More stuff about Aqueous Equilibria: CH.17, Part 6

Factors Affecting Solubility

- pH: If a substance has a basic anion, it will be more soluble in an acidic solution

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$$
$$F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$$

* F^- is a base so it reacts with H^+ to form HF, removing it from the first equilibrium, which shifts right on purpose

increasing solubility with basic anion

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^-(aq)$$
Chalk

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 1.4 \times 10^{-8}$$

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$$
$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \quad K_{sp} = 2.07 \times 10^{-33}$$

$$PO_4^{3-}(aq) + H^+(aq) \rightleftharpoons HPO_4^{2-}(aq)$$ still base

$$+ 3H^+ \rightleftharpoons H_3PO_4(aq)$$

- Transition metal ions can react w/ Lewis bases to form complex ions, increasing solubility of their salts

How Complex Ion formation Affects Solubility

- Silver chloride is quite insoluble ($K_{sp} = 1.6 \times 10^{-10}$)
- In presence of NH_3, solubility greatly increases because Ag^+ forms complex ions with NH_3

$$Ag^+ + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$$

~~Dissolving AgCl in NH_3~~

~~$AgCl(s) \rightleftharpoons Ag$~~

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]_2} = 1.7 \times 10^7$$

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.6 \times 10^{-10}$

$\underline{x\,Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+ \quad K_f = 1.7 \times 10^7}$

$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-(aq) \quad K_{net} = K_{sp} \cdot K_f$

$= 2.8 \times 10^{-3}$

How much $AgCl(s)$ dissolves in 1L H_2O?

$K_{sp} = 1.6 \times 10^{-10} = x^2 \qquad x = 1.3 \times 10^{-5}\ M$

1.3×10^{-5} moles AgCl dissolves

How much dissolves in 1L of 0.5M NH_3?

$$K_{net} = 2.8 \times 10^{-3} = \frac{[Ag(NH_3)]^+[Cl^-]}{[NH_3]^2} = \frac{x^2}{(0.5)^2}$$

$x = 0.026\ M$

0.026 moles AgCl dissolves

Factors Affecting Solubility

- Amphoteric species can react as an acid or as a base
- Many metals (ie. Cu, Zn, Sn, Pb, Al) form amphoteric oxides or hydroxides
- Solubility of amphoteric species will be increased in both acid and base

Example: $Al(OH)_3$

As a base: $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$

As an acid: $Al(OH)_3 + OH^- \rightarrow \underbrace{Al(OH)_4^-}_{\text{complex ion}}$

Will a precipitate form?

- Calculate the reaction quotient, Q, and compare it to the solubility product constant, ksp.
  - ✓ If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  - ✓ If $Q < K_{sp}$, more solid can dissolve, so no precipitate forms.
  - ✓ If $Q > K_{sp}$, a precipitate will form

1.0×10^{-4} M Pb^{2+}, 1.0×10^{-4} M Ag^+ in solution.
S^{2-} is added. What metal will precipitate first?

① K_{sp} for $PbS = 7 \times 10^{-29}$ $\quad PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$
② K_{sp} for $Ag_2S = 1.6 \times 10^{-49}$ $\quad Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$

① $K_{sp} = [Pb^{2+}][S^{2-}] = 7 \times 10^{-29}$

$$[S^{2-}] = \frac{7 \times 10^{-29}}{\underset{\uparrow\, 1.0 \times 10^{-4}}{[Pb^{2+}]}} = 7 \times 10^{-25} M \leftarrow \text{when } Pb^{2+} \text{ precipitates}$$

solving for $[S^{2-}]$ at which $Q = K_{sp}$

② $K_{sp} = [Ag^+]^2[S^{2-}] = 1.6 \times 10^{-49}$ $\quad$ when Ag^+ precipitates

$$[S^{2-}] = \frac{1.6 \times 10^{-49}}{(1.0 \times 10^{-4})^2} = 1.6 \times 10^{-41} M$$

Selective Precipitation of Ions

- Differences in solubility of salts can be used to separate ions in a mixture
- "Qualitative Analysis" of ions in a solution

(ex) $Ni(NO_3)_2$ $\quad 1.5 \times 10^{-6}$ M

Add solid Na_2CO_3 $\quad$ How much can we add before we get a precipitate?

$NiCO_3$ $\quad K_{sp} = 1.4 \times 10^{-7}$

$K_{sp} = [Ni^{2+}][CO_3^{2-}]$ $\quad NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$

$= 1.5 \times 10^{-6} = [CO_3^{2-}]$

$[CO_3^{2-}] = 9.3 \times 10^{-2}$ M at $Q = K$