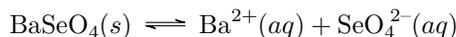# Suggested Problems: Chapter 15

15.3: There is no change in the concentrations of Ag^+ or CrO_4^{2-} because the solid, Ag_2CrO_4, does not appear in the equilibrium constant expression and, therefore, does not affect the position of the equilibrium.

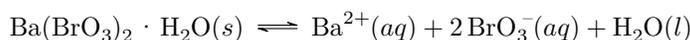**15.11:** For (a), the solubility reaction is

$$BaSeO_4(s) \rightleftharpoons Ba^{2+}(aq) + SeO_4^{2-}(aq)$$

for which the solubiity product is $K_{sp} = [Ba^{2+}][SeO_4^{2-}]$. The molar solubility of $BaSeO_4$ is

$$S = \frac{0.0118 \text{ g/L}}{280.28 \text{ g/mol}} = 4.21 \times 10^{-5} \text{ M}$$

Given the solubility reaction, we know $[Ba^{2+}] = [SeO_4^{2-}] = S$, which gives

$$K_{sp} = [Ba^{2+}][SeO_4^{2-}] = (4.21 \times 10^{-5})(4.21 \times 10^{-5}) = 1.77 \times 10^{-9}$$

For (b), the solubility reaction is

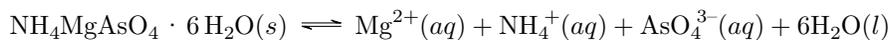$$Ba(BrO_3)_2 \cdot H_2O(s) \rightleftharpoons Ba^{2+}(aq) + 2 BrO_3^-(aq) + H_2O(l)$$

for which the solubility product is $K_{sp} = [Ba^{2+}][BrO_3^-]^2$. The molar solubility of $Ba(BrO_3)_2 \cdot H_2O$ is

$$S = \frac{3.0 \text{ g/L}}{411.147 \text{ g/mol}} = 7.3 \times 10^{-3} \text{ M}$$

Given the solubility reaction, we know $[Ba^{2+}] = S$ and that $[BrO_3^-] = 2S$, which gives

$$K_{sp} = [Ba^{2+}][BrO_3^-]^2 = (7.3 \times 10^{-3})(2 \times (7.3 \times 10^{-3}))^2 = 1.6 \times 10^{-6}$$

For (c), the solubility reaction is

$$NH_4MgAsO_4 \cdot 6 H_2O(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + AsO_4^{3-}(aq) + 6H_2O(l)$$

for which the solubility product is $K_{sp} = [Mg^{2+}][NH_4^+][AsO_4^{3-}]$. The molar solubility of $NH_4MgAsO_4 \cdot 6 H_2O$ is

$$S = \frac{0.38 \text{ g/L}}{289.3544 \text{ g/mol}} = 1.3 \times 10^{-3} \text{ M}$$

Given the solubility reaction, we know $[Mg^{2+}] = [NH_4^+] = [AsO_4^{3-}] = S$, which gives

$$K_{sp} = [Mg^{2+}][NH_4^+][AsO_4^{3-}] = (1.3 \times 10^{-3})^3 = 2.2 \times 10^{-9}$$

For (d), the solubility reaction is

$$La_2(MoO_4)_3(s) \rightleftharpoons 2La^{3+}(aq) + 3MoO_4^{2-}(aq)$$

for which the solubility product is $K_{sp} = [\text{La}^{3+}]^2[\text{MoO}_4^{2-}]^3$. The molar solubility of $\text{La}_2(\text{MoO}_4)_3$ is

$$S = \frac{0.0179 \text{ g/L}}{757.62 \text{ g/mol}} = 2.36 \times 10^{-5} \text{ M}$$

Given the solubility reaction, we know $[\text{La}^{3+}] = 2S$ and that $[\text{MoO}_4^{2-}] = 3S$, which gives

$$K_{sp} = [\text{La}^{3+}]^2[\text{MoO}_4^{2-}]^3 = (2 \times (2.36 \times 10^{-5}))^2(3 \times (2.36 \times 10^{-5}))^3 = 7.91 \times 10^{-22}$$

15.13: For (a), the solubility reaction is

$$\text{KHC}_4\text{H}_4\text{O}_6(s) \rightleftharpoons \text{K}^+(aq) + \text{HC}_4\text{H}_4\text{O}_6^-(aq)$$
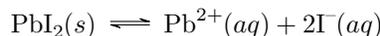
for which $K_{sp} = [\text{K}^+][\text{HC}_4\text{HO}_6^-] = 3 \times 10^{-4}$. Given the solubility reaction, we know that $S = [\text{K}^+]$ and that $[\text{HC}_4\text{HO}_6^-] = [\text{K}^+]$. Substituting into the K_{sp} expression

$$K_{sp} = [\text{K}^+][\text{HC}_4\text{HO}_6^-] = (S)(S) = 3 \times 10^{-4}$$

and solving gives $S = 2 \times 10^{-2}$ M.

For (b), the solubility reaction is

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

for which $K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = 8.7 \times 10^{-9}$. Given the solubility reaction, we know that $S = [\text{Pb}^{2+}]$ and that $[\text{I}^-] = 2 \times [\text{Pb}^{2+}]$. Substituting into the K_{sp} expression

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = (S)(2S)^2 = 4S^3 = 8.7 \times 10^{-9}$$

and solving gives $S = 1.3 \times 10^{-3}$ M.

For (c), the solubility reaction is

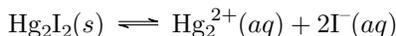$$\text{Ag}_4[\text{Fe(CN)}_6](s) \rightleftharpoons 4\text{Ag}^+(aq) + \text{Fe(CN)}_6^{3-}(aq)$$

for which $K_{sp} = [\text{Ag}^+]^4[\text{Fe(CN)}_6^{3-}] = 1.55 \times 10^{-41}$. Given the solubility reaction, we know that $S = [\text{Fe(CN)}_6^{3-}]$ and that $[\text{Ag}^+] = 4 \times [\text{Fe(CN)}_6^{3-}]$. Substituting into the K_{sp} expression

$$K_{sp} = [\text{Ag}^+]^4[\text{Fe(CN)}_6^{3-}] = (4S)^4(S) = 1.55 \times 10^{-41}$$

and solving gives $S = 2.27 \times 10^{-9}$ M.

For (d), the solubility reaction is

$$\text{Hg}_2\text{I}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{I}^-(aq)$$
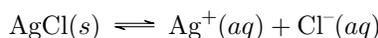
for which $K_{sp} = [\text{Hg}_2^{2+}][\text{I}^-]^2 = 4.5 \times 10^{-29}$. Given the solubility reaction, we know that $S = [\text{Hg}_2^{2+}]$ and that $[\text{I}^-] = 2 \times [\text{Hg}_2^{2+}]$. Substituting into the K_{sp} expression

$$K_{sp} = [\text{Hg}_2^{2+}][\text{I}^-]^2 = (S)(2S)^2 = 4S^3 = 4.5 \times 10^{-29}$$

and solving gives $S = 2.2 \times 10^{-10}$ M.

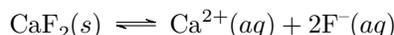**15.15:** For (a), the solubility reaction is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

If we assume that the initial concentration of Ag^+ is 0 and that the initial concentration of Cl^- is 0.025 M, then the equilibrium concentration of Ag^+ is x and the equilibrium concentration of Cl^- is $0.025 + x$. Substituting into the equilibrium constant expression and making the assumption that $0.025 + x \approx 0.025$

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = (x)(0.025 + x) \approx (x)(0.025)$$

gives $x = [Ag^+] = 7.2 \times 10^{-9}$ M and $[Cl^-] = 0.025 + 7.2 \times 10^{-9} \approx 0.025$ M. A check of the simplifying assumption shows that it introduces an error of $2.9 \times 10^{-5}\%$.

For (b), the solubility reaction is

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

If we assume that the initial concentration of Ca^{2+} is 0 and that the initial concentration of F^- is 0.00133 M, then the equilibrium concentration of Ca^{2+} is x and the equilibrium concentration of F^- is $0.00133 + 2x$. Substituting into the equilibrium constant expression and making the assumption that $0.00133 + 2x \approx 0.00133$

$$K_{sp} = 3.9 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (x)(0.00133 + 2x)^2 \approx (x)(0.00133)^2$$

gives $x = [Ca^{2+}] = 2.2 \times 10^{-5}$ M and $[F^-] = 0.00133 + 2 \times (2.2 \times 10^{-5}) \approx 0.00133$ M. A check of the simplifying assumption shows that it introduces an error of 1.7%.

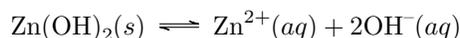For (c), the solubility reaction is

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^-(aq)$$

If we assume that the initial concentration of Ag^+ is 0 and that the initial concentration of CrO_4^- is 0.2238 M (19.50 g K_2SO_4 in 0.500 L), then the equilibrium concentration of Ag^+ is $2x$ and the equilibrium concentration of CrO_4^- is $0.2238 + x$. Substituting into the equilibrium constant expression and making the assumption that $0.2238 + x \approx 0.2238$

$$K_{sp} = 1.18 \times 10^{-18} = [Ag^+]^2[CrO_4^-] = (2x)^2(0.2238) + x \approx (2x)^2(0.2388)$$

gives $x = 1.15 \times 10^{-9}$; thus $[Ag^+] = 2x = 2.30 \times 10^{-9}$ M and $[CrO_4^-] = 0.2238 + 1.15 \times 10^{-9} \approx 0.2238$ M. A check of the simplifying assumption shows that it introduces an error of $5.1 \times 10^{-7}\%$.

For (d), the solubility reaction is

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

If we assume that the initial concentration of Zn^{2+} is 0 and that the initial concentration of OH^- is 2.8×10^{-3} M (a pH of 11.45), then the equilibrium concentration of Zn^{2+} is x and the equilibrium concentration of OH^- is 2.8×10^{-3} (no change, because the pH is fixed by buffering). Substituting into the equilibrium constant expression

$$K_{sp} = 4.5 \times 10^{-17} = [Zn^{2+}][OH^-]^2 = (x)(2.8 \times 10^{-3})^2$$

gives $x = [\text{Zn}^{2+}] = 5.7 \times 10^{-12}$ M and $[\text{OH}^-] = 2.8 \times 10^{-3}$ M.

15.25: The solubility reaction is

$$\text{CaSO}_4 \cdot 2\,\text{H}_2\text{O}(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 2\text{H}_2\text{O}(l)$$
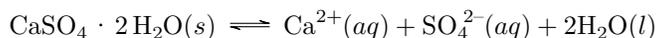
for which $K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5}$. The initial concentration of Ca^{2+} is 0 and the initial concentration of SO_4^{2-} is 0.010 M. The equilibrium concentration of Ca^{2+} is x and the equilibrium concentration of SO_4^{2-} is $0.010 + x$. If we assume that $0.010 + x \approx 0.010$, then

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (x)(0.010 - x) \approx (x)(0.010) = 2.4 \times 10^{-5}$$

and $x = 0.0024$, which gives an error of 24%, which is too large. From here we can retreat and solve rigorously, or we can try a new assumption. Let's do the latter here just to see how it works. Our new assumption is that $0.010 + x \approx 0.01 + 0.0024 = 0.0124$; this gives

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (x)(0.0124) = 2.4 \times 10^{-5}$$

and $x = 0.0019$, which gives an error of 4%, which is an error we can accept. If the equilibrium concentration of Ca^{2+} is 0.0019 M, then this is the concentration of dissolved $\text{CaSO}_4 \cdot 2\,\text{H}_2\text{O}$; at 172.16 g/mol, this is 0.34 g of $\text{CaSO}_4 \cdot 2\,\text{H}_2\text{O}$.

15.64: *Note: there is a typo in this problem. The volume of 0.100 M NH_3 is 0.150 L, not 1.150 L.* The complexation reaction is

$$\text{Cd}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cd}(\text{NH}_3)_4^{2+}(aq)$$
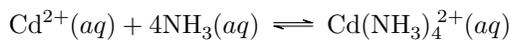
for which

$$\beta_4 = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = 4.0 \times 10^6$$

The initial concentrations of the reactants and products are

$$[\text{Cd}^{2+}] = \frac{(0.100\ \text{L})(0.0100\ \text{M})}{0.250\ \text{L}} = 0.00400\ \text{M}$$

$$[\text{NH}_3] = \frac{(0.150\ \text{L})(0.100\ \text{M})}{0.250\ \text{L}} = 0.0600\ \text{M}$$

$$[\text{Cd}(\text{NH}_3)_4^{2+}] = 0\ \text{M}$$

Because the equilibrium constant is so large and the initial concentration of the one product is so small (as in zero), it is best to allow the system to react to completion, using up the limiting reagent, which is Cd^{2+}; thus, the new set of initial concentrations is

$$0.00400\ \text{M} - 0.00400\ \text{M} = 0\ \text{M}$$

$$[\text{NH}_3] = 0.0600\ \text{M} - 4 \times 0.00400\ \text{M} = 0.0440\ \text{M}$$

$$[\text{Cd(NH}_3)_4^{2+}] = 0 \text{ M} + 0.00400 \text{ M} = 0.00400 \text{ M}$$

and the equilibrium concentrations are

$[\text{Cd}^{2+}] = x$

$$[\text{NH}_3] = 0.0440 + 4x$$

$$[\text{Cd(NH}_3)_4^{2+}] = 0.00400 - x$$

Substituting into the equillibrium constant expression and making two simplifying assumptions gives

$$\beta_4 = \frac{[\text{Cd(NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = \frac{0.00400 - x}{(x)(0.0440 + 4x)^4} \approx \frac{0.00400}{(x)(0.0440)^4} = 4.0 \times 10^6$$

which we solve for x obtaining a value of 2.668×10^{-4}. Checking the error in the assumption gives an error of 6.7% for $\text{Cd(NH}_3)_4^{2+}$ and error of 2.4% for NH_3. To refine our calculation, we assume that

$$[\text{Cd(NH}_3)_4^{2+}] = 0.00400 - x \approx 0.00400 - 2.668 \times 10^{-4} = 0.0037$$

and that

$$[\text{NH}_3] = 0.0440 + 4x \approx 0.0451$$

Substituting into the equillibrium constant expression

$$\beta_4 = \frac{[\text{Cd(NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = \frac{0.00400 - x}{(x)(0.0440 + 4x)^4} \approx \frac{0.0037}{(x)(0.0451)^4} = 4.0 \times 10^6$$

gives x as 2.24×10^{-4}. The error in our new assumption now is approximately 1%, which is acceptable. The concentration of Cd^{2+} is 2.24×10^{-4} M.