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

$$Ag_2S(s) + H_2O(l) \rightleftharpoons 2Ag^+(aq) + HS^-(aq) + OH^-(aq) \qquad K_{sp}$$

$$HS^-(aq) + H^+(aq) \rightleftharpoons H_2S(aq) \qquad 1/K_{a1}$$

$$2[Ag^+(aq) + 2Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)] \qquad K_f^2$$

H+(aq) + OH-(aq) <=> H2O(l) 1/Kw

$$Ag_2S(s) + H_2O(l) + H^+(aq) + 4Cl^-(aq) \rightleftharpoons 2AgCl_2^-(aq) + H_2S(aq) + OH\text{-}(aq)$$

~~Add $H^+(aq)$ to each side to obtain the overall reaction~~ really need to add in water equil. above

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

$$K = \frac{K_{sp} \times K_f^2}{K_{a1}\ Kw} = \frac{(6 \times 10^{-51})(1.1 \times 10^5)^2}{(9.5 \times 10^{-8})\ (1.0\ x10\text{^}-14)} = \cancel{7.64 \times 10^{-34}} = \cancel{8 \times 10^{-34}} = 7.64\ x\ 10\text{^}-20$$

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 $Ca(OH)_2(s)$.

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$; $K_{sp} = [Ca^{2+}][OH^-]^2$

$Q = [Ca^{2+}][OH^-]^2$; $[Ca^{2+}] = 0.050\ M$; 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)

$Q < K_{sp}$, no $Ca(OH)_2$ precipitates.

(b) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$; $K_{sp} = [Ag+]^2[SO_4^{2-}]$

$$[Ag^+] = \frac{0.050\ M \times 100\ mL}{110\ mL} = 4.545 \times 10^{-2} = 4.5 \times 10^{-2}\ M$$

$$[SO_4^{2-}] = \frac{0.050\ M \times 10\ mL}{110\ mL} = 4.545 \times 10^{-3} = 4.5 \times 10^{-3}\ M$$

$Q = (4.545 \times 10^{-2})^2\ (4.545 \times 10^{-3}) = 9.4 \times 10^{-6}$; $K_{sp} = 1.5 \times 10^{-5}$

$Q < K_{sp}$, no Ag_2SO_4 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; $[OH^-] = 10^{-5.5} = 3.16 \times 10^{-6} = 3 \times 10^{-6}\ M$

$Q = (0.020)(3.16 \times 10^{-6})^2 = 2 \times 10^{-13}$; $Q > K_{sp}$, $Co(OH)_2$ will precipitate.

(b) $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$; $K_{sp} = [Ag+][IO_3^-] = 3.1 \times 10^{-8}$

$$[Ag^+] = \frac{0.010\ M\ Ag^+ \times 0.020\ L}{0.030\ L} = 6.667 \times 10^{-3} = 6.7 \times 10^{-3}\ M$$