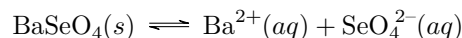


## Suggested Problems: Chapter 15

**15.3:** There is no change in the concentrations of  $\text{Ag}^+$  or  $\text{CrO}_4^{2-}$  because the solid,  $\text{Ag}_2\text{CrO}_4$ , 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



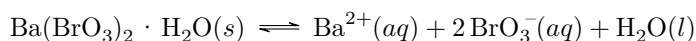
for which the solubility product is  $K_{sp} = [\text{Ba}^{2+}][\text{SeO}_4^{2-}]$ . The molar solubility of  $\text{BaSeO}_4$  is

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

Given the solubility reaction, we know  $[\text{Ba}^{2+}] = [\text{SeO}_4^{2-}] = S$ , which gives

$$K_{sp} = [\text{Ba}^{2+}][\text{SeO}_4^{2-}] = (4.21 \times 10^{-5})(4.21 \times 10^{-5}) = 1.77 \times 10^{-9}$$

For (b), the solubility reaction is



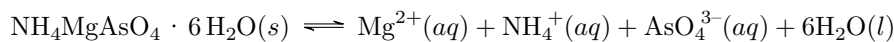
for which the solubility product is  $K_{sp} = [\text{Ba}^{2+}][\text{BrO}_3^-]^2$ . The molar solubility of  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$  is

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

Given the solubility reaction, we know  $[\text{Ba}^{2+}] = S$  and that  $[\text{BrO}_3^-] = 2S$ , which gives

$$K_{sp} = [\text{Ba}^{2+}][\text{BrO}_3^-]^2 = (7.3 \times 10^{-3})(2 \times (7.3 \times 10^{-3}))^2 = 1.6 \times 10^{-6}$$

For (c), the solubility reaction is



for which the solubility product is  $K_{sp} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{AsO}_4^{3-}]$ . The molar solubility of  $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$  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  $[\text{Mg}^{2+}] = [\text{NH}_4^+] = [\text{AsO}_4^{3-}] = S$ , which gives

$$K_{sp} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{AsO}_4^{3-}] = (1.3 \times 10^{-3})^3 = 2.2 \times 10^{-9}$$

For (d), the solubility reaction is



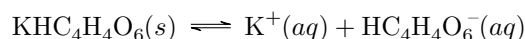
for which the solubility product is  $K_{sp} = [\text{La}^{3+}]^2[\text{MoO}_4^{2-}]^3$ . The molar solubility of  $\text{La}_2(\text{MoO}_4)_3$  is

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

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

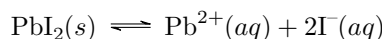


for which  $K_{sp} = [\text{K}^+][\text{HC}_4\text{HO}_6^-] = 3 \times 10^{-4}$ . Given the solubility reaction, we know that  $S = [\text{K}^+]$  and that  $[\text{HC}_4\text{HO}_6^-] = [\text{K}^+]$ . Substituting into the  $K_{sp}$  expression

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

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

For (b), the solubility reaction is



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  $S = 1.3 \times 10^{-3} \text{ M}$ .

For (c), the solubility reaction is

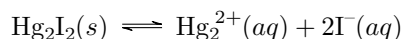


for which  $K_{sp} = [\text{Ag}^+]^4[\text{Fe}(\text{CN})_6^{3-}] = 1.55 \times 10^{-41}$ . Given the solubility reaction, we know that  $S = [\text{Fe}(\text{CN})_6^{3-}]$  and that  $[\text{Ag}^+] = 4 \times [\text{Fe}(\text{CN})_6^{3-}]$ . Substituting into the  $K_{sp}$  expression

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

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

For (d), the solubility reaction is

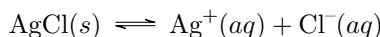


for which  $K_{sp} = [\text{Hg}_2^{2+}][\text{I}^-]^2 = 4.5 \times 10^{-29}$ . Given the solubility reaction, we know that  $S = [\text{Hg}_2^{2+}]$  and that  $[\text{I}^-] = 2 \times [\text{Hg}_2^{2+}]$ . Substituting into the  $K_{sp}$  expression

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

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

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

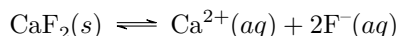


If we assume that the initial concentration of  $\text{Ag}^+$  is 0 and that the initial concentration of  $\text{Cl}^-$  is 0.025 M, then the equilibrium concentration of  $\text{Ag}^+$  is  $x$  and the equilibrium concentration of  $\text{Cl}^-$  is  $0.025 + x$ . Substituting into the equilibrium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

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

gives  $x = [\text{Ag}^+] = 7.2 \times 10^{-9}$  M and  $[\text{Cl}^-] = 0.025 + 7.2 \times 10^{-9} \approx 0.025$  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



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

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

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

For (c), the solubility reaction is

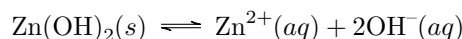


If we assume that the initial concentration of  $\text{Ag}^+$  is 0 and that the initial concentration of  $\text{CrO}_4^{2-}$  is 0.2238 M (19.50 g  $\text{K}_2\text{SO}_4$  in 0.500 L), then the equilibrium concentration of  $\text{Ag}^+$  is  $2x$  and the equilibrium concentration of  $\text{CrO}_4^{2-}$  is  $0.2238 + x$ . Substituting into the equilibrium constant expression and making the assumption that  $0.2238 + x \approx 0.2238$

$$K_{sp} = 1.18 \times 10^{-18} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2x)^2(0.2238 + x) \approx (2x)^2(0.2238)$$

gives  $x = 1.15 \times 10^{-9}$ ; thus  $[\text{Ag}^+] = 2x = 2.30 \times 10^{-9}$  M and  $[\text{CrO}_4^{2-}] = 0.2238 + 1.15 \times 10^{-9} \approx 0.2238$  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

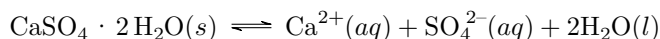


If we assume that the initial concentration of  $\text{Zn}^{2+}$  is 0 and that the initial concentration of  $\text{OH}^-$  is  $2.8 \times 10^{-3}$  M (a pH of 11.45), then the equilibrium concentration of  $\text{Zn}^{2+}$  is  $x$  and the equilibrium concentration of  $\text{OH}^-$  is  $2.8 \times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

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

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

**15.25:** The solubility reaction is



for which  $K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5}$ . The initial concentration of  $\text{Ca}^{2+}$  is 0 and the initial concentration of  $\text{SO}_4^{2-}$  is 0.010 M. The equilibrium concentration of  $\text{Ca}^{2+}$  is  $x$  and the equilibrium concentration of  $\text{SO}_4^{2-}$  is  $0.010 + x$ . If we assume that  $0.010 + x \approx 0.010$ , then

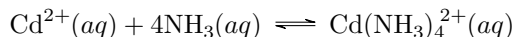
$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (x)(0.010 - x) \approx (x)(0.010) = 2.4 \times 10^{-5}$$

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  $\text{Ca}^{2+}$  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  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

**15.63:** The complexation reaction is



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  $\text{Cd}^{2+}$ ; thus, the new set of initial concentrations is

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

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

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

and the equilibrium concentrations are

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

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

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

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

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

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

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

and that

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

Substituting into the equilibrium constant expression

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

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