CHEMISTRY 1220
SOLUBILITY
STUDY SESSION

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K_{sp} & MOLAR SOLUBILITY

Question #1

The solubility product expression for $La_2(CO_3)_3$ is K_{sp} = ?

First, write the equilibrium expression. The subscript following each atom in the solid is the number of ions of that atom in solution. The total charges must add to zero:

$$La_2(CO_3)_3(s) \rightleftharpoons 2La^{3+}(aq) + 3CO_3^{2-}(aq)$$

Given the information above and the equilibrium expression:

$$\boxed{K_{sp}=[La^{3+}]^2\,[CO_3^{2-}]^3}$$

Question #2

The solubility of BaF_2 is 1.3 g/L. What is the solubility product constant?

Conversely, K_{sp} can be calculated from either solubility or molar solubility. First, convert solubility in g/L to mol/L (M) since the concentrations used in K_{sp} are in mol/L (M). If the given solubility is already in mol/L, this step is unnecessary:

$$\frac{1.3\text{ g }BaF_2}{1\text{ L}} \times \frac{1\text{ mol }BaF_2}{175.33\text{ g }BaF_2} = 0.0074\text{ mol/L} = 0.0074\text{ M }BaF_2$$

From this molar concentration and the equilibrium expression, we can calculate the equilibrium concentrations of each ion using their respective coefficients in the equilibrium:

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$

$$0.0074\text{ M }BaF_2 \times \frac{1\text{ mol }Ba^{2+}}{1\text{ mol }BaF_2} = 0.0074\text{ M }Ba^{2+}$$

$$0.0074\text{ M }BaF_2 \times \frac{2\text{ mol }F^-}{1\text{ mol }BaF_2} = 0.0148\text{ M }F^-$$

With these concentrations and the solubility-product expression, we can calculate K_{sp}. Don't forget the exponents!

$$K_{sp}=[Ba^{2+}]\,[F^-]^2=(0.0074)(0.0148)^2=\boxed{1.6 \times 10^{-6}}$$

Question #3

Which compound is the least soluble (mol/L) in water?

- **(a) $CaCO_3$ $K_{sp} = 2.8 \times 10^{-9}$**
- **(b) PbI_2 $K_{sp} = 8.7 \times 10^{-9}$**
- **(c) AgBr $K_{sp} = 5.0 \times 10^{-13}$**
- **(d) $Fe(OH)_2$ $K_{sp} = 8.0 \times 10^{-16}$**
- **(e) $Co(OH)_2$ $K_{sp} = 1.6 \times 10^{-15}$**

You can directly compare solids with the **same** ratio of cation to anion (i.e. higher K_{sp}, more soluble) to eliminate some possible answer choices. However, if the ratios differ, the molar solubility (x) for EACH compound must be calculated using an ICE table because the lowest K_{sp} does not necessarily correspond to the lowest molar solubility.

(a) 5.29×10^{-5} mol/L
(b) 1.30×10^{-3} mol/L
(c) 7.07×10^{-7} mol/L
(d) 5.85×10^{-6} mol/L
(e) 7.37×10^{-6} mol/L

Of these values, (c) is the lowest. So AgBr is the least soluble (even though its K_{sp} is not the lowest).

Question #4

Which of the following salts has the <u>highest</u> concentration of silver ion when dissolved in water?

AgCl $K_{sp} = 1.6 \times 10^{-10}$
Ag_2CO_3 $K_{sp} = 8.1 \times 10^{-12}$
AgBr $K_{sp} = 5.0 \times 10^{-13}$

Calculate the molar concentration of **silver ion** for each of the salts.

(a) 1.26×10^{-5} M
(b) 2.53×10^{-4} M (make sure to multiply x by 2!)
(c) 7.07×10^{-7} M

Of these concentrations, (b) is the highest. So Ag_2CO_3 has the highest concentration of silver ion (Note: this is not just because silver has a subscript of 2 after it in Ag_2CO_3; you must calculate the actual concentration for each compound).

FACTORS INFLUENCING SOLUBILITY

Question #1
A solution is saturated with silver acetate, $AgC_2H_3O_2$ (K_{sp} = 1.9 x 10^{-3}). Which of the following reagents will increase the solubility of silver acetate?

$NaC_2H_3O_2$ **HNO_3** **NH_3** **$AgNO_3$**

For problems like these, first write out the solubility equilibrium expression and see how the various reagents will influence the equilibrium. Remember, a common-ion will decrease solubility, the effect of a change in pH will depend on the particular equilibrium, and formation of a complex ion will increase solubility, trumping both the common-ion and pH effects:

$$AgC_2H_3O_2\,(s) \rightleftharpoons Ag^+(aq) + C_2H_3O_2^-(aq)$$

$NaC_2H_3O_2$-common ion, therefore decreases solubility.

HNO_3- $C_2H_3O_2^-$ is the conjugate base of a **weak** acid ($HC_2H_3O_2$), and is therefore a weak base itself. It can be neutralized by HNO_3, a strong acid, thereby decreasing the concentration of $C_2H_3O_2^-$ and shifting the equilibrium to the right, **increasing solubility**.

NH_3- Ag^+ forms the complex ion $Ag(NH_3)_2^+$, **increasing solubility.**

$AgNO_3$- common ion, therefore decreases solubility.

Question #2
How many of the following salts would be more soluble in acidic solution that in pure water?

BaC_2O_4 **CaS** **$AuCl_3$** **PbF_2** **$ZnCO_3$**

For an acidic solution to increase solubility, it must neutralize a **weak** base. Therefore the anion must be the conjugate base of a **weak** acid. Remember, conjugate salts of **strong** acids/bases are NOT influenced by addition of acids/bases or pH changes:

BaC_2O_4- $C_2O_4^-$ is the conjugate base of the weak acid HC_2O_4. **Solubility increases**.

CaS- S^{2-} is the conjugate base of the weak acid HS^-. **Solubility increases**.
$AuCl_3$- Cl^- is the conjugate base of the strong acid HCl. Solubility is NOT affected.

PbF_2- F^- is the conjugate base of the weak acid HF. **Solubility increases**.

$ZnCO_3$- CO_3^{2-} is the conjugate base of the weak acid HCO_3^-. **Solubility increases**.

Question #3
Would each of the following reagents increase, decrease, of have no effect on the solubility of $Cu(OH)_2$?

$CuCl_2$ **HCl** **NH_3** **NaOH**

$$Cu(OH)_2\,(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^{-}(aq)$$

$CuCl_2$-common ion, therefore decreases solubility.

HCl- H^+ neutralizes OH^-, decreasing the concentration of OH^- and shifting the equilibrium to the right, **increasing solubility**.

NH_3- Cu^{2+} forms the complex ion $Cu(NH_3)_4^{2+}$, **increasing solubility.**

NaOH- common ion, therefore decreases solubility.

Question #4
Which salt solubility would be most sensitive to pH?

$Ca(NO_3)_2$ **CaF_2** **$CaCl_2$** **$CaBr_2$** **CaI_2**

All of the cations are Ca^{2+}, the conjugate salt of the strong base $Ca(OH)_2$. It cannot be neutralized by changes in pH. Of all the anions, only F^- is the conjugate base of a **weak** acid. The rest are conjugate bases of strong acids. Therefore **CaF_2** is most sensitive to pH.

Question #5
The solubility of which of the listed salts would be unaffected by the presence of a strong acid?

$KClO_4$ **BaF_2** **$FePO_4$** **SnI_2**

Conjugate bases of **strong** acids will be unaffected by addition of a strong acid. The salts with this type of conjugate base include **$KClO_4$** ($HClO_4$ is a strong acid) and **SnI_2** (HI is a strong acid). BaF_2 and $FePO_4$ contain conjugate bases of **weak** acids and are therefore influenced by a strong acid addition.

Question #6
How many of the following reagents, when added to a solution in contact with solid $NiCO_3$ would change the solubility of $NiCO_3$?

HCl **$NiCl_2$** **NaCl** **Na_2CO_3** **NH_3**

$$NiCO_3\,(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$$

HCl- This strong acid can neutralize CO_3^{2-} because this anion is the conjugate base of a weak acid. This removes CO_3^{2-}, shifting the reaction to the right and **increasing solubility**.

$NiCl_2$- common ion, therefore **decreases solubility.**

NaCl- no effect.

Na_2CO_3- common ion, therefore **decreases solubility.**

NH_3- Ni^+ forms the complex ion $Ni(NH_3)_6^{2+}$, **increasing solubility.**

Question #7

The solubility of how many of the following salts will be affected by strong acid?

AgBr **$Cu_3(PO_4)_2$** **$NaNO_3$** **BaF_2**

Conjugate bases of **weak** acids will be affected by strong acid. This includes: **$Cu_3(PO_4)_2$ and BaF_2.**

Question #8

Zinc oxalate is a slightly soluble salt. How many of the following reagents would be expected to decrease the solubility of ZnC_2O_4?

$Na_2C_2O_4$ **NH_3** **NaOH** **HCl** **$ZnCl_2$**

$$ZnC_2O_4\,(s) \rightleftharpoons Zn^{2+}(aq) + C_2O_4^{2-}(aq)$$

$Na_2C_2O_4$-common ion, therefore **decreases solubility**.

NH_3- Zn^{2+} forms the complex ion $Zn(NH_3)_4^{2+}$, increasing solubility.

NaOH- Zn^{2+} forms the complex ion $Zn(OH)_4^{2-}$, increasing solubility.

HCl- $C_2O_4^{2-}$ is the conjugate base of a weak acid ($HC_2O_4^-$), and is therefore a weak base itself. It can be neutralized by HCl, a strong acid, thereby decreasing the concentration of $C_2O_4^{2-}$ and shifting the equilibrium to the right and increasing solubility.

$ZnCl_2$- common ion, therefore **decreases solubility**.

COMMON ION EFFECT

Question #1

What is the molar solubility of MgF_2 in 0.40 M F^-? K_{sp} MgF_2 = 6.4×10^{-9}

	$MgF_2(s)$ $\rightleftharpoons$	$Mg^{2+}(aq)$ +	$2F^-(aq)$
Initial	-----	0 M	**0.40 M**
Change	-----	+1x M	+2x M
Equilibrium	-----	x M	2x**+0.40** M

$$K_{sp}=[Mg^{2+}][F^-]^2=(x)(\cancel{2x}+0.40)^2=(x)(0.40)^2=6.4 \times 10^{-9}$$

$$x=\boxed{4.0 \times 10^{-8}\ M}$$

Question #2

The solubility product constant for BiI_3 is 8.1×10^{-19}. Calculate the molar solubility of BiI_3 in 0.20 M $Bi(NO_3)_3$.

Be careful! Here, the common ion is the **cation**, unlike in the previous problems:

	$BiI_3(s)$ $\rightleftharpoons$	$Bi^{3+}(aq)$ +	$3I^-(aq)$
Initial	-----	**0.20 M**	0 M
Change	-----	+1x M	+3x M
Equilibrium	-----	x+ **0.20** M	3x M

$$K_{sp}=[Bi^{3+}][I^-]^3=(\cancel{x}+0.20)(3x)^3=(0.20)(27x^3)=8.1 \times 10^{-19}$$

$$x=\boxed{5.3 \times 10^{-7}\ M}$$

pH & SOLUBILITY

Question #1

The K_{sp} for $Zn(OH)_2$ is 5.0×10^{-17}. Determine the molar solubility of $Zn(OH)_2$ in buffered solution with a pH of 11.50?

First, determine the concentration of OH^- when the pH is 11.50:

$$pH=-\log[H^+]=11.50$$
$$[H^+]=3.16 \text{ x } 10^{-12}\text{ M}$$
$$[H^+][OH^-]=1.0 \text{ x } 10^{-14} \text{ (always true)}$$
$$(3.16 \text{ x } 10^{-12}\text{ M})^+][OH^-]=1.0 \text{ x } 10^{-14}$$
$$[OH^-]=3.16 \text{ x } 10^{-3}\text{ M}$$

Now, the problem is similar to a common-ion problem. However, because the solution is buffered, it **resists changes in pH.** Therefore, **the concentration of OH^- does NOT change**:

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

Initial	-----	0 M	**$3.16 \text{ x } 10^{-3}$ M**
Change	-----	+1x M	NO CHANGE
Equilibrium	-----	x M	**$3.16 \text{ x } 10^{-3}$ M**

$$K_{sp}=[Zn^{2+}][OH^-]^2=(x)(3.16 \text{ x } 10^{-3})^2=5.0 \text{ x } 10^{-17}$$
$$x = 5.0 \text{ x } 10^{-12}\text{ M}$$

Question #2

What is the pH of a saturated solution of $Cu(OH)_2$ ($K_{sp} = 2.6 \times 10^{-19}$)?

To determine the pH, we need to determine the concentration of H^+ using an ICE table:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

Initial	-----	0 M	0 M
Change	-----	+1x M	+2x M
Equilibrium	-----	x M	2x M

$$K_{sp}=[Cu^{2+}][OH^-]^2=(x)(2x)^2=4x^3=2.6 \text{ x } 10^{-19}$$
$$x= 4.0 \text{ x } 10^{-7}\text{ M}$$

*Remember to multiply x by 2 in this problem because the equilibrium concentration of OH^- is **2**x:

$$[OH^-]=\mathbf{2}x=2(4.0 \text{ x } 10^{-7}\text{ M})= 8.0 \text{ x } 10^{-7}\text{ M}$$
$$[H^+][OH^-]=1.0 \text{ x } 10^{-14}$$
$$[H^+](8.0 \text{ x } 10^{-7}\text{ M})=1.0 \text{ x } 10^{-14}$$
$$[H^+]=1.2 \text{ x } 10^{-8}\text{ M}$$
$$pH=-\log[H^+]=-\log(1.2 \text{ x } 10^{-8})=\boxed{7.9}$$

Question #3

What is the molar solubility (mol/L) of $Cr(OH)_3$ at pH = 10.00? K_{sp} for $Cr(OH)_3$ is 6.3×10^{-31} and K_f for $Cr(OH)_4^-$ is 8×10^{29}.

In this problem, a **complex ion** is formed. This effect **increases** solubility and **trumps both the common-ion and pH effects**. To determine the molar solubility of a solid whose ion forms a complex ion, we need to find the overall equilibrium expression and "overall K" for both the dissolution of the solid and the formation of the complex-ion. Identical species on opposite sides of the equilibrium arrow cancel. When "adding" two equilibria, the overall K is the product of the individual K values:

$$\begin{array}{ll}
Cr(OH)_3(s) \rightleftharpoons \cancel{Cr^{3+}(aq)} + \cancel{3OH^-(aq)} & K_{sp}=6.3 \times 10^{-31} \\
\underline{\cancel{Cr^{3+}(aq)} + \cancel{4}OH^-(aq) \rightleftharpoons Cr(OH_4)^-(aq)} & \underline{K_f=8.0 \times 10^{29}} \\
Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons Cr(OH_4)^-(aq) & \mathbf{K = K_{sp} \times K_f} \\
 & =(6.3 \times 10^{-31})(8.0 \times 10^{29}) \\
 & =5.04 \times 10^{-1}
\end{array}$$

Calculate the initial concentration of OH^- from the given pH:

$$pH=-\log[H^+]=10.00$$
$$[H^+]=1.0 \times 10^{-10}\ M$$
$$[H^+][OH^-]=1.0 \times 10^{-14} \text{ (always true)}$$
$$(1.0 \times 10^{-10}\ M)^+][OH^-]=1.0 \times 10^{-14}$$
$$[OH^-]=1.0 \times 10^{-4}\ M$$

Now, set up an ICE table for the overall expression using the overall K. Assuming the solution is **buffered** at a pH of 10.00, the concentration of OH^- will **not change**:

	$Cr(OH)_3(s)$ +	$OH^-(aq)$ $\rightleftharpoons$	$Cr(OH_4)^-(aq)$
Initial	-----	1.0×10^{-4} M	0 M
Change	-----	NO CHANGE	+x M
Equilibrium	-----	1.0×10^{-4} M	x M

$$K=\frac{[Cr(OH_4)^-]}{[OH^-]}=\frac{x}{1.0 \times 10^{-4}} = 5.04 \times 10^{-1}$$

$$x= \boxed{5.0 \times 10^{-5}\ M}$$

COMPLEX ION FORMATION

Question #1

Calculate the concentration of free cadmium ion, $[Cd^{2+}]$, in a solution that contains 0.20 M $Cd(NO_3)_2$ in 2.0 M NaCN. Cadmium ion forms the complex ion, $Cd(CN)_4^{2-}$ for which K_f is 6.0×10^{18}.

To solve problems like this, you need to take a 2-step approach. First, assume **all** of the Cd^{2+} is converted to the complex ion:

	$Cd^{2+}(aq)$	$+\quad 4CN^-(aq)\quad \rightleftharpoons$	$Cd(CN)_4^{2-}(aq)$
Initial	0.20 M	2.0 M	0 M
Change	-0.20 M	-4(0.20) M	+0.20 M
Final (NOT equilibrium)	0 M	1.2 M	0.20 M

Next, use the FINAL concentrations from the first table as the INITIAL concentrations for a new table of the REVERSE reaction (dissociation of the complex ion) to determine the equilibrium concentration of free Cd^{2+}:

	$Cd(CN)_4^{2-}(aq)\quad \Longleftarrow$	$Cd^{2+}(aq)\quad +$	$4CN^-(aq)$
Initial	0.20 M	0 M	1.2 M
Change	-x M	+x M	+4x M
Equilibrium	0.20-x M	x M	1.2+4x M

These equilibrium concentrations refer to the reverse reaction, so they do not correspond to K_f, instead they correspond to **K_d, the dissociation constant**, which is $1/K_f$ (K for a reverse reaction always equals the inverse of K for the forward reaction):

$$K_d=\frac{[Cd^{2+}][CN^-]^4}{[Cd(CN)_4^{2-}]}=\frac{(x)(1.2+\cancel{4x})^4}{(0.20-\cancel{x})}=\frac{2.07x}{0.20}=\frac{1}{6.0 \times 10^{18}}$$

$$x=\boxed{1.6 \times 10^{-20}\ M}$$

Question #2

35. Calculate the molar solubility of $CdCO_3$ in 1.5 M NH_3. Note that Cd^{2+} forms the $Cd(NH_3)_4^{2+}$ complex ion for which K_f is 1.3×10^7. K_{sp} for $CdCO_3$ is 5.2×10^{-12}.

$$\begin{aligned}
&CdCO_3(s) \Longleftarrow \cancel{Cd^{2+}(aq)} + CO_3^{2-}(aq) && K_{sp}=5.2 \times 10^{-12}\\
&\cancel{Cd^{2+}(aq)} + 4NH_3(aq) \Longleftarrow Cd(NH_3)_4^{2+}(aq) && K_f=1.3 \times 10^{7}\\
&CdCO_3(s) + 4NH_3(aq) \Longleftarrow Cd(NH_3)_4^{2+}(aq) + CO_3^{2-}(aq) && \mathbf{K = K_{sp} \times K_f}\\
& && =(5.2 \times 10^{-12})(1.3 \times 10^{7})\\
& && =6.76 \times 10^{-5}
\end{aligned}$$

	$CdCO_3(s)\quad +$	$4NH_3(aq)\quad \Longleftarrow$	$Cd(NH_3)_4^{2+}(aq)\quad +$	$CO_3^{2-}(aq)$
Initial	------	1.5 M	0 M	0 M
Change	------	-4x M	+x M	+x M
Equilibrium	------	1.5-4x M	x M	x M

$$K=\frac{[Cd(NH_3)_4^{2+}][CO_3^{2-}]}{[NH_3]^4}=\frac{x^2}{(1.5-\cancel{4x})^4}=6.76 \times 10^{-5}$$

$$x=\boxed{1.8 \times 10^{-2}\ M}$$

Question #3

Calculate the molar solubility of AgCl in 12 M NH_3.

K_{sp} AgCl = 1.8×10^{-10} $\quad$ K_f $Ag(NH_3)_2$ = 1.7×10^{7}

$AgCl(s) \Longleftarrow \cancel{Ag^+(aq)} + Cl^-(aq) \qquad K_{sp}=1.8 \times 10^{-10}$

$\underline{\cancel{Ag^+(aq)} + 2NH_3(aq) \Longleftarrow Ag(NH_3)_2^+(aq) \qquad K_f=1.7 \times 10^{7}}$

$AgCl(s) + 2NH_3(aq) \Longleftarrow Ag(NH_3)_2^+ + Cl^-(aq) \qquad$ **$K= K_{sp} \times K_f$**

$=3.06 \times 10^{-3}$

	$AgCl(s)$ +	$2NH_3(aq)$ $\Longleftarrow$	$Ag(NH_3)_2^+$ +	$Cl^-(aq)$
Initial	------	12 M	0 M	0 M
Change	------	-2x M	+x M	+x M
Equilibrium	------	12-2x M	x M	x M

$$K=\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}=\frac{x^2}{(12-\cancel{2x})^2}=3.06 \times 10^{-3}$$

$$x=\boxed{6.6 \times 10^{-1}\text{ M}}$$

Question #4

The Ag^+ ion forms the complex ion $AgCl_2^-$ for which $K_f = 2.5 \times 10^5$. Determine the equilibrium constant for the solubility of AgCl in the presence of excess chloride ion. K_{sp} of AgCl is 1.8×10^{-10}.

$AgCl(s) \Longleftarrow \cancel{Ag^+(aq)} + \cancel{Cl^-(aq)} \qquad K_{sp}=1.8 \times 10^{-10}$

$\underline{\cancel{Ag^+(aq)} + \cancel{2}Cl^-(aq) \Longleftarrow AgCl_2^-(aq) \qquad K_f=2.5 \times 10^{5}}$

$AgCl(s) + Cl^-(aq) \Longleftarrow AgCl_2^- \qquad$ **$K= K_{sp} \times K_f$**

$\boxed{K=4.5 \times 10^{-5}}$

Question #5

Use the information from problem 41 to calculate the molar solubility of AgCl in 8.5 M HCl.

	$AgCl(s)$ +	$Cl^-(aq)$	$AgCl_2^-(aq)$
Initial	------	8.5 M	0 M
Change	------	-x M	+x M
Equilibrium	------	8.5-x M	x M

$$K=\frac{[AgCl_2^-]}{[Cl^-]}=\frac{x}{(8.5-\cancel{x})}=4.5 \times 10^{-5}$$

$$x=\boxed{3.8 \times 10^{-4}\text{ M}}$$

PRECIPITATION AND SEPARATION OF IONS

Question #1

To determine whether or not precipitation occurs, you need to compare K_{sp} to **Q**, the **reaction quotient.** The equation for Q appears the same as that for K_{sp}:

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$

However, these concentrations can be at **any** point and do **not** necessarily correspond to equilibrium concentrations, as they do for K_{sp}. K_{sp} can be thought of as a *specific* Q value that occurs at equilibrium. Q for given concentrations can be compared to K_{sp} to determine whether or not precipitation will occur:

If $Q<K_{sp}$, there are not enough products. The solution is **unsaturated, and the reaction will shift to the right, so NO precipitate is formed. More solid can be dissolved.
If $Q=K_{sp}$, the reaction is at equilibrium. The solution is **saturated.
If $Q>K_{sp}$, there are too many products. The solution is **supersaturated, and the reaction will shift to the left, so a precipitate will form.

A solution contains Ca^{2+} at a concentration of 2.0×10^{-4} M. If 40.0 mL of this solution is added to 25.0 mL of 5.0×10^{-3} M NaF, will a precipitate form? If 40.0 mL of the Ca^{2+} solution is added to 25.0 mL of 5.0×10^{-3} M Na_3PO_4 will a precipitate form?

For CaF_2, $K_{sp} = 3.9 \times 10^{-11}$
For $Ca_3(PO_4)_2$, $K_{sp} = 2.0 \times 10^{-29}$

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

The concentrations of each ion must be calculated because the volumes change once they are added together:

$$[Ca^{2+}] = \frac{(2.0 \times 10^{-4}\ \text{mol/L})(0.040\ \text{L})}{(0.040\ \text{L} + 0.0250\ \text{L})} = 1.23 \times 10^{-4}\ \text{M}$$

$$[F^-] = \frac{(5.0 \times 10^{-3}\ \text{mol/L})(0.025\ \text{L})}{(0.040\ \text{L} + 0.0250\ \text{L})} = 1.92 \times 10^{-3}\ \text{M}$$

$$Q = [Ca^{2+}][F^-]^2 = (1.23 \times 10^{-4}\ \text{M})(1.92 \times 10^{-3}\ \text{M})^2 = 4.55 \times 10^{-10}$$

$Q>K_{sp}$, therefore equilibrium will shift left and a **precipitate forms.**

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$[Ca^{2+}]=\frac{(2.0 \times 10^{-4}\ mol/L)(0.040\ L)}{(0.040\ L + 0.0250\ L)}=1.23 \times 10^{-4}\ M$$

$$[PO_4^{3-}]=\frac{(5.0 \times 10^{-3}\ mol/L)(0.025\ L)}{(0.040\ L + 0.0250\ L)}=1.92 \times 10^{-3}\ M$$

$$Q=[Ca^{2+}]^3[\ PO_4^{3-}]^2=(1.23 \times 10^{-4}\ M)^3(\ 1.92 \times 10^{-3}\ M)^2=6.86 \times 10^{-18}$$

$Q>K_{sp}$, therefore equilibrium will shift left and a **precipitate forms.**

Question #2

Which salt precipitates first and what is the minimum concentration of Ag^+ necessary to cause this precipitation in a solution containing 7.5 mL of 0.025 M NaCl and 7.5 mL of 0.025 M Na_3PO_4?

K_{sp} AgCl = 1.8×10^{-10} K_{sp} Ag_3PO_4 = 1.3×10^{-20}

To determine which salt precipitates first, we need to look at Q, **not** K_{sp}, because precipitation occurs when $Q>K_{sp}$, which is **not** at equilibrium. We can, however, set Q equal to K_{sp} and solve for the minimum concentration of the ion required for precipitation to occur. Whichever concentration is **lower,** that solid will **precipitate first**:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$[Cl^-]=\frac{(0.025\ mol/L)(0.0075\ L)}{(0.0075\ L + 0.0075\ L)}=1.25 \times 10^{-2}\ M$$

$$Q=[Ag^+][Cl^-]$$
$$1.8 \times 10^{-10}=[Ag^+](1.25 \times 10^{-2}\ M)$$
$$\boxed{[Ag^+]=1.4 \times 10^{-8}\ M \text{ needed for AgCl to ppt.}}$$

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$$

$$[PO_4^{3-}]=\frac{(0.025\ mol/L)(0.0075\ L)}{(0.0075\ L + 0.0075\ L)}=1.25 \times 10^{-2}\ M$$

$$Q=[Ag^+]^3[PO_4^{3-}]$$
$$1.3 \times 10^{-20}=[Ag^+]^3(1.25 \times 10^{-2}\ M)$$
$$\boxed{[Ag^+]=1.0 \times 10^{-6}\ M \text{ needed for } Ag_3PO_4 \text{to ppt.}}$$

***Since the concentration of Ag^+ needed for AgCl to precipitate is lower, it will precipitate first.**

Question #3

A solution contains 0.10 M $Mg(NO_3)_2$ and 0.10 M $Ca(NO_3)_2$. If solid sodium oxalate, $Na_2C_2O_4$, is added to the solution, what is $[Ca^{2+}]$ (M) when MgC_2O_4 begins to precipitate? (Assume no volume changes.) At 25 ^{o}C, K_{sp} of CaC_2O_4 is 2.3×10^{-9} and K_{sp} of MgC_2O_4 is 8.6×10^{-5}.

First, calculate the concentration of $C_2O_4^{2-}$ when MgC_2O_4 begins to precipitate:

$$MgC_2O_4(s) \rightleftharpoons Mg^{2+}(aq) + C_2O_4^{2-}(aq)$$

$$Q=[\,Mg^{2+}][\,C_2O_4^{2-}]$$
$$8.6 \times 10^{-5}=(0.10\text{ M})[\,C_2O_4^{2-}]$$
$$\boxed{[C_2O_4^{2-}]=8.6 \times 10^{-4}\text{ M needed for }MgC_2O_4\text{ to ppt.}}$$

Now, use this concentration of $C_2O_4^{2-}$ in the K_{sp} expression for CaC_2O_4 to determine the concentration of Ca^{2+} at this point:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

$$K_{sp}=[\,Ca^{2+}][\,C_2O_4^{2-}]$$
$$2.3 \times 10^{-9}[\,Ca^{2+}](8.6 \times 10^{-4}\text{ M})$$
$$\boxed{[Ca^{2+}]=2.7 \times 10^{-6}\text{ M}}$$

Question #4

A solution contains 0.010 M Al^{3+} and 0.010 M Ag^{+}. Solid Na_3PO_4 is slowly added to separate the two cations. K_{sp} for $AlPO_4$ is 1.3×10^{-20} and K_{sp} for Ag_3PO_4 is 1.3×10^{-20}. Which cation would precipitate first, and after it precipitates, what concentration of PO_4^{3-} ion should be obtained in the solution for the best separation?

$$AlPO_4(s) \rightleftharpoons Al^{3+}(aq) + PO_4^{3-}(aq)$$
$$Q=[Al^{3+}][PO_4^{3-}]$$
$$1.3 \times 10^{-20}=(0.010\text{ M})[PO_4^{3-}]$$
$$\boxed{[PO_4^{3-}]=1.3 \times 10^{-18}\text{ M needed for }AlPO_4\text{ to ppt.}}$$

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^{+}(aq) + PO_4^{3-}(aq)$$
$$Q=[Ag^{+}]^3[PO_4^{3-}]$$
$$1.3 \times 10^{-20}=(0.010\text{ M})^3[PO_4^{3-}]$$
$$\boxed{[PO_4^{3-}]=1.3 \times 10^{-14}\text{ M needed for }Ag_3PO_4\text{to ppt.}}$$

***Since the concentration of PO_4^{3-} needed for $AlPO_4$ to precipitate is lower, it will precipitate first. To ensure the best separation, $[PO_4^{3-}]$ should be as close to the higher concentration (1.3×10^{-14} M) WITHOUT going over that concentration. This ensures that virtually all of $AlPO_4$ will be solid, but no Ag^{+} will have precipitated yet into Ag_3PO_4.**