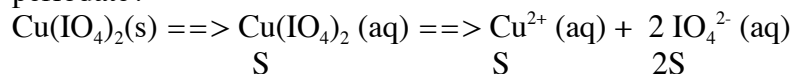Answers to Problem set #10

1. A 0.1L sample of a saturated solution of copper (II) periodate $[Cu(IO_4)_2]$ contains 0.146 g/L of the dissolved salt. What is the Ksp of copper (II) periodate?

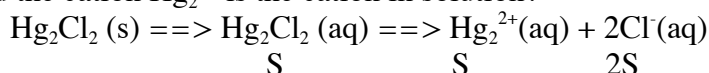$Cu(IO_4)_2(s) ==> Cu(IO_4)_2 \ (aq) ==> Cu^{2+} \ (aq) + \ 2 \ IO_4^{2-} \ (aq)$
$\qquad\qquad\qquad\qquad S \qquad\qquad\quad S \qquad\qquad 2S$

$K_{sp} = S(2S)^2 = 4S^3$
M.W. $(Cu(IO_4)_2 = 445.5$ g/mol); 1.46 g/L= 3.27 x 10^{-3} moles/liter = S
$K_{sp} = 4(3.27x10^{-4})^3 = 1.4 \ x10^{-7}$

2. What is the solubility of Hg_2Cl_2 in moles/liter and g/liter if Ksp = $1.1x10^{-18}$ and the cation Hg_2^{2+} is the cation in solution?
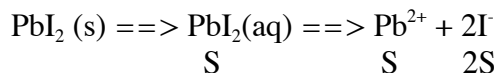
$Hg_2Cl_2 \ (s) ==> Hg_2Cl_2 \ (aq) ==> Hg_2^{2+}(aq) + 2Cl^-(aq)$
$\qquad\qquad\qquad\qquad S \qquad\qquad\quad S \qquad\qquad 2S$

$K_{sp} = (2S)^2S = 4S^3 = 1.1 \ x \ 10^{-18}$; **S=6.5 x 10^{-7} mole/liter**
M.W. $(Hg_2Cl_2) = 472.09$ g/mol; **S=6.5 x 10^{-7} mole/liter *472.09 g/mol = 3.07x10^{-4} g/liter.**

3. The Ksp for lead iodide (PbI_2) is $1.4x10^{-8}$. Calculate the solubility of lead iodide in

    a. Water
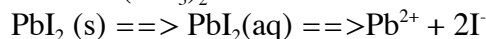 $PbI_2 \ (s) ==> PbI_2(aq) ==> Pb^{2+} + 2I^-$
    $\qquad\qquad\qquad\quad S \qquad\qquad S \quad\ 2S \quad K_{sp} = S(2S)^2 = 4S^3 = 1.4 \ x10^{-8}$
    S=0.0015 moles/liter

    b. 0.1M $Pb(NO_3)_2$
    $PbI_2 \ (s) ==> PbI_2(aq) ==>Pb^{2+} + 2I^-$
    Initial: $\qquad\qquad\qquad\qquad 0.1M \quad OM$
    Eq. $\qquad\qquad\qquad\qquad 0.1 +x \quad 2x$
    $K_{sp} = 1.4 \ x \ 10^{-8} = (0.1 + x)(2x)^2$; assume x<<<0.1 ;$4x^2 = 1.4 \ x \ 10^{-8}$
    x=1.9 x10^{-4}
    Thus, 2x=2S=3.7 x 10^{-4} , S=1.9x10^{-4}moles/liter
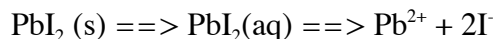
    c. 0.01M NaI
    $PbI_2 \ (s) ==> PbI_2(aq) ==> Pb^{2+} + 2I^-$
    Initial: $\qquad\qquad\qquad\qquad\qquad 0M \quad 0.01M$
    Eq. $\qquad\qquad\qquad\qquad\qquad x \qquad 0.01+2x$
    $K_{sp} = 1.4 \ x \ 10^{-8} = (0.01 + 2x)^2(x)$; assume x<<0.01 ; x=1.4 x10^{-4}
    Thus, S=x=~1.4 x 10^{-4} moles/liter

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})

$(0.1L)(0.02M\ Pb(NO_3)_2) = 0.002\ mol\ Pb^{2+}/0.2L = 0.01M\ Pb^{2+}$

$(0.1L)(0.02M\ NaCl) = 0.002\ mol\ Cl^-/0.2L = 0.01M\ Cl^-$

$$PbCl_2 ==> Pb^{2+}\ (aq) + 2\ Cl^-(aq)$$
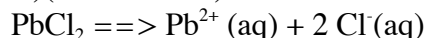
Initial: 0.01M   0.01M

$K_{sp} = [Pb^{2+}]_{eq}[\ Cl^-]_{eq}^2$

$Q = (0.01)(0.01)^2 = 1x10^{-6} < K_{sp}$

No precipitate will form. Thus $[Pb^{2+}]_{eq} = 0.01M$ and $[\ Cl^-]_{eq} = 0.01M$

b. 75mL of 0.02M $BaCl_2$ and 125ml of 0.04M Na_2SO_4
(assume $BaCl_2$ and Na_2SO_4 are freely soluble in water and that
Ksp $(BaSO_4) = 1.1\ x\ 10^{-10})$

$(.075L)\ (0.02M\ BaCl_2) = .0015\ mol\ Ba^{2+}\ /\ .2L = .0075\ M$

$(0.125L)(0.04\ M\ Na_2SO_4) = 0.005\ mol\ SO_4^{2-}\ /\ 0.2L = .025\ M$

$$BaSO_4\ (s) ==> Ba^{2+}\ (aq) + SO_4^{2-}(aq)$$
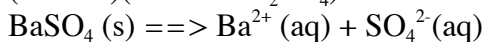
Initial: 0.0075M   0.025M

$K_{sp} = 1.1x10^{-10} = [Ba^{2+}]_{eq}[SO_4^{2-}]_{eq}$; $Q = (0.0075)(0.025) = 1.8x10^{-4} >> K_{sp}$

Thus, a precipitate will form. Assuming maximum precipitate formation, all Ba^{2+}
will be consumed

$$BaSO_4\ (s) ==> Ba^{2+}\ (aq) + SO_4^{2-}(aq)$$
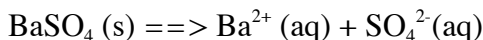
New initial: 0M   + 0.0175M

Equilibrium: x   0.0175 +x

$K_{sp} = 1.1x10^{-10} = (x)(0.0175+x)$; assume $x << 0.0175$; $x = 6.28\ x\ 10^{-9}$

Thus, $[Ba^{2+}]_{eq} = 6.28x10^{-9}M$; $[SO_4^{2-}]_{eq} = 0.0175M$

$BaSO_4$ 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. PbI_2

$$PbI_2 ==> Pb^{2+}\ (aq) + 2I^-(aq)$$
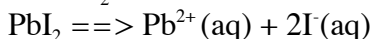
Since I^- is the conjugate base of a strong acid (HI), solubility will remain
unchanged as the solution is made acidic.

    b. AgOH

$$AgOH(s) ==> Ag^+\ (aq) + HO^-(aq)$$

Since HO^- is the conjugate base of a weak acid (H_2O) and is thus a strong
base, solubility will increase as the solution is made acidic, since OH is
consumed by the added acid.

    c. $Ca_3(PO_4)_2$

$$Ca_3(PO_4)_2 ==> 3Ca^{2+}\ (aq) + 2PO_4^{3-}\ (aq)$$
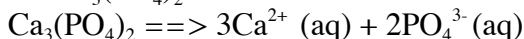
Since PO_4^{3-} is the conjugate base of a weak acid (HPO_4^{2-}), the solubility
will increase as the solution is made acidic

6. The cations in an aqueous solution that contains 0.1M $Hg_2(NO_3)_2$ and 0.05M Pb $(NO_3)_2$ are to be separated by taking advantage of the difference in the solubilities of their iodides Ksp $(PbI_2) = 1.4 \times 10^{-8}$; Ksp $(Hg_2I_2) = 1.2 \times 10^{-28}$. 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 Hg_2^{2+} is the cation in solution from $Hg_2(NO_3)_2$.

Clearly,PbI_2 is more soluble than Hg_2I_2. We need to figure out what concentration of iodide will just precipitate the PbI_2

$PbI_2(s) ==> Pb^{2+}(aq) + 2I^-(aq)$
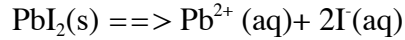
$K_{sp} = [Pb^{2+}]_{eq}[I^-]_{eq}^2 = (0.05M)[I^-]_{eq}^2 = 1.4 \times 10^{-8}$; **[I⁻] = 5.3 x10⁻⁴M**

Note that at this concentration:

$Hg_2I_2 ==> Hg_2^{2+}(aq) + 2I^-(aq)$
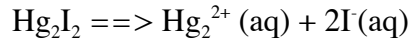
$Q(Hg_2I_2) = (0.1M)(5.3 \times 10^{-4}M)^2 = 2.8 \times 10^{-8} >> K_{sp}(Hg_2I_2)$

In contrast, the minimum required concentration of iodide required to precipitate Hg_2^{2+} is

$K_{sp} = [Hg_2^{2+}]_{eq}[I^-]_{eq}^2 = (0.1M)(x)^2 = 1.2 \times 10^{-28}$; $[I^-] = 3.4 \times 10^{-14}M$

Thus , Hg_2^{2+} will be selectively precipitated out of solution until the iodide concentration rises to **5.3 x10⁻⁴M**

7. When 50 mL of 0.1M $AgNO_3$ and 30 mL of 0.06M Na_2CrO_4 are mixed, a precipitate of of silver chromate (Ag_2CrO_4) is formed. The Ksp of silver chromate in water is 1.9×10^{-12}. Calculate the $[Ag^+]$ and $[CrO_4^{2-}]$ remaining in solution at equilibrium.

50 mL of 0.1M $AgNO_3 = .005$ mol Ag^+ / .08L = 0.0625M

30 mL of 0.06M $Na_2CrO_4 = .0018$mol CrO_4^{2-} / .08L = 0.0225 M

$Ag_2CrO_4(s) ==> 2Ag^+(aq) + CrO_4^{2-}(aq)$
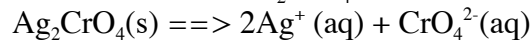
$K_{sp} = 1.9 \times 10^{-12} = [Ag^+]_{eq}^2[CrO_4^{2-}]_{eq}$

$Q = (0.0625M)^2 (0.0225M) = 8.8 \times 10^{-5} >> K_{sp}$

$$Ag_2CrO_4(s) ==> 2Ag^+(aq) + CrO_4^{2-}(aq)$$

Initial:	0.0625M	0.0225M
New initial:	0.0175M	0M
Eq.	0.0175M+2x	x

$K_{sp} = 1.9 \times 10^{-12} = (0.0175M+2x)^2(x)$; assume 2x<<<0.0175M

$x = 6.2 \times 10^{-9}$

Thus, **[CrO₄²⁻]= 6.2x10⁻⁹M**

[Ag⁺]=0.0175M+2x = 0.0175M

8. The enamel of your teeth contains hydroxyapatite $(Ca_5(PO_4)_3OH$, $K_{sp}= 6.8 \times 10^{-37}$) 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 $Ca_5(PO_4)_3F$ ($K_{sp}=1 \times 10^{-60}$). How does this prevent tooth decay?

$Ca_5(PO_4)_3OH(s) ==> 5 Ca^{2+}(aq) + 4 PO_4^{3-}(aq) + HO^-(aq)$
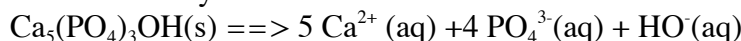
$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^4[HO^-] = 6.8 \times 10^{-37}$$

Organic acids, though weak, can react completely with the strong base HO^-, thus increasing the solubility of hydroxyapatite, which results in enamel/tooth decay
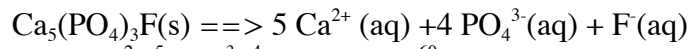
$$Ca_5(PO_4)_3F(s) ==> 5\ Ca^{2+}\ (aq) + 4\ PO_4^{3-}(aq) + F^-(aq)$$
$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^4[F^-] = 1 \times 10^{-60}$$

Fluoride is clearly a much weaker base than HO^-, with a poor tendency to react with weak acids; also comparing K_{sp} values, $Ca_5(PO_4)_3F$ has much poorer solubility in water than $Ca_5(PO_4)_3OH$. Both of these features combined prevent tooth decay