

# **CHEMISTRY 1220**

## **SOLUBILITY**

### **STUDY SESSION**

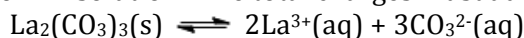
- ☐  **$K_{sp}$  & MOLAR SOLUBILITY**
- ☐ **FACTORS INFLUENCING SOLUBILITY**
- ☐ **COMMON ION EFFECT**
- ☐ **pH & SOLUBILITY**
- ☐ **COMPLEX ION FORMATION**
- ☐ **PRECIPITATION AND SEPARATION OF IONS**
- ☐ **EXAM PREP**

# K<sub>sp</sub> & MOLAR SOLUBILITY

## Question #1

The solubility product expression for La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> is K<sub>sp</sub> = ?

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:

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

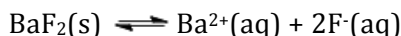
## Question #2

The solubility of BaF<sub>2</sub> is 1.3 g/L. What is the solubility product constant?

Conversely, K<sub>sp</sub> 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<sub>sp</sub> 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<sub>sp</sub>. 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) CaCO<sub>3</sub> K<sub>sp</sub> = 2.8 x 10<sup>-9</sup>
- (b) PbI<sub>2</sub> K<sub>sp</sub> = 8.7 x 10<sup>-9</sup>
- (c) AgBr K<sub>sp</sub> = 5.0 x 10<sup>-13</sup>
- (d) Fe(OH)<sub>2</sub> K<sub>sp</sub> = 8.0 x 10<sup>-16</sup>
- (e) Co(OH)<sub>2</sub> K<sub>sp</sub> = 1.6 x 10<sup>-15</sup>

You can directly compare solids with the **same** ratio of cation to anion (i.e. higher K<sub>sp</sub>, 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?

<b>AgCl</b>	<b><math>K_{sp} = 1.6 \times 10^{-10}</math></b>
<b>Ag<sub>2</sub>CO<sub>3</sub></b>	<b><math>K_{sp} = 8.1 \times 10^{-12}</math></b>
<b>AgBr</b>	<b><math>K_{sp} = 5.0 \times 10^{-13}</math></b>

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 Ag<sub>2</sub>CO<sub>3</sub> has the highest concentration of silver ion (Note: this is not just because silver has a subscript of 2 after it in Ag<sub>2</sub>CO<sub>3</sub>; you must calculate the actual concentration for each compound).

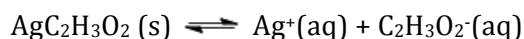
# FACTORS INFLUENCING SOLUBILITY

## 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.

$\text{HNO}_3$ -  $\text{C}_2\text{H}_3\text{O}_2^-$  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  $\text{HNO}_3$ , 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**.

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

$\text{AgNO}_3$ - 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:

$\text{BaC}_2\text{O}_4$ -  $\text{C}_2\text{O}_4^{2-}$  is the conjugate base of the weak acid  $\text{HC}_2\text{O}_4$ . **Solubility increases**.

$\text{CaS}$ -  $\text{S}^{2-}$  is the conjugate base of the weak acid  $\text{HS}^-$ . **Solubility increases**.

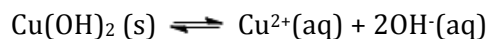
$\text{AuCl}_3$ -  $\text{Cl}^-$  is the conjugate base of the strong acid  $\text{HCl}$ . Solubility is NOT affected.

$\text{PbF}_2$ -  $\text{F}^-$  is the conjugate base of the weak acid  $\text{HF}$ . **Solubility increases**.

$\text{ZnCO}_3$ -  $\text{CO}_3^{2-}$  is the conjugate base of the weak acid  $\text{HCO}_3^-$ . **Solubility increases**.

### Question #3

Would each of the following reagents increase, decrease, or have no effect on the solubility of  $\text{Cu}(\text{OH})_2$ ?



$\text{CuCl}_2$ -common ion, therefore decreases solubility.

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

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

$\text{NaOH}$ - common ion, therefore decreases solubility.

### Question #4

Which salt solubility would be most sensitive to pH?



All of the cations are  $\text{Ca}^{2+}$ , 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  $\text{F}^-$  is the conjugate base of a **weak** acid. The rest are conjugate bases of strong acids. Therefore  **$\text{CaF}_2$**  is most sensitive to pH.

### Question #5

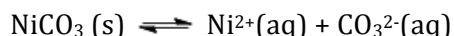
The solubility of which of the listed salts would be unaffected by the presence of a strong acid?



Conjugate bases of **strong** acids will be unaffected by addition of a strong acid. The salts with this type of conjugate base include  **$\text{KClO}_4$**  ( $\text{HClO}_4$  is a strong acid) and  **$\text{SnI}_2$**  ( $\text{HI}$  is a strong acid).  $\text{BaF}_2$  and  $\text{FePO}_4$  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  $\text{NiCO}_3$  would change the solubility of  $\text{NiCO}_3$ ?



$\text{HCl}$ - This strong acid can neutralize  $\text{CO}_3^{2-}$  because this anion is the conjugate base of a weak acid. This removes  $\text{CO}_3^{2-}$ , shifting the reaction to the right and **increasing solubility**.

$\text{NiCl}_2$ - common ion, therefore **decreases solubility**.

$\text{NaCl}$ - no effect.

$\text{Na}_2\text{CO}_3$ - common ion, therefore **decreases solubility**.

$\text{NH}_3$ -  $\text{Ni}^+$  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**

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

**$\text{NaNO}_3$**

**$\text{BaF}_2$**

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

### Question #8

Zinc oxalate is a slightly soluble salt. How many of the following reagents would be expected to decrease the solubility of  $\text{ZnC}_2\text{O}_4$ ?

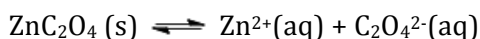
**$\text{Na}_2\text{C}_2\text{O}_4$**

**$\text{NH}_3$**

**$\text{NaOH}$**

**$\text{HCl}$**

**$\text{ZnCl}_2$**



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

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

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

$\text{HCl}$ -  $\text{C}_2\text{O}_4^{2-}$  is the conjugate base of a weak acid ( $\text{HC}_2\text{O}_4^-$ ), and is therefore a weak base itself. It can be neutralized by  $\text{HCl}$ , 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.

$\text{ZnCl}_2$ - common ion, therefore **decreases solubility**.

# COMMON ION EFFECT

## Question #1

What is the molar solubility of  $\text{MgF}_2$  in  $0.40 \text{ M F}^-$ ?  $K_{\text{sp}} \text{MgF}_2 = 6.4 \times 10^{-9}$

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

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

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

## Question #2

The solubility product constant for  $\text{BiI}_3$  is  $8.1 \times 10^{-19}$ . Calculate the molar solubility of  $\text{BiI}_3$  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	-----		<b>0.20 M</b>		0 M
Change	-----		+1x M		+3x M
Equilibrium	-----		x+ <b>0.20 M</b>		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  $5.0 \times 10^{-17}$ . 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		<b><math>3.16 \times 10^{-3} M</math></b>
Change	-----		+1x M		NO CHANGE
Equilibrium	-----		x M		<b><math>3.16 \times 10^{-3} M</math></b>

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

## 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:

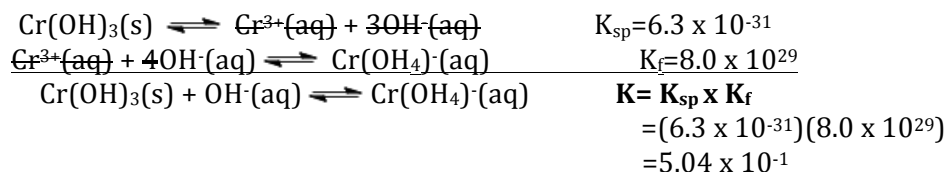
$$\begin{aligned} [OH^-] &= 2x = 2(4.0 \times 10^{-7} M) = 8.0 \times 10^{-7} M \\ [H^+][OH^-] &= 1.0 \times 10^{-14} \\ [H^+](8.0 \times 10^{-7} M) &= 1.0 \times 10^{-14} \\ [H^+] &= 1.2 \times 10^{-8} M \\ pH &= -\log[H^+] = -\log(1.2 \times 10^{-8}) = \boxed{7.9} \end{aligned}$$



### Question #3

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

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  $\text{OH}^-$  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  $\text{OH}^-$  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,  $[\text{Cd}^{2+}]$ , in a solution that contains 0.20 M  $\text{Cd}(\text{NO}_3)_2$  in 2.0 M NaCN. Cadmium ion forms the complex ion,  $\text{Cd}(\text{CN})_4^{2-}$  for which  $K_f$  is  $6.0 \times 10^{18}$ .

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

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

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

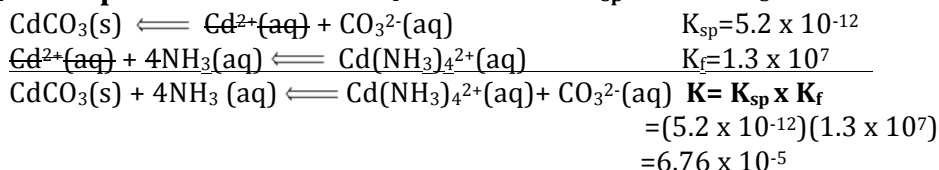
These equilibrium concentrations refer to the reverse reaction, so they do not correspond to  $K_f$ , instead they correspond to  $K_d$ , **the dissociation constant**, which is  $1/K_f$  (K for a reverse reaction always equals the inverse of K for the forward reaction):

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

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

## Question #2

35. Calculate the molar solubility of  $\text{CdCO}_3$  in 1.5 M  $\text{NH}_3$ . Note that  $\text{Cd}^{2+}$  forms the  $\text{Cd}(\text{NH}_3)_4^{2+}$  complex ion for which  $K_f$  is  $1.3 \times 10^7$ .  $K_{sp}$  for  $\text{CdCO}_3$  is  $5.2 \times 10^{-12}$ .



	$\text{CdCO}_3(\text{s})$	+	$4\text{NH}_3(\text{aq})$	$\rightleftharpoons$	$\text{Cd}(\text{NH}_3)_4^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
Initial	-----		1.5 M		0 M		0 M
Change	-----		-4x M		+x M		+x M
Equilibrium	-----		1.5-4x M		x M		x M

$$K = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}][\text{CO}_3^{2-}]}{[\text{NH}_3]^4} = \frac{x^2}{(1.5-4x)^4} = 6.76 \times 10^{-5}$$

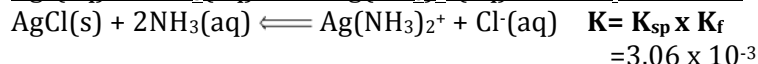
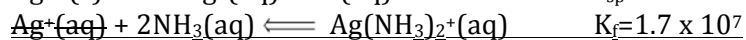
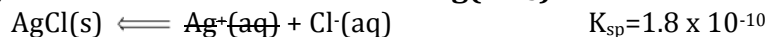
$$x = 1.8 \times 10^{-2} \text{ M}$$

**Question #3**

Calculate the molar solubility of AgCl in 12 M NH<sub>3</sub>.

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

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



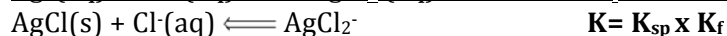
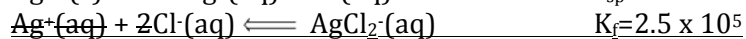
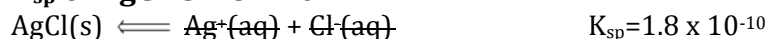
	AgCl(s)	+	2NH <sub>3</sub> (aq)	⇌	Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	+	Cl <sup>-</sup> (aq)
Initial	-----		12 M		0 M		0 M
Change	-----		-2x M		+x M		+x M
Equilibrium	-----		12-2x M		x M		x M

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

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

**Question #4**

The Ag<sup>+</sup> ion forms the complex ion AgCl<sub>2</sub><sup>-</sup> for which K<sub>f</sub> = 2.5 x 10<sup>5</sup>. Determine the equilibrium constant for the solubility of AgCl in the presence of excess chloride ion. K<sub>sp</sub> of AgCl is 1.8 x 10<sup>-10</sup>.



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

**Question #5**

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

	AgCl(s)	+	Cl <sup>-</sup> (aq)	⇌	AgCl <sub>2</sub> <sup>-</sup> (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:

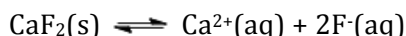
\*\*If  $Q < K_{sp}$ , there are not enough products. The solution is **unsaturated**, and the reaction will shift to the right, so NO precipitate is formed. More solid can be dissolved.

\*\*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  $\text{Ca}^{2+}$  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  $\text{Ca}^{2+}$  solution is added to 25.0 mL of  $5.0 \times 10^{-3} \text{ M Na}_3\text{PO}_4$  will a precipitate form?**

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



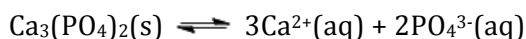
The concentrations of each ion must be calculated because the volumes change once they are added together:

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

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

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

$Q > K_{sp}$ , 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  $\text{Ag}^+$  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  $\text{Na}_3\text{PO}_4$ ?**

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

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

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



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

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

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

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



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

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

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

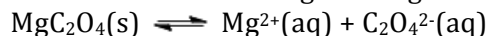
$$[\text{Ag}^+] = 1.0 \times 10^{-6} \text{ M needed for Ag}_3\text{PO}_4 \text{ to ppt.}$$

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

### Question #3

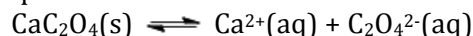
A solution contains 0.10 M  $\text{Mg}(\text{NO}_3)_2$  and 0.10 M  $\text{Ca}(\text{NO}_3)_2$ . If solid sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , is added to the solution, what is  $[\text{Ca}^{2+}]$  (M) when  $\text{MgC}_2\text{O}_4$  begins to precipitate? (Assume no volume changes.) At 25 °C,  $K_{\text{sp}}$  of  $\text{CaC}_2\text{O}_4$  is  $2.3 \times 10^{-9}$  and  $K_{\text{sp}}$  of  $\text{MgC}_2\text{O}_4$  is  $8.6 \times 10^{-5}$ .

First, calculate the concentration of  $\text{C}_2\text{O}_4^{2-}$  when  $\text{MgC}_2\text{O}_4$  begins to precipitate:



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

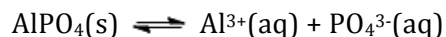
Now, use this concentration of  $\text{C}_2\text{O}_4^{2-}$  in the  $K_{\text{sp}}$  expression for  $\text{CaC}_2\text{O}_4$  to determine the concentration of  $\text{Ca}^{2+}$  at this point:



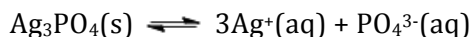
$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] \\ 2.3 \times 10^{-9} &= [\text{Ca}^{2+}](8.6 \times 10^{-4} \text{ M}) \\ [\text{Ca}^{2+}] &= 2.7 \times 10^{-6} \text{ M} \end{aligned}$$

### Question #4

A solution contains 0.010 M  $\text{Al}^{3+}$  and 0.010 M  $\text{Ag}^+$ . Solid  $\text{Na}_3\text{PO}_4$  is slowly added to separate the two cations.  $K_{\text{sp}}$  for  $\text{AlPO}_4$  is  $1.3 \times 10^{-20}$  and  $K_{\text{sp}}$  for  $\text{Ag}_3\text{PO}_4$  is  $1.3 \times 10^{-20}$ . Which cation would precipitate first, and after it precipitates, what concentration of  $\text{PO}_4^{3-}$  ion should be obtained in the solution for the best separation?



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



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

\*Since the concentration of  $\text{PO}_4^{3-}$  needed for  $\text{AlPO}_4$  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  $\text{AlPO}_4$  will be solid, but no  $\text{Ag}^+$  will have precipitated yet into  $\text{Ag}_3\text{PO}_4$ .