0.50 M concentration originally present.

11.56 At pH 14.0, if we assume $\text{Zn}(\text{OH})_2(s)$ is present, we have

$$[\text{Zn}^{2+}][\text{OH}^-]^2 = K_{\text{sp}} = 4.5 \times 10^{-17}$$

$$[\text{Zn}^{2+}] = \frac{4.5 \times 10^{-17}}{(1.0)^2} = 4.5 \times 10^{-17} \text{ M}$$

$$\frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{Zn}^{2+}][\text{OH}^-]^4} = K_f = 5 \times 10^{14}$$

$$[\text{Zn}(\text{OH})_4^{2-}] = K_f[\text{Zn}^{2+}][\text{OH}^-]^4 = (5 \times 10^{14})(4.5 \times 10^{-17})(1.0)^4 = 2.2 \times 10^{-2}$$

$$[\text{Zn}(\text{OH})_4^{2-}] + [\text{Zn}^{2+}] = 2.2 \times 10^{-2} + 4.5 \times 10^{-17} = 0.022 \text{ M} > 0.01 \text{ M}$$

so that there is a contradiction. Thus our assumption was false and no precipitate forms. We must therefore recalculate the concentrations using

$$\frac{[\text{Zn}^{2+}]}{[\text{Zn}(\text{OH})_4^{2-}]} = \frac{1}{K_f[\text{OH}^-]^4} = 2 \times 10^{-15}$$

$$[\text{Zn}(\text{OH})_4^{2-}] = 0.010 \text{ M and } [\text{Zn}^{2+}] = 2 \times 10^{-17} \text{ M}$$

In the second case,

$$[\text{Zn}^{2+}] = \frac{(4.5 \times 10^{-17})}{(0.10)^2} = 4.5 \times 10^{-15} \text{ M}$$

$$[\text{Zn}(\text{OH})_4^{2-}] = (5 \times 10^{14})(4.5 \times 10^{-15})(0.1)^4 = 2.2 \times 10^{-4}$$

$$[\text{Zn}(\text{OH})_4^{2-}] + [\text{Zn}^{2+}] = 2.2 \times 10^{-4} < 0.10 \text{ M}$$

so that in this case our assumption was correct and a precipitate forms.

11.66 (a) If all but 0.1 percent of the Fe^{3+} ion has been precipitated, then

$$[\text{Fe}^{3+}] = 0.001(0.01 \text{ M}) = 1 \times 10^{-5} \text{ M}$$

Since the solution is saturated with $\text{Fe}(\text{OH})_3$,

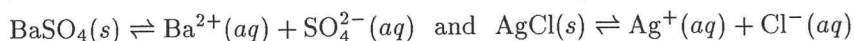
$$[\text{OH}^-]^3 = \frac{10^{-36}}{1 \times 10^{-5}} = 10^{-31}$$

$$[\text{OH}^-] = 5 \times 10^{-11} \text{ M and } [\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{5 \times 10^{-11}} = 2 \times 10^{-4} \text{ M}$$

for a pH of 3.7. At any higher pH, an even smaller fraction of the Fe^{3+} ion will remain in solution.

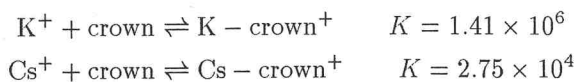
(b) $\text{Ni}(\text{OH})_2$ tends to precipitate when $[\text{Ni}^{2+}][\text{OH}^-]^2 \geq 6 \times 10^{-18}$. With Ni^{2+} at 0.01 M, this means that $[\text{OH}^-]^2 < 6 \times 10^{-16}$ to avoid precipitation of $\text{Ni}(\text{OH})_2$, or $[\text{OH}^-] < 2.4 \times 10^{-8}$ M. This corresponds to $[\text{H}_3\text{O}^+] > 4 \times 10^{-7}$ M, or pH < 6.4. Thus, between pH 3.7 and 6.4, Fe^{3+} and Ni^{2+} could, in principle, be separated effectively by precipitation of $\text{Fe}(\text{OH})_3$.

11.68 Two dissolution-precipitation equilibria take place simultaneously. They are:



We mix solutions of Ag_2SO_4 and BaCl_2 , both of which are dissociated into ions. The concentrations of the four ions after the mixing, but before any precipitation has occurred are $[\text{Ba}^{2+}] = 0.020 \text{ M}$, $[\text{Ag}^+] = 0.020 \text{ M}$, $[\text{Cl}^-] = 0.040 \text{ M}$, and $[\text{SO}_4^{2-}] = 0.010 \text{ M}$. Assume that the Ba^{2+} and the SO_4^{2-} react completely to form $\text{BaSO}_4(s)$. Then the concentration of the sulfate is zero, and the concentration of the barium ion, which is in excess in the precipitation reaction, is 0.010 M. Substituting this 0.010 M into the K_{sp} expression gives $[\text{SO}_4^{2-}] = 1.1 \times 10^{-8} \text{ M}$, which is indeed very close to zero. In the same way, Cl^- is in excess relative to Ag^+ . At equilibrium, its concentration will be 0.020 M. The K_{sp} for AgCl then gives $[\text{Ag}^+] = 8.0 \times 10^{-9} \text{ M}$.

11.46 Let us abbreviate the 18-crown-6 as "crown." We have the two equilibria:



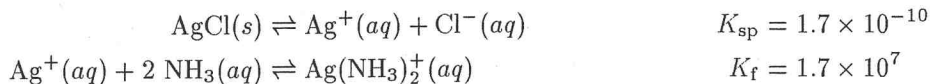
Both equilibrium constants for the formation of crown complexes are large, so both equilibria lie far to the right. The crown compound is in excess in the solution. Thus, effectively all of the K^+ and Cs^+ ion are consumed leaving $0.30 - 0.020 - 0.020 = 0.26 \text{ mol L}^{-1}$ of crown and forming 0.020 mol L^{-1} of K-crown^+ and 0.020 mol L^{-1} of Cs-crown^+ . We construct the appropriate equilibrium expressions and substitute the concentrations just listed:

$$K = \frac{[\text{Kcrown}^+]}{[\text{K}^+][\text{crown}]} = 1.41 \times 10^6$$

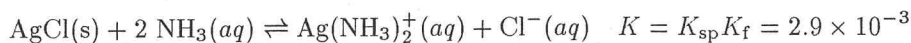
$$1.41 \times 10^6 = \frac{0.020}{[\text{K}^+]0.26}; \quad [\text{K}^+] = 5.5 \times 10^{-8} \text{ M}$$

A similar computation on the Cs^+ equilibrium gives $[\text{Cs}^+] = 2.8 \times 10^{-6} \text{ M}$.

11.48



Adding the second equation to the first gives



$$[\text{NH}_3] = 1.0 - 2x \quad \text{and} \quad [\text{Ag}(\text{NH}_3)_2^+] = x = [\text{Cl}^-]$$

$$\frac{x^2}{(1.0 - 2x)^2} = 2.9 \times 10^{-3}$$

$$\frac{x}{1.0 - 2x} = 0.054 \quad \text{so that} \quad x = 0.049 = [\text{Ag}(\text{NH}_3)_2^+]$$

0.049 mol AgCl dissolves per liter, or $(0.049 \text{ mol})(143.3 \text{ g mol}^{-1}) = 7.0 \text{ g}$.