

CHEMISTRY 1220

SOLUBILITY

STUDY SESSION

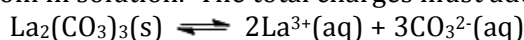
- ☐ **K_{sp} & MOLAR SOLUBILITY**
- ☐ **FACTORS INFLUENCING SOLUBILITY**
- ☐ **COMMON ION EFFECT**
- ☐ **pH & SOLUBILITY**
- ☐ **COMPLEX ION FORMATION**
- ☐ **PRECIPITATION AND SEPARATION OF IONS**
- ☐ **EXAM PREP**

K_{sp} & MOLAR SOLUBILITY

Question #1

The solubility product expression for La₂(CO₃)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:



Given the information above and the equilibrium expression:

$$K_{\text{sp}} = [\text{La}^{3+}]^2 [\text{CO}_3^{2-}]^3$$

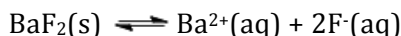
Question #2

The solubility of BaF₂ 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:



$$0.0074 \text{ M BaF}_2 \times \frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaF}_2} = 0.0074 \text{ M Ba}^{2+}$$

$$0.0074 \text{ M BaF}_2 \times \frac{2 \text{ mol F}^{-}}{1 \text{ mol BaF}_2} = 0.0148 \text{ M F}^{-}$$

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

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

Question #3

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

- (a) CaCO₃ K_{sp} = 2.8 x 10⁻⁹
- (b) PbI₂ K_{sp} = 8.7 x 10⁻⁹
- (c) AgBr K_{sp} = 5.0 x 10⁻¹³
- (d) Fe(OH)₂ K_{sp} = 8.0 x 10⁻¹⁶
- (e) Co(OH)₂ K_{sp} = 1.6 x 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) $5.29 \times 10^{-5} \text{ mol/L}$
- (b) $1.30 \times 10^{-3} \text{ mol/L}$
- (c) $7.07 \times 10^{-7} \text{ mol/L}$
- (d) $5.85 \times 10^{-6} \text{ mol/L}$
- (e) $7.37 \times 10^{-6} \text{ mol/L}$

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 highest concentration of silver ion when dissolved in water?

AgCl	$K_{sp} = 1.6 \times 10^{-10}$
Ag₂CO₃	$K_{sp} = 8.1 \times 10^{-12}$
AgBr	$K_{sp} = 5.0 \times 10^{-13}$

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

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

Of these concentrations, (b) is the highest. So Ag₂CO₃ has the highest concentration of silver ion (Note: this is not just because silver has a subscript of 2 after it in Ag₂CO₃; you must calculate the actual concentration for each compound).

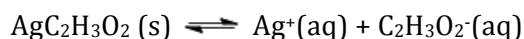
FACTORS INFLUENCING SOLUBILITY

Question #1

A solution is saturated with silver acetate, $\text{AgC}_2\text{H}_3\text{O}_2$ ($K_{\text{sp}} = 1.9 \times 10^{-3}$). Which of the following reagents will increase the solubility of silver acetate?



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:



$\text{NaC}_2\text{H}_3\text{O}_2$ -common ion, therefore decreases solubility.

HNO_3 - $\text{C}_2\text{H}_3\text{O}_2^-$ is the conjugate base of a **weak** acid ($\text{HC}_2\text{H}_3\text{O}_2$), and is therefore a weak base itself. It can be neutralized by HNO_3 , a strong acid, thereby decreasing the concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ and shifting the equilibrium to the right, **increasing solubility**.

NH_3 - Ag^+ forms the complex ion $\text{Ag}(\text{NH}_3)_2^+$, **increasing solubility**.

AgNO_3 - common ion, therefore decreases solubility.

Question #2

How many of the following salts would be more soluble in acidic solution than in pure water?



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 - $\text{C}_2\text{O}_4^{2-}$ 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**.

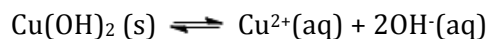
AuCl_3 - Cl^- is the conjugate base of the strong acid HCl . Solubility is NOT affected.

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, or have no effect on the solubility of $\text{Cu}(\text{OH})_2$?



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 $\text{Cu}(\text{NH}_3)_4^{2+}$, **increasing solubility**.

NaOH - common ion, therefore decreases solubility.

Question #4

Which salt solubility would be most sensitive to pH?



All of the cations are Ca^{2+} , the conjugate salt of the strong base $\text{Ca}(\text{OH})_2$. 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

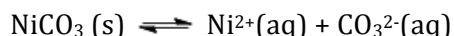
The solubility of which of the listed salts would be unaffected by the presence of a strong acid?



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 - 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 $\text{Ni}(\text{NH}_3)_6^{2+}$, **increasing solubility**.

Question #7

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

AgBr

$\text{Cu}_3(\text{PO}_4)_2$

NaNO_3

BaF_2

Conjugate bases of **weak** acids will be affected by strong acid. This includes: **$\text{Cu}_3(\text{PO}_4)_2$ 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 ?

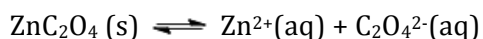
$\text{Na}_2\text{C}_2\text{O}_4$

NH_3

NaOH

HCl

ZnCl_2



$\text{Na}_2\text{C}_2\text{O}_4$ -common ion, therefore **decreases solubility**.

NH_3 - Zn^{2+} forms the complex ion $\text{Zn}(\text{NH}_3)_4^{2+}$, increasing solubility.

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

HCl - $\text{C}_2\text{O}_4^{2-}$ 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 $\text{C}_2\text{O}_4^{2-}$ 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^- ? $K_{\text{sp}} \text{MgF}_2 = 6.4 \times 10^{-9}$

	$\text{MgF}_2(\text{s})$	\rightleftharpoons	$\text{Mg}^{2+}(\text{aq})$	+	$2\text{F}^-(\text{aq})$
Initial	-----		0 M		0.40 M
Change	-----		+1x M		+2x M
Equilibrium	-----		x M		2x+ 0.40 M

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

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

Question #2

The solubility product constant for BiI_3 is 8.1×10^{-19} . Calculate the molar solubility of BiI_3 in $0.20 \text{ M Bi(NO}_3)_3$.

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

	$\text{BiI}_3(\text{s})$	\rightleftharpoons	$\text{Bi}^{3+}(\text{aq})$	+	$3\text{I}^-(\text{aq})$
Initial	-----		0.20 M		0 M
Change	-----		+1x M		+3x M
Equilibrium	-----		x+ 0.20 M		3x M

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

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

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:

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

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		$3.16 \times 10^{-3} M$
Change	-----		+1x M		NO CHANGE
Equilibrium	-----		x M		$3.16 \times 10^{-3} M$

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

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

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

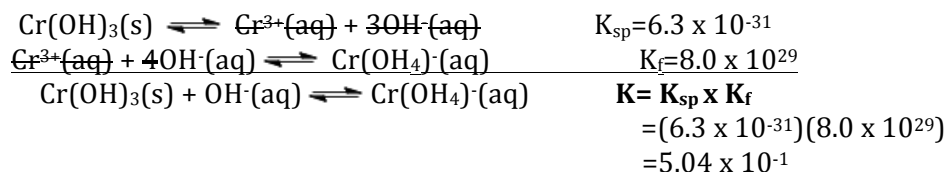
*Remember to multiply x by 2 in this problem because the equilibrium concentration of OH^- is 2x:

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

Question #3

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



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

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

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**:

	$\text{Cr}(\text{OH})_3(\text{s})$	+	$\text{OH}^-(\text{aq})$	\rightleftharpoons	$\text{Cr}(\text{OH})_4^-(\text{aq})$
Initial	-----		$1.0 \times 10^{-4} \text{ M}$		0 M
Change	-----		NO CHANGE		+x M
Equilibrium	-----		$1.0 \times 10^{-4} \text{ M}$		x M

$$K = \frac{[\text{Cr}(\text{OH})_4^-]}{[\text{OH}^-]} = \frac{x}{1.0 \times 10^{-4}} = 5.04 \times 10^{-1}$$

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

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:

	$Cd^{2+}(aq)$	+	$4CN^-(aq)$	\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+} :

	$Cd(CN)_4^{2-}(aq)$	\rightleftharpoons	$Cd^{2+}(aq)$	+	$4CN^-(aq)$
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

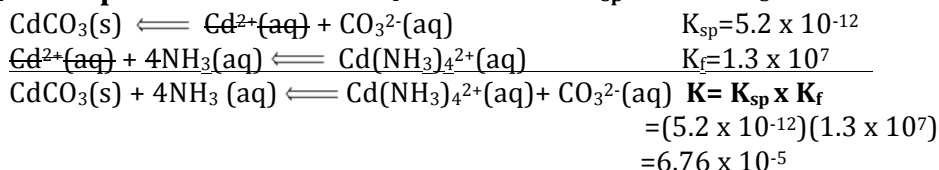
These equilibrium concentrations refer to the reverse reaction, so they do not correspond to K_f , instead they correspond to K_d , the **dissociation constant**, which is $1/K_f$ (K for a reverse reaction always equals the inverse of K for the forward reaction):

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

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

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} .



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

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

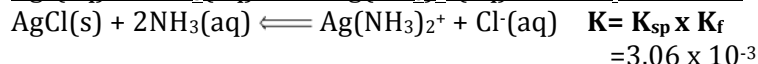
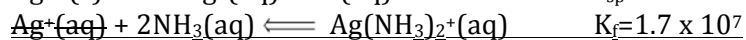
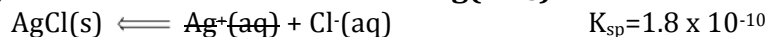
$$x = 1.8 \times 10^{-2} M$$

Question #3

Calculate the molar solubility of AgCl in 12 M NH₃.

$$K_{sp} \text{ AgCl} = 1.8 \times 10^{-10}$$

$$K_f \text{ Ag(NH}_3)_2 = 1.7 \times 10^7$$



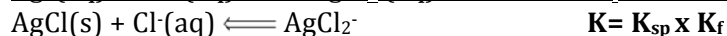
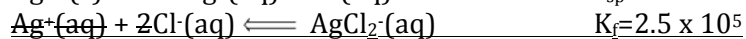
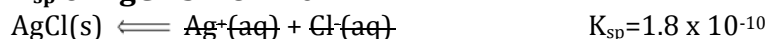
	AgCl(s)	+	2NH ₃ (aq)	⇌	Ag(NH ₃) ₂ ⁺	+	Cl ⁻ (aq)
Initial	-----		12 M		0 M		0 M
Change	-----		-2x M		+x M		+x M
Equilibrium	-----		12-2x M		x M		x M

$$K = \frac{[\text{Ag(NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{x^2}{(12-2x)^2} = 3.06 \times 10^{-3}$$

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

Question #4

The Ag⁺ ion forms the complex ion AgCl₂⁻ for which K_f = 2.5 x 10⁵. Determine the equilibrium constant for the solubility of AgCl in the presence of excess chloride ion. K_{sp} of AgCl is 1.8 x 10⁻¹⁰.



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

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

$$K = \frac{[\text{AgCl}_2^-]}{[\text{Cl}^-]} = \frac{x}{(8.5-x)} = 4.5 \times 10^{-5}$$

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

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:

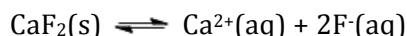
If $Q < K_{sp}$, there are not enough products. The solution is **unsaturated, and the reaction will shift to the right, so NO precipitate is formed. More solid can be dissolved.

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 $2.0 \times 10^{-4} \text{ M}$. If 40.0 mL of this solution is added to 25.0 mL of $5.0 \times 10^{-3} \text{ M NaF}$, will a precipitate form? If 40.0 mL of the Ca^{2+} solution is added to 25.0 mL of $5.0 \times 10^{-3} \text{ M Na}_3\text{PO}_4$ will a precipitate form?

$$\begin{array}{ll} \text{For CaF}_2, & K_{sp} = 3.9 \times 10^{-11} \\ \text{For Ca}_3(\text{PO}_4)_2, & K_{sp} = 2.0 \times 10^{-29} \end{array}$$



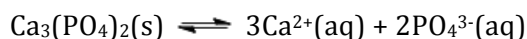
The concentrations of each ion must be calculated because the volumes change once they are added together:

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

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

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

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



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

$$[\text{PO}_4^{3-}] = \frac{(5.0 \times 10^{-3} \text{ mol/L})(0.025 \text{ L})}{(0.040 \text{ L} + 0.0250 \text{ L})} = 1.92 \times 10^{-3} \text{ M}$$

$$Q = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (1.23 \times 10^{-4} \text{ M})^3 (1.92 \times 10^{-3} \text{ M})^2 = 6.86 \times 10^{-18}$$

$Q > K_{\text{sp}}$, 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 ?

$$K_{\text{sp}} \text{ AgCl} = 1.8 \times 10^{-10}$$

$$K_{\text{sp}} \text{ Ag}_3\text{PO}_4 = 1.3 \times 10^{-20}$$

To determine which salt precipitates first, we need to look at Q , **not** K_{sp} , because precipitation occurs when $Q > K_{\text{sp}}$, 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**:

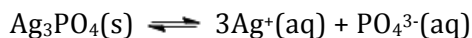


$$[\text{Cl}^-] = \frac{(0.025 \text{ mol/L})(0.0075 \text{ L})}{(0.0075 \text{ L} + 0.0075 \text{ L})} = 1.25 \times 10^{-2} \text{ M}$$

$$Q = [\text{Ag}^+][\text{Cl}^-]$$

$$1.8 \times 10^{-10} = [\text{Ag}^+](1.25 \times 10^{-2} \text{ M})$$

$$[\text{Ag}^+] = 1.4 \times 10^{-8} \text{ M needed for AgCl to ppt.}$$



$$[\text{PO}_4^{3-}] = \frac{(0.025 \text{ mol/L})(0.0075 \text{ L})}{(0.0075 \text{ L} + 0.0075 \text{ L})} = 1.25 \times 10^{-2} \text{ M}$$

$$Q = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

$$1.3 \times 10^{-20} = [\text{Ag}^+]^3 (1.25 \times 10^{-2} \text{ M})$$

$$[\text{Ag}^+] = 1.0 \times 10^{-6} \text{ M needed for Ag}_3\text{PO}_4 \text{ to ppt.}$$

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

Question #3

A solution contains 0.10 M $\text{Mg}(\text{NO}_3)_2$ and 0.10 M $\text{Ca}(\text{NO}_3)_2$. If solid sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, is added to the solution, what is $[\text{Ca}^{2+}]$ (M) when MgC_2O_4 begins to precipitate? (Assume no volume changes.) At 25 °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 $\text{C}_2\text{O}_4^{2-}$ when MgC_2O_4 begins to precipitate:

$$\begin{aligned}\text{MgC}_2\text{O}_4(\text{s}) &\rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \\ Q &= [\text{Mg}^{2+}][\text{C}_2\text{O}_4^{2-}] \\ 8.6 \times 10^{-5} &= (0.10 \text{ M})[\text{C}_2\text{O}_4^{2-}] \\ [\text{C}_2\text{O}_4^{2-}] &= 8.6 \times 10^{-4} \text{ M needed for MgC}_2\text{O}_4 \text{ to ppt.}\end{aligned}$$

Now, use this concentration of $\text{C}_2\text{O}_4^{2-}$ in the K_{sp} expression for CaC_2O_4 to determine the concentration of Ca^{2+} at this point:

$$\begin{aligned}\text{CaC}_2\text{O}_4(\text{s}) &\rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \\ K_{\text{sp}} &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] \\ 2.3 \times 10^{-9} &= [\text{Ca}^{2+}](8.6 \times 10^{-4} \text{ M}) \\ [\text{Ca}^{2+}] &= 2.7 \times 10^{-6} \text{ M}\end{aligned}$$

Question #4

A solution contains 0.005 M AsO_4^{3-} , 0.005 M I^- , and 0.005 M CO_3^{2-} . If AgNO_3 is slowly added, in what order would the silver salts precipitate?

$$\begin{array}{ll}\text{For Ag}_3\text{AsO}_4, & K_{\text{sp}} = 1.0 \times 10^{-22} \\ \text{For AgI,} & K_{\text{sp}} = 8.3 \times 10^{-17} \\ \text{For Ag}_2\text{CO}_3, & K_{\text{sp}} = 8.1 \times 10^{-12}\end{array}$$

$$\begin{aligned}\text{Ag}_3\text{AsO}_4(\text{s}) &\rightleftharpoons 3\text{Ag}^+(\text{aq}) + \text{AsO}_4^{3-}(\text{aq}) \\ Q &= [\text{Ag}^+]^3[\text{AsO}_4^{3-}] \\ 1.0 \times 10^{-22} &= [\text{Ag}^+]^3(0.005 \text{ M}) \\ [\text{Ag}^+] &= 2.71 \times 10^{-7} \text{ M needed for Ag}_3\text{AsO}_4 \text{ to ppt.}\end{aligned}$$

$$\begin{aligned}\text{AgI}(\text{s}) &\rightleftharpoons \text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \\ Q &= [\text{Ag}^+][\text{I}^-] \\ 8.3 \times 10^{-17} &= [\text{Ag}^+](0.005 \text{ M}) \\ [\text{Ag}^+] &= 1.66 \times 10^{-14} \text{ M needed for AgI to ppt.}\end{aligned}$$

$$\begin{aligned}\text{Ag}_2\text{CO}_3(\text{s}) &\rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \\ Q &= [\text{Ag}^+]^2[\text{CO}_3^{2-}] \\ 8.1 \times 10^{-12} &= [\text{Ag}^+]^2(0.005 \text{ M}) \\ [\text{Ag}^+] &= 4.02 \times 10^{-5} \text{ M needed for Ag}_2\text{CO}_3 \text{ to ppt.}\end{aligned}$$

***Lowest concentration will precipitate first: AgI precipitates first, then Ag_3AsO_4 , then Ag_2CO_3 .**

Question #5

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?

$$\begin{aligned}\text{AlPO}_4(\text{s}) &\rightleftharpoons \text{Al}^{3+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \\ Q &= [\text{Al}^{3+}][\text{PO}_4^{3-}] \\ 1.3 \times 10^{-20} &= (0.010 \text{ M})[\text{PO}_4^{3-}] \\ \boxed{[\text{PO}_4^{3-}] = 1.3 \times 10^{-18} \text{ M needed for AlPO}_4 \text{ to ppt.}}\end{aligned}$$

$$\begin{aligned}\text{Ag}_3\text{PO}_4(\text{s}) &\rightleftharpoons 3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \\ Q &= [\text{Ag}^+]^3[\text{PO}_4^{3-}] \\ 1.3 \times 10^{-20} &= (0.010 \text{ M})^3[\text{PO}_4^{3-}] \\ \boxed{[\text{PO}_4^{3-}] = 1.3 \times 10^{-14} \text{ M needed for Ag}_3\text{PO}_4 \text{ to ppt.}}\end{aligned}$$

*Since the concentration of PO_4^{3-} needed for AlPO_4 to precipitate is lower, it will precipitate first. To ensure the best separation, $[\text{PO}_4^{3-}]$ should be as close to the higher concentration ($1.3 \times 10^{-14} \text{ M}$) 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 .