17.68 According Appendix D.3, K_{sp} for $Ag_2S(s)$ is of the type

$$Ag_{2}S(s) + H_{2}O(l) \rightleftharpoons 2Ag^{+}(aq) + HS^{-}(aq) + OH^{-}(aq) \qquad K_{sp}$$

$$HS^{-}(aq) + H^{+}(aq) \rightleftharpoons H_{2}S(aq) \qquad 1/K_{al}$$

$$2[Ag^{+}(aq) + 2Cl^{-}(aq) \rightleftharpoons AgCl_{2}^{-}(aq)] \qquad K_{f}^{2}$$

$$H^{+}(aq) \qquad OH^{-}(aq) \qquad <=> H2O(1) \qquad 1/K_{bl}$$

$$Ag_{s}S(s) + H_{s}O(l) + H^{+}(aq) + 4Cl^{-}(aq) \rightleftharpoons 2AgCl_{s}^{-}(aq) + H_{s}S(aq)$$

Add H (aq) to each side to obtain the overall reacation water equil. above

$$Ag_2S(s) + 2H^{\dagger}(aq) + 4Cl^{\dagger}(aq) \rightleftharpoons 2AgCl_2^{\dagger}(aq) + H_2S(aq)$$

$$K = \frac{K_{sp} \times K_f^2}{K_{a1} \text{ Kw}} = \frac{(6 \times 10^{-51})(1.1 \times 10^5)^2}{(9.5 \times 10^{-8})(1.0 \times 10^5 - 14)} = 7.64 \times 10^{-34} = 8 \times 10^{-34} = 7.64 \times 10^5 - 20$$

Precipitation and Separation of Ions (Section 17.6)

- 17.69 Analyze/Plan. Follow the logic in Sample Exercise 17.16. Precipitation conditions: will Q (see Chapter 15) exceed K_{sp} for the compound? Solve.
 - (a) In base, Ca^{2^+} can form $Ca(OH)_2(s)$. $Ca(OH)_2(s) \iff Ca^{2^+}(aq) + 2OH^-(aq); \quad K_{sp} = [Ca^{2^+}][OH^-]^2$ $Q = [Ca^{2^+}][OH^-]^2; [Ca^{2^+}] = 0.050 \, M; pOH = 14 8.0 = 6.0; [OH^-] = 1.0 \times 10^{-6} \, M$ $Q = (0.050)(1.0 \times 10^{-6})^2 = 5.0 \times 10^{-14}; K_{sp} = 6.5 \times 10^{-6} \, (Appendix D.3)$ $Q < K_{sp}, \text{ no Ca}(OH)_2 \text{ precipitates.}$
 - (b) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{-2}(aq); K_{sp} = [Ag+]^2[SO_4^{-2}]$ $[Ag^+] = \frac{0.050 M \times 100 \text{ mL}}{110 \text{ mL}} = 4.545 \times 10^{-2} = 4.5 \times 10^{-2} M$ $[SO_4^{-2}] = \frac{0.050 M \times 10 \text{ mL}}{110 \text{ mL}} = 4.545 \times 10^{-3} = 4.5 \times 10^{-3} M$ $Q = (4.545 \times 10^{-2})^2 (4.545 \times 10^{-3}) = 9.4 \times 10^{-6}; K_{sp} = 1.5 \times 10^{-5}$ $Q < K_{sp}, \text{ no } Ag_2SO_4 \text{ precipitates.}$
- 17.70 (a) $Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2OH^-(aq); K_{sp} = [Co^{2+}][OH^-]^2 = 1.3 \times 10^{-15}$ $pH = 8.5; pOH = 14 - 8.5 = 5.5; [OH^-] = 10^{-5.5} = 3.16 \times 10^{-6} = 3 \times 10^{-6} M$ $Q = (0.020)(3.16 \times 10^{-6})^2 = 2 \times 10^{-13}; Q > K_{sp}, Co(OH), will precipitate.$
 - (b) $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq); K_{sp} = [Ag+][IO_3^-] = 3.1 \times 10^{-8}$ $[Ag^+] = \frac{0.010 M Ag^+ \times 0.020 L}{0.030 L} = 6.667 \times 10^{-3} = 6.7 \times 10^{-3} M$