Answers to Problem set #10

1. A 0.1L sample of a saturated solution of copper (II) periodate \([\text{Cu(IO}_4^2]_2)\) contains 0.146 g/L of the dissolved salt. What is the Ksp of copper (II) periodate?

\[
\text{Cu(IO}_4^2]_2(s) \rightleftharpoons \text{Cu(IO}_4^2]_2(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + 2 \text{IO}_4^{2-}(aq)
\]

\[
K_{sp} = S(2S)^2 = 4S^3
\]

M.W. (Cu(IO}_4^2]_2 = 445.5 g/mol; 1.46 g/L = 3.27 x 10^{-3} moles/liter = S

\[
K_{sp} = 4(3.27x10^{-3})^3 = 1.4 \times 10^{-7}
\]

2. What is the solubility of Hg\(_2\)Cl\(_2\) in moles/liter and g/liter if Ksp = 1.1x10^{-18} and the cation Hg\(_{2}^{2+}\) is the cation in solution?

\[
\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2\text{Cl}_2(aq) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{Cl}^{-}(aq)
\]

\[
S \quad S \quad 2S
\]

\[
K_{sp} = (2S)^2S = 4S^3 = 1.1 \times 10^{-18}; \quad S=6.5 \times 10^{-7} \text{ mole/liter}
\]

M.W. (Hg\(_2\)Cl\(_2\) = 472.09 g/mol; S=6.5 \times 10^{-7} \text{ mole/liter} \times 472.09 \text{ g/mol} = 3.07 \times 10^{-4} \text{ g/liter}.

3. The Ksp for lead iodide (PbI\(_2\)) is 1.4x10^{-8}. Calculate the solubility of lead iodide in

a. Water

\[
\text{PbI}_2(s) \rightleftharpoons \text{PbI}_2(aq) \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^{-}
\]

\[
S = 0.0015 \text{ moles/liter}
\]

b. 0.1M Pb(NO\(_3\))\(_2\)

\[
\text{PbI}_2(s) \rightleftharpoons \text{PbI}_2(aq) \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^{-}
\]

Initial: \[0.1M \quad 0M\]

Eq. \(0.1 + x \quad 2x\)

\[
K_{sp} = 1.4 \times 10^{-8} = (0.1 + x)(2x)^2; \text{ assume } x<<0.1; 4x^2 = 1.4 \times 10^{-8}
\]

\[x = 1.9 \times 10^{-4}\]

Thus, \(2x = 2S = 3.7 \times 10^{-4}\), \(S = 1.9 \times 10^{-4} \text{ moles/liter}\)

c. 0.01M NaI

\[
\text{PbI}_2(s) \rightleftharpoons \text{PbI}_2(aq) \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^{-}
\]

Initial: \[0M \quad 0.01M\]

Eq. \[x \quad 0.01 + 2x\]

\[
K_{sp} = 1.4 \times 10^{-8} = (0.01 + 2x)^2(x); \text{ assume } x<<0.01; x = 1.4 \times 10^{-4}
\]

Thus, \(S = x = 1.4 \times 10^{-4} \text{ moles/liter}\)

4. What are the concentrations of all ions in solution after the following solutions are mixed and have reached equilibrium? Will a precipitate form? If so, how many grams of solid are formed?

a. 100 mL of 0.02M Pb(NO\(_3\))\(_2\) and 100.0 mL of 0.02M NaCl (assume both NaCl and Pb(NO\(_3\))\(_2\) are freely soluble in water and Ksp PbCl\(_2\)=1.6x10^{-5})
(0.1L)(0.02M Pb(NO₃)₂) = 0.002 mol Pb²⁺/0.2L = 0.01M Pb²⁺
(0.1L)(0.02M NaCl) = 0.002 mol Cl⁻/0.2L = 0.01M Cl⁻
PbCl₂ ==> Pb²⁺ (aq) + 2 Cl⁻(aq)

Initial: 0.01M  0.01M
Ksp = [Pb²⁺]_{eq}[Cl⁻]_{eq}²
Q = (0.01)(0.01)² = 1x10⁻⁶ < Ksp
No precipitate will form. Thus [Pb²⁺]_{eq} = 0.01M and [ Cl⁻]_{eq} = 0.01M

b. 75mL of 0.02M BaCl₂ and 125ml of 0.04M Na₂SO₄
(assume BaCl₂ and Na₂SO₄ are freely soluble in water and that
Ksp (BaSO₄) = 1.1 x 10⁻¹⁰)
(.075L) (0.02M BaCl₂) = .0015 mol Ba²⁺ / .2L = .0075 M
(0.125L)(0.04 M Na₂SO₄) = 0.005 mol SO₄²⁻ / 0.2L = .025 M
BaSO₄ (s) ==> Ba²⁺ (aq) + SO₄²⁻(aq)

Initial: 0.0075M  0.025M
Ksp = 1.1 x 10⁻¹⁰ = [Ba²⁺]_{eq}[SO₄²⁻]_{eq}; Q = (0.0075)(0.025) = 1.8 x 10⁻⁴ >> Ksp
Thus, a precipitate will form. Assuming maximum precipitate formation, all Ba²⁺
will be consumed

BaSO₄ (s) ==> Ba²⁺ (aq) + SO₄²⁻(aq)
New initial: 0M  +  0.0175M
Equilibrium: x  0.0175 +x
Ksp = 1.1 x 10⁻¹⁰ = (x)(0.0175 + x); assume x << 0.0175; x = 6.28 x 10⁻⁹
Thus, [Ba²⁺]_{eq} = 6.28 x 10⁻⁹M; [SO₄²⁻]_{eq} = 0.0175M
BaSO₄ precipitated = 0.0075M * 0.2L = 0.0015 moles

5. For each of the following ionic compounds, state whether the solubility will
increase, decrease, or remain unchanged as a solution at pH 7 is made acidic.

a. PbI₂
PbI₂ ==> Pb²⁺ (aq) + 2I⁻(aq)
Since I⁻ is the conjugate base of a strong acid (HI), solubility will remain
unchanged as the solution is made acidic.

b. AgOH
AgOH(s) ==> Ag⁺ (aq) + HO⁻(aq)
Since HO⁻ is the conjugate base of a weak acid (H₂O) and is thus a strong
base, solubility will increase as the solution is made acidic, since OH is
consumed by the added acid.

c. Ca₃(PO₄)₂
Ca₃(PO₄)₂ ==> 3Ca²⁺ (aq) + 2PO₄³⁻(aq)
Since PO₄³⁻ is the conjugate base of a weak acid (HPO₄²⁻), the solubility
will increase as the solution is made acidic.
6. The cations in an aqueous solution that contains 0.1M Hg(NO₃)₂ and 0.05M Pb(NO₃)₂ are to be separated by taking advantage of the difference in the solubilities of their iodides Ksp (PbI₂) = 1.4 x 10⁻⁸; Ksp (Hg₂I₂) = 1.2 x 10⁻²⁸. What should be the concentration of iodide ion for the best separation (one in which one of the cations should remain entirely in solution and the other should precipitate as fully as possible)? Assume Hg²⁺ is the cation in solution from Hg₂(NO₃)₂.

Clearly, PbI₂ is more soluble than Hg₂I₂. We need to figure out what concentration of iodide will just precipitate the PbI₂

PbI₂(s) ===> Pb²⁺(aq) + 2I⁻(aq)

Ksp = [Pb²⁺]eq[I⁻]eq² = (0.05M)[I⁻]eq² = 1.4 x 10⁻⁸; [I⁻] = 5.3 x 10⁻⁴ M

Note that at this concentration:

Hg₂I₂ ===> Hg₂²⁺(aq) + 2I⁻(aq)

Q(Hg₂I₂) = (0.1M)(5.3 x 10⁻⁴ M)² = 2.8 x 10⁻⁸ >> Ksp(Hg₂I₂)

In contrast, the minimum required concentration of iodide required to precipitate Hg₂⁺ is

Ksp = [Hg₂⁺]eq[I⁻]eq² = (0.1M)(x)² = 1.2 x 10⁻²⁸; [I⁻] = 3.4 x 10⁻¹⁴ M

Thus, Hg₂⁺ will be selectively precipitated out of solution until the iodide concentration rises to 5.3 x 10⁻⁴ M.

7. When 50 mL of 0.1M AgNO₃ and 30 mL of 0.06M Na₂CrO₄ are mixed, a precipitate of silver chromate (Ag₂CrO₄) is formed. The Ksp of silver chromate in water is 1.9 x 10⁻¹². Calculate the [Ag⁺] and [CrO₄²⁻] remaining in solution at equilibrium.

50 mL of 0.1M AgNO₃ = 0.005 mol Ag⁺ / 0.08L = 0.0625 M
30 mL of 0.06M Na₂CrO₄ = 0.018mol CrO₄²⁻ / 0.08L = 0.0225 M

Ag₂CrO₄(s) ===> 2Ag⁺(aq) + CrO₄²⁻(aq)

Ksp = 1.9 x 10⁻¹² = [Ag⁺]²[CrO₄²⁻]eq

Q=(0.0625M)²(0.0225M) = 8.8 x 10⁻⁵ >> Ksp

Ag₂CrO₄(s) ===> 2Ag⁺(aq) + CrO₄²⁻(aq)

Initial:
0.0625 M  0.0225 M
New initial:
0.0175 M  0 M
Eq.
0.0175M+2x  x
Ksp = 1.9 x 10⁻¹² = (0.0175M+2x)²(x) ; assume 2x<<0.0175 M
x = 6.2 x 10⁻⁹

Thus, [CrO₄²⁻] = 6.2 x 10⁻⁹ M

[Ag⁺] = 0.175 + 2x = 0.0175 M

8. The enamel of your teeth contains hydroxyapatite (Ca₅(PO₄)₃OH, Ksp = 6.8 x 10⁻³⁷) write out the chemical equation & solubility product expression for the dissolution of this substance in water. It is known that tooth decay starts when bacteria in the mouth convert sugar into organic acids. Why might this be so? Flouridation of drinking water (0.7 to 1.2 ppm) and in dental products converts hydroxyapatite to Ca₅(PO₄)₃F (Ksp=1 x 10⁻⁶⁰). How does this prevent tooth decay?

Ca₅(PO₄)₃OH(s) ===> 5Ca²⁺(aq) + 3PO₄³⁻(aq) + HO⁻(aq)
\[ K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^4[\text{HO}^-] = 6.8 \times 10^{-37} \]

Organic acids, though weak, can react completely with the strong base HO\(^-\), thus increasing the solubility of hydroxyapatite, which results in enamel/tooth decay.

\[
\text{Ca}_5(\text{PO}_4)_3\text{F(s)} \rightarrow 5 \text{Ca}^{2+} (\text{aq}) + 4 \text{PO}_4^{3-}(\text{aq}) + \text{F}^- (\text{aq})
\]

\[ K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^4[\text{F}^-] = 1 \times 10^{-60} \]

Fluoride is clearly a much weaker base than HO\(^-\), with a poor tendency to react with weak acids; also comparing \(K_{sp}\) values, \(\text{Ca}_5(\text{PO}_4)_3\text{F}\) has much poorer solubility in water than \(\text{Ca}_5(\text{PO}_4)_3\text{OH}\). Both of these features combined prevent tooth decay.