AP Solubility Set I

1. (80-8) Account for the difference in solubility described in each of the following experimental observations (write reactions!):
   
   (a) BaCO₃, BaSO₃, and BaSO₄ are only slightly soluble in water, but the first two dissolve in HCl solution whereas BaSO₄ does not.
   (b) AgCl, Hg₂Cl₂, and PbCl₂ are only slightly soluble in water, but AgCl does dissolve in ammonia solution whereas the other two do not.
   (c) Fe(OH)₃ and Al(OH)₃ are only slightly soluble in water, but Al(OH)₃ dissolves in concentrated NaOH whereas Fe(OH)₃ does not.

2. (84-6) Given solid samples of KI and of (NH₄)₂CO₃. Briefly describe four simple laboratory tests by which these two compounds can be distinguished. For each test, report the expected result for each compound.

3. (85-1) At 25 °C the solubility product constant, K_{sp}, for strontium sulfate, SrSO₄, is 7.6 x 10⁻⁷. The solubility product constant for strontium fluoride, SrF₂, is 7.9 x 10⁻¹⁰
   
   (a) What is the molar solubility of SrSO₄ in pure water at 25 °C?
   (b) What is the molar solubility of SrF₂ in pure water at 25 °C?
   (c) An aqueous solution of Sr(NO₃)₂ is added slowly to 1.0 liter of a well-stirred solution containing 0.020 mole F⁻ and 0.10 mole SO₄²⁻ at 25 °C. (You may assume that the added Sr(NO₃)₂ solution does not materially affect the total volume of the system.) Which salt precipitates first? What is the concentration of strontium ion, Sr²⁺, in the solution when the first precipitate begins to form?
   (d) As more Sr(NO₃)₂ is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?

4. (90-1) The solubility of iron(II) hydroxide, Fe(OH)₂, is 1.43 x 10⁻³ gram per liter at 25 °C.
   
   (a) Write a balanced equation for the solubility equilibrium.
   (b) Write the expression for the solubility product constant, K_{sp}, and calculate its value.
   (c) Calculate the pH of the saturated solution of Fe(OH)₂ at 25 °C.
   (d) A 50.0-milliliter sample of 3.00 x 10⁻³ molar FeSO₄ solution is added to 50.0 milliliters of 4.00 x 10⁻⁶ molar NaOH solution. Does a precipitate of Fe(OH)₂ form? Explain and show calculations to support your answer.

5. (94-1) MgF₂(s) ⇌ Mg²⁺(aq) + 2 F⁻(aq)

   In a saturated solution of MgF₂ at 18° C, the concentration of Mg²⁺ is 1.21 x 10⁻³ molar. The equilibrium is represented by the equation above.
   
   (a) Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18° C.
   (b) Calculate the equilibrium concentration of Mg²⁺ in 1.000 liter of saturated MgF₂ solution at 18°C to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
   (c) Predict whether a precipitate of MgF₂ will form when 100.0 milliliters of a 3.00 x 10⁻³ molar Mg(NO₃)₂ solution is mixed with 200.0 milliliters of a 2.00 x 10⁻³ molar NaF solution at 18°C. Calculations to support your prediction must be shown.
   (d) At 27°C the concentration of Mg²⁺ in a saturated solution of MgF₂ is 1.17 x 10⁻³ molar. Is the dissolving of MgF₂ in water an endothermic or an exothermic process? Give an explanation to support your conclusion.
Solutions

1. (a) \( \text{BaCO}_3(s) \rightleftharpoons \text{Ba}^{2+} + \text{CO}_3^{2-} \)
   \( \text{BaSO}_3(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_3^{2-} \)
   \( \text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-} \)

   Dissolving takes place if equilibrium is shifted to the right.

   \[ \text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) \]
   \[ \text{SO}_3^{2-} + \text{H}^+ \rightarrow \text{HSO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{SO}_2(g) \]

   In these two cases, equilibrium is shifted to the right by the production of a removed product (a gas).

   \( \text{SO}_4^{2-} + \text{H}^+ \) do not react since \( \text{SO}_4^{2-} \) is a weak Bronsted base.

(b) Warm dilute \( \text{HNO}_3 \) oxidizes \( S^2- \) to \( S^0 \) (or higher). This reaction shifts the equilibrium between \( \text{CuS}(s) \) and its ions toward the ions.

(c) \( \text{AgCl}(s) + 2 \text{NH}_3 \rightarrow [\text{Ag(NH}_3)_2]^+ + \text{Cl}^- \)

   silver ions complex with ammonia to form the soluble \( [\text{Ag(NH}_3)_2]^+ \), neither \( \text{Hg}_2^{2+} \) nor \( \text{Pb}^{2+} \) form such complexes.

(d) \( \text{Al(OH)}_3(s) + \text{OH}^- \rightarrow \text{Al(OH)}_4^- \) (or similar)

   \( \text{Al(OH)}_3 \) is amphoteric. The product is a hydroxoaluminate ion, \( \text{Fe(OH)}_3 \) is not amphoteric.

2. Answers vary. Start with looking at the solubility rules and find counterions that provide exclusive precipitates.

3. (a) \( \text{SrSO}_4(s) \rightleftharpoons \text{Sr}^{2+}(aq) + \text{SO}_4^{2-}(aq) \)

   At equilibrium: \( [\text{Sr}^{2+}] = X \text{ M} = [\text{SO}_4^{2-}] \)

   \[ X^2 = \text{K}_{sp} = 7.6 \times 10^{-7} \]

   \( X = 8.7 \times 10^{-4} \text{ mol/L} \), solubility of \( \text{SrSO}_4 \)

(b) \( \text{SrF}_2(s) \rightleftharpoons \text{Sr}^{2+}(aq) + 2 \text{F}^-(aq) \)

   At equilibrium: \( [\text{Sr}^{2+}] = X \text{ M} = [\text{F}^-] = 2X \text{ M} \)

   \[ \text{K}_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2 = (X)(2X)^2 = 7.9 \times 10^{-10} \]

   \( X = 5.8 \times 10^{-4} \text{ mol/L} \), solubility of \( \text{SrF}_2 \)

(c) Solve for \( [\text{Sr}^{2+}] \) required for precipitation of each salt.

   \[ \text{K}_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2 = 7.9 \times 10^{-10} = X \times \frac{0.020 \text{ mol}}{1 \text{ mol}} ; X = 2.0 \times 10^{-6} \text{ M} \]

   \[ \text{K}_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = 7.6 \times 10^{-7} = Y \times \frac{0.010 \text{ mol}}{1.0 \text{ L}} ; y = 7.6 \times 10^{-6} \text{ M} \]

   Since \( 2.0 \times 10^{-6} \text{ M} < 7.6 \times 10^{-6} \text{ M} \), \( \text{SrF}_2 \) must precipitate first.

   When \( \text{SrF}_2 \) precipitates, \( [\text{Sr}^{2+}] = 2.0 \times 10^{-6} \text{ M} \)

(d) The second precipitate to form is \( \text{SrSO}_4 \), which appears when \( [\text{Sr}^{2+}] = 7.6 \times 10^{-6} \text{ M} \) (based on calculations in Part c.)

   When \( [\text{Sr}^{2+}] = 7.6 \times 10^{-6} \text{ M}, [\text{F}^-] \) is determined as follows:

   \[ \text{K}_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2 = 7.9 \times 10^{-10} \]

   \[ = (7.6 \times 10^{-6} \text{ mol})^2 = 7.9 \times 10^{-10} ; z = 1.0 \times 10^{-2} \text{ M} \]

   \[ \% \text{ F}^- \text{ still in solution} = \frac{1.0 \times 10^{-2}}{2.0 \times 10^{-2}} \times 100 = 50.0\% \]

4. (a) \( \text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3 \text{OH}^-(aq) \)
(b) $K_{sp} = [Fe^{2+}][OH^{-}]^2$

$[Fe^{2+}] = (1.43 \times 10^{-3} \text{ g Fe(OH)}_2/\text{L})(1 \text{ mol Fe(OH)}_2/91.8617 \text{ g Fe(OH)}_2) = 1.55 \times 10^{-5} \text{ M}$

$K_{sp} = [1.55 \times 10^{-5}][2(1.55 \times 10^{-5})]^2 = 1.50 \times 10^{-14}$

(c) pH means you are solving for [OH⁻], but you’ve already been given that $(2 \times 1.55 \times 10^{-5}) = 3.11 \times 10^{-5} \text{ M}$

$pH = 14 - pOH = 14 - (-\log (3.11 \times 10^{-5})) = 9.49$

(d) Use the Ksp expression to calculate Q:

$$Q_{sp} = [Fe^{2+}][OH^{-}]^2 = (0.0015)(2 \times 10^{-6})^2 = 6 \times 10^{-15}$$

Q<sub>sp</sub> < K<sub>sp</sub>, so no ppt forms.

5. (a) $K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2.42 \times 10^{-3})^2$

= 7.09 \times 10^{-9}

(b) $x = \text{concentration of Mg}^{2+} \text{ ion (by equilibrium)}$

$2x = \text{concentration of F}^- \text{ ion (by equilibrium)}$

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

$[F^-] = (0.100 + 2x) \text{ M}$

since $X$ is a small number then $(0.100 + 2x) = 0.100$

$K_{sp} = 7.09 \times 10^{-9} = (x)(0.100)^2$

$X = 7.09 \times 10^{-9}$

$[Mg^{2+}] = 1.21 \times 10^{-3} - 1.20929 \times 10^{-3} = 7.09 \times 10^{-7} \text{ M}$

(c) $[Mg^{2+}] = 3.00 \times 10^{-3} \text{ M}$

$[F^-] = 2.00 \times 10^{-3} \text{ M}$

trial $K_{sp} = (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.78 \times 10^{-9}$

trial $K_{sp} < = 7.09 \times 10^{-9}$, :: no ppt.

(d) @ 18ºC, 1.21 \times 10^{-3} \text{ M MgF}_2 \text{ dissolves}$

@ 27ºC, 1.17 \times 10^{-3} \text{ M MgF}_2 \text{ dissolves}$

MgF₂ ⇌ Mg²⁺ + 2 F⁻ + heat

dissolving is exothermic; if heat is increased it forces the equilibrium to shift left (according to LeChatelier’s Principle) and less MgF₂ will dissolve.