SUBJECTIVE SOLVED EXAMPLES

Example - 1 *A solution contains a mixture of* $Ag^+(0.1M)$ *and* Hg_2^{2+} $(0.10\ M)$ *which are separated by selective precipitation. Calculate maximum concentration of Iodide ion at which one of them gets precipitated almost completely. What % age of that metal ion is precipitated ?* $\left(K_{sp\ AgI} = 8.5\times10^{-17}\ M\ ;\ \ K_{sp\ Hg_2I_2} = 2.5\times10^{-26}\right)$

SOLUTION :

First determine, which ion starts precipitating first

$$[I^-]_{\text{Min. for AgI}} = \frac{K_{sp}\text{ of AgI}}{[Ag^+]}$$

$$= \frac{8.5\times10^{-17}}{0.1} = 8.5\times10^{-16}\ \text{M}$$

$$[I^-]_{\text{Min. for }Hg_2I_2} = \sqrt{\frac{K_{sp}\text{ of }Hg_2I_2}{[Hg_2^{2+}]}}$$

$$= \sqrt{\frac{2.5\times10^{-26}}{0.1}} = 5\times10^{-13}\ \text{M}$$

This means that AgI will be precipitated first as $[I^-]$ required for AgI is less.

But when $[I^-]$ reaches 5×10^{-13} M then precipitation of Hg_2I_2 also starts.

So $[Ag^+]$ left at that stage is given as :

$$[Ag^+] = \frac{K_{sp}\text{ of AgI}}{[I^-]_{Hg_2I_2}} = \frac{8.5\times10^{-17}}{5.0\times10^{-13}} = 1.7\times10^{-4}\text{M}$$

$$\%\text{ of }Ag^+\text{ left un-precipitated} = \frac{1.7\times10^{-4}}{0.1}\times100 = 0.17\%$$

$\Rightarrow$ % age of Ag^+ precipitated $= 99.83\ \%$

This means when Hg_2I_2 starts precipitating, Ag^+ is almost precipitated.

Example - 2 *Carbonic acid,* H_2CO_3*, is a diprotic acid for which* $K_1 = 10^{-7}$ *and* $K_2 = 10^{-11}$*. Which solution will produce a pH closest to 9?*

(A) $0.1\ M\ H_2CO_3$ **(B)** $0.1\ M\ Na_2CO_3$ **(C)** $0.1\ M\ NaHCO_3$ **(D)** $0.1\ M\ NaHCO_3$ *and* $0.1\ M\ Na_2CO_3$

SOLUTION : (C)

Amphiprotic salt is a salt that can donate proton as well as can accept a proton. For example : NaHS, $NaHCO_3$ etc.

$$NaHS \longrightarrow Na^+ + HS^-$$

$$HS^- + H^+ \rightleftharpoons H_2S$$

$$HS^- \rightleftharpoons S^{2-} + H^+$$

pH of amphiprotic salt of weak acid is calculated by using following expression.

$$pH = \frac{1}{2}\left[pK_{a_1} + pK_{a_2}\right]$$

$$pH = \frac{1}{2}\left[pK_{a_1} + pK_{a_2}\right] = \frac{1}{2}[7+11] = 9$$

Example - 3 *For the reaction* $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$, *in an aqueous medium, the equilibrium constant,* K_C *at* 25°C *is* 4×10^{-19}. *Calculate the* Ag^+ *ion concentration in the solution which was originally* 0.1 *M in KCN and* 0.03 *M* $AgNO_3$.

SOLUTION :

0.1 M KCN and 0.03 M $AgNO_3$ are mixed.

Since K_{eq} for $Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$ is very-very high $\left(K = \frac{1}{4}\times 10^{19}\right)$, first assume that whole of Ag^+ is converted to $Ag(CN)_2^-$.

$$\begin{array}{cccc} Ag^+ & + \quad 2CN^- & \longrightarrow & Ag(CN)_2^- \\ 0.03\text{ M} & 0.1\text{ M} & & 0 \\ 0 & 0.1 - 2\times 0.03\text{ M} & & 0.03\text{ M} \end{array}$$

Now, 0.03 M $Ag(CN)_2^-$ $(K_{eq} = 4 \times 10^{-19})$

dissociate as follows :

$$\begin{array}{cccc} Ag(CN)_2^- & \rightleftharpoons & Ag^+ & + \quad 2CN^- \\ 0.03\text{ M} & & - & 0.04\text{ M} \\ 0.03 - x & & x & (0.04 + 2x) \end{array}$$

$$K_C = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = 4 \times 10^{-19}$$

$$\Rightarrow \quad [Ag^+] = \frac{K_C[Ag(CN)_2^-]}{[CN^-]^2}$$

$$= \frac{4\times10^{-19}[0.03 - x]}{(0.04 + 2x)^2}$$

Solve the above equation by assuming 'x' to be very small.

$$\Rightarrow \quad [Ag^+] = \frac{4\times10^{-19}[0.03]}{(0.04)^2} = 7.5\times10^{-18}\text{ M}$$

[Verify the approximation yourself]

Example - 4 *Calculate* $[NH_4^+]$ *(derived from* NH_4Cl*) needed to prevent* $Mg(OH)_2$ *from precipitating in a litre of solution which contains* 0.2 *mole of ammonia and* 0.001 *mole of* Mg^{2+} *ions. The ionisation constant of ammonia is* 2.0×10^{-5} *and* K_{sp} *of* $Mg(OH)_2$ *is* 1.0×10^{-11}.

SOLUTION :

Note that aq. ammonia is NH_4OH.

First check whether we need to add NH_4Cl.

$$[OH^-]_{\text{From } NH_3} = \sqrt{K_b c} = 2\times10^{-3}\text{ M}$$

$$\left[\because\ \alpha = \sqrt{\frac{K_b}{c}} = 10^{-2} \Rightarrow 1-\alpha \sim 1\right]$$

$$\Rightarrow \quad I.P_{Mg(OH)_2} = 10^{-3}\times(2\times10^{-3})^2 = 4\times10^{-9} > K_{sp}$$

Thus, precipitation will take place if NH_4Cl is not added and hence, NH_4Cl is required to be added so as to suppress the dissociation of NH_4OH. As a result, $[OH^-]$ will decrease.

Now, calculate the concentration of OH^- ions in equilibrium with Mg^{2+} ions from Ksp of $Mg(OH)_2$.

$$K_{sp} \text{ of } Mg(OH)_2 = [Mg^{2+}]\,[OH^-]^2$$

$$\Rightarrow \quad [OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.0\times10^{-11}}{0.001}} = 1.0\times10^{-4}$$

If $[OH^-] \le 1.0\times10^{-4}$M, Mg^{2+} ions will not be precipitated. So, maximum concentration of OH^- in the solution should be 1.0×10^{-4} M. As $[OH^-]$ is derived from dissociation of ammonia, consider dissociation of ammonia.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$\Rightarrow \quad [NH_4^+] = \frac{K_b[NH_4OH]}{[OH^-]}$$

$$\Rightarrow \quad [NH_4^+]_{min} = \frac{(2.0\times10^{-5})(0.2)}{[1.0\times10^{-4}]} = 4.0\times10^{-2}\text{ M}$$

For this much concentration of NH_4^+ ions, Mg^{2+} will not be precipitated.

Example - 5 *When a 40 mL of a 0.1 M weak base, BOH is titrated with 0.10 M HCl, the pH of the solution at the end point is 5.5. What will be the pH if 10 mL of 0.10 M NaOH is added to the resulting solution ?*

SOLUTION :

At the end point, pH = 5.5 (i.e. an acidic solution). It means salt formed at the end of neutralisation undergoes hydrolysis.

For 4 millimoles (40×0.1) of weak base, 4 millimoles of acid is required at the end point.

$$\begin{array}{cccc} BOH & + HCl & \rightleftharpoons & BCl + H_2O \\ 4 & 4 & & \\ - & - & & 4 \end{array}$$

$\Rightarrow$ millimoles of salt (BCl) formed = 4

$\Rightarrow$ $[BCl] = 4/V$ where $V = V_{HCl} + V_{base}$

At the end point : $4 = 0.10 \times V_{HCl}$

$\Rightarrow$ $V_{HCl} = 40\,mL$

$\Rightarrow$ $V = 40 + 40 = 80\,mL$

$\Rightarrow$ $[BCl] = 4/80 = 0.05\,M$

Note that BCl is a salt of strong acid and weak base.

$$\Rightarrow \quad [H^+] = \sqrt{\frac{K_w\ c}{K_b}}$$

$$\Rightarrow \quad K_b = \frac{K_w\ c}{[H^+]^2} = \frac{(10^{-14}) \times (0.05)}{(10^{-5.5})^2} = 5.0 \times 10^{-5}$$

When 10 mL of 0.12 M NaOH is added :

$$\begin{array}{lllll} & BCl & + \ NaOH & \longrightarrow BOH & + \ NaCl \\ \text{Initially} & 4\ \text{m.moles} & 10 \times 0.10 & & \\ \text{Finally} & 4 - 10 \times 0.10 & & & \\ & 4 - 1 = 3.0 & - & 1.0 & \end{array}$$

It means a basic buffer containing 3.0 m.moles of BCl and 1.0 m.moles of BOH is fomed. Find the pH by using Henderson's equation for basic buffer.

$$pOH = pK_b + \log \frac{[BCl]}{[BOH]}$$

$$\Rightarrow \quad pOH = -\log(5 \times 10^{-5}) + \log \frac{[3.0/V]}{[1.0/V]}$$

$$\Rightarrow \quad pOH = 4.77 \qquad (pK_b = 4.3)$$

$$\Rightarrow \quad pH = 14 - pOH = 9.22$$

Example - 6 *It is given that 0.001 mol each of Cd^{2+} and Fe^{2+} ions are contained in 1.0 L of 0.02M HCl solution. This solution is now saturated with H_2S gas at 25°C.*

(a) *Determine whether or not each of these ions will be precipitated as sulphide ?*

(b) *How much Cd^{2+} ions remain in the solution at equilibrium ?*

$$K_1(H_2S) = 1.0 \times 10^{-7} \ ; \ K_2(H_2S) = 1.0 \times 10^{-14} \ ; \ K_{sp}(CdS) = 8 \times 10^{-27} \ ; \ K_{sp}(FeS) = 3.7 \times 10^{-19}$$

SOLUTION :

Note that two salts are of same type (i.e., AB type) and K_{sp} of CdS is lower than that of FeS. This means CdS will precipitate first if at all any precipitation takes place.

Calculate the minimum concentration of Sulphide ion required to initiate the precipitation of each of the metal sulphide.

$$[S^{2-}]_{\text{Min for CdS}} = \frac{K_{sp}\,CdS}{[Cd^{2+}]} = \frac{8 \times 10^{-27}}{0.001} = 8 \times 10^{-24}\,M$$

$$[S^{2-}]_{\text{Min for FeS}} = \frac{K_{sp}\,FeS}{[Fe^{2+}]} = \frac{3.7 \times 10^{-19}}{0.001} = 3.7 \times 10^{-16}\,M$$

Now calculate the sulphide ion concentration in the saturated solution, using :

$$K_a = K_1 \times K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = 10^{-21}$$

$$\Rightarrow \quad [S^{2-}] = \frac{10^{-21} \times 0.1}{0.02^2} = 2.5 \times 10^{-19}\,M$$

$$\Rightarrow \quad [Cd^{2+}]_{\text{Left}} = \frac{8 \times 10^{-27}}{2.5 \times 10^{-19}} = 3.2 \times 10^{-8}\,M$$

Thus, only CdS will get precipitated.

To calculate the remaining concentration of Cd^{2+} ion (more accurately) in the solution, first assume that whole of the Cd^{2+} has been precipitated as :

$$Cd^{2+} + H_2S \longrightarrow CdS + 2\,H^+$$

Thus, $[H^+]_{new} = 0.02 + 0.001 \times 2 = 0.022$ M

$$\Rightarrow \quad [S^{2-}]_{\text{At new equilibrium}} = \frac{10^{-21} \times 0.1}{0.022^2}$$

$$= 2.07 \times 10^{-19}\ \text{M}$$

$$\Rightarrow \quad [Cd^{2+}]_{\text{Left}} = \frac{8 \times 10^{-27}}{2.07 \times 10^{-19}} = 3.86 \times 10^{-8}\ \text{M}$$

Note : FeS will not be precipitated at all.

Example - 7 *The solubility product, K_{sp} of $Ca(OH)_2$ at 25°C is 4.0×10^{-6}. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH solution. How much $Ca(OH)_2$ in milligrams is precipitated ?*

SOLUTION :

First find the concentration of Ca^{2+} ions at saturation using K_{sp} of $Ca(OH)_2$.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$\Rightarrow \quad K_{sp} = [Ca^{2+}]\,[OH^-]^2$$

Let $[Ca^{2+}] = x$ mol/L $\quad \Rightarrow \quad [OH^-] = 2x$

$$\Rightarrow \quad K_{sp} = 4x^3 \quad \text{or} \quad x = \sqrt[3]{\frac{K_{sp}}{4}} = 0.01\ \text{M}$$

$$\Rightarrow \quad [Ca^{2+}] = 0.01\ \text{M and } [OH^-] = 0.02\ \text{M}$$

As equal volumes of saturated solution and 0.4 M NaOH are mixed :

$$[Ca^{2+}] = \frac{0.01}{2} = 5 \times 10^{-3}\ \text{M}$$

and $$[OH^-]_{\text{Total}} = \frac{0.02}{2} + \frac{0.4}{2} = 0.21\text{M}$$

$$[\because \ [OH^-]_{\text{Total}} = [OH^-]_{\text{NaOH}} + [OH^-]_{\text{From}\,Ca(OH)_2}]$$

Now, calculate $I.P._{Ca(OH)_2} = [Ca^{2+}]\,[OH^-]^2$

$$= (5 \times 10^{-3})\,(0.21)^2 = 2.2 \times 10^{-4} > K_{sp}$$

Since concentration of OH^- is quite high, Ca^{2+} will be precipitated till a new saturation state is reached.

Let at new saturated state, $[OH^-] = 0.21$ M

(Assuming no change in $[OH^-]$)

$$[Ca^{2+}]_{\text{left}} = \frac{K_{sp}}{[OH^-]^2} = \frac{(4 \times 10^{-6})}{(0.21)^2} = 9.07 \times 10^{-5}\ \text{M}$$

$$\Rightarrow \quad [Ca^{2+}]\ \text{precipitated} = 5 \times 10^{-3} - 9.07 \times 10^{-5}\ \text{M}$$

$$= 4.91 \times 10^{-3}\ \text{M}$$

$$\Rightarrow \quad \text{amount of } Ca^{2+} = 4.91 \times 10^{-3} \times 74 \times 10^3\ \text{mg/L}$$

$$= 363.3\ \text{mg/L}$$

Check the approximation : $[OH^-]_{\text{left}} \sim 0.21$ M. How ??

Find out the $[OH^-]_{\text{used}} = 2\,[Ca^{2+}]_{\text{used}}$

(see Reaction's Stoichiometry)

$$= 2 \times 4.91 \times 10^{-3}\ \text{M} = 9.8 \times 10^{-3}\ \text{M}$$

$$\Rightarrow \quad [OH^-]_{\text{left}} = 0.21 - 9.8 \times 10^{-3}\ \text{M} = 0.2\ \text{M} \approx 0.21\ \text{M}$$

Alternate Approach :

		$Ca(OH)_2\,(s) \rightleftharpoons$	$Ca^{2+}\,(aq)$ +	$2\,OH^-\,(aq)$	
$t = t_{eq}$:	concentration :		0.01	0.02	I.P. = K_{sp}
$t = 0$ (new) :	concentration :		5×10^{-3}	0.21	I.P. > K_{sp}
(After mixing equal volumes with NaOH)					
$t = t_{eq}$ (new)			$5 \times 10^{-3} - x$	$0.21 - 2x$	I.P. = K_{sp}

Now, I.P. = K_{sp} at equilibrium

$(5 \times 10^{-3} - x)\,(0.21 - 2x)^2 = 4 \times 10^{-6}$ $\Rightarrow$ This equation in 'x' is clearly a cubic.

To solve the above equation approximately, assume $0.21 - 2x \sim 0.21$ which is what has been done in the previous approach.

Example - 8 *The solubility product of $Ag_2C_2O_4$ at 25°C is 1.20×10^{-11}. A solution of $K_2C_2O_4$ containing 0.15 moles in 500 ml water is mixed with excess of Ag_2CO_3 till the following equilibrium is established :*

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3.$$

At equilibrium, the solution contains 0.03 mole of K_2CO_3. Assuming that the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. [Take 100% ionisation of $K_2C_2O_4$ and K_2CO_3]

SOLUTION :

$$\underset{\text{initial}}{[K_2C_2O_4]} = \frac{0.15}{0.5} = 0.30\,M = P$$

and $$\underset{\text{final}}{[K_2CO_3]} = \frac{0.03}{0.5} = 0.06\,M = x$$

$$\begin{array}{lcl} Ag_2CO_3 + K_2C_2O_4 & \rightleftharpoons & K_2CO_3 + Ag_2C_2O_4 \\ \quad P & & \quad - \\ \quad P - x & & \quad x \end{array}$$

1 mol K_2CO_3 $\equiv$ 1 mol $K_2C_2O_4$ and since both are completely ionized :

Now find $[Ag^+]$ at equilibrium as :

$$[Ag^+] = \sqrt{\frac{K_{sp} \text{ of } Ag_2C_2O_4}{[C_2O_4^{2-}]}}$$

$$= \sqrt{\frac{1.20 \times 10^{-11}}{P - x}} = \sqrt{\frac{1.20 \times 10^{-11}}{0.3 - 0.06}} = 7.07 \times 10^{-6}\,M$$

$$[CO_3^{2-}]_{\text{final}} = x = 0.06\,M$$

Now, K_{sp} of $Ag_2CO_3 = [Ag^+]^2\,[CO_3^{2}]$

$\Rightarrow$ K_{sp} of $Ag_2CO_3 = (7.07 \times 10^{-6})^2 \times 0.06$

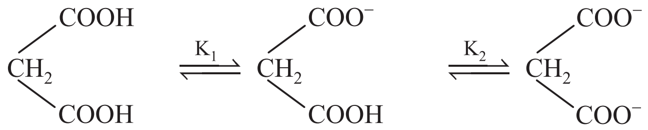
$= 3 \times 10^{-12}$

Example - 9 *Malonic acid is an organic dibasic acid like H_2S having first ionisation constant, $K_1 = 1.42 \times 10^{-3}$ and second ionisation constant, $K_2 = 2.0 \times 10^{-6}$. Compute the divalent malonate ion concentration in :*

(a) *0.001 M Malonic acid* **(b)** *in a solution that is 0.0001 M in malonic acid and 0.0004 M HCl.*

(c) *in a solution that is 0.0001 M in malonic acid and 0.1 M HCl.*

SOLUTION :



(a) Consider malonic acid to be H_2A, where malonate ion is A^{2-}. For dibasic acids, we consider ionisation in two stages as follows :

$$\begin{array}{lcccc} H_2A & \rightleftharpoons & H^+ & + & HA^- \\ c - x & & x & & x \end{array}$$

; First ionisation constant = $K_1 = 1.42 \times 10^{-3}$

c = initial concentration = 0.001 M.

$$\Rightarrow \quad K_1 = \frac{[H^+][HA^-]}{[H_2A]} = \frac{x^2}{c - x} = 1.42 \times 10^{-3}$$

Solving the quadratic, $x^2 + 1.42 \times 10^{-3}x - 1.42 \times 10^{-6} = 0$ $\Rightarrow$ $x = 6.75 \times 10^{-4}$ M

Note that $K_1 >> K_2$, so concentration of H^+ in solution is considered only from first dissociation, i.e., $[H^+] = x$ M *(neglect H^+ concentration from second ionisation).*

Consider second ionisation :

$$\begin{array}{lcccc} HA^- & \longrightarrow & H^+ & + & A^{2-} \\ x & & x & & - \\ x - y & & x + y & & y \end{array}$$

; Second ionisation constant = $K_1 = 2.0 \times 10^{-6}$

$$\Rightarrow \qquad K_2 = \frac{[H^+][A^2\ \ ]}{[HA^-]} = \frac{(x+y)\,y}{x-y}$$

Note : $[H^+] = x + y \approx x$ $\qquad [HA^-] = x - y \approx x$ $\qquad (y << x)$

$$\Rightarrow \qquad K_2 = y = [A^{2-}] = 2.0 \times 10^{-6}\ M$$

Note : Usually, $[A^{2-}]$ for H_2A (dibasic acid) can be approximately taken to be K_2.

(b) Here $c = 10^{-4}$ M, $[H^+] = 4 \times 10^{-4}$ M (From HCl)

$$\Rightarrow \qquad K_1 = \frac{[H^+][HA^-]}{[H_2A]} = \frac{(4\times 10^{-4} + x)(x)}{10^{-4} - x} = 1.42 \times 10^{-3}$$

Important : *Note that, we can not go for approximation in this case, since the concentration of HCl is so low that* H^+ *is considered both from HCl and malonic acid.*

Solving the quadratic, $x^2 + 1.82 \times 10^{-3}\,x - 1.42 \times 10^{-7} = 0 \quad \Rightarrow \quad x = 7.5 \times 10^{-5}$ M

Now consider, second ionisation and substitute for value of x.

$$K_2 = \frac{[H^+][A^{2-}]}{[HA^-]} = \frac{(4\times 10^{-4} + x)\,y}{x} = 2.0 \times 10^{-6}$$

$$\Rightarrow \qquad \frac{(4\times 10^{-4} + 7.5\times 10^{-5})\ y}{7.5\times 10^{-5}} = 2.0 \times 10^{-6} \qquad \Rightarrow \qquad y = [A^{2-}] = 3.2 \times 10^{-7}\ M$$

(c) Here $c = 10^{-4}$ M, $[H^+] = 0.1$ M

$$\Rightarrow \qquad K_a = K_1K_2 = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = \frac{(0.1)^2[A^{2-}]}{10^{-4}} = 2.84\times 10^{-9} \qquad \Rightarrow \qquad [A^{2-}] = 2.84 \times 10^{-11}\ M$$

Important : *Note that, we will do the approximation in this case, since the concentration of HCl is so high that* H^+ *is considered from malonic acid is negligible*. Recall the ionization of H_2S (g) in an acidic solution.

Example - 10 *Calculate the* $[F^-]$ *in a solution saturated with respect to* MgF_2 *and* SrF_2.

$K_{sp}\,(MgF_2) = 6.0 \times 10^{-9}$; $K_{sp}\,(SrF_2) = 3.0 \times 10^{-9}$

SOLUTION :

In this case, please note that the K_{sp} values of two salts are very similar. So the concentration of F^- ions (the common ion) can not be calculated from a single salt alone.

Let the simultaneous solubilities of MgF_2 and SrF_2 be x and y respectively in mol/L.

$$\underset{}{MgF_2\,(s)} \rightleftharpoons \underset{x}{Mg^{2+}} + \underset{2x}{2\,F^-}$$

$$\underset{}{SrF_2\,(s)} \rightleftharpoons \underset{y}{Sr^{2+}} + \underset{2y}{2\,F^-}$$

At eq : $[F^-] = 2x + 2y$; $\quad [Mg^{2+}] = x$; $\quad [Sr^{2+}] = y$

$$\Rightarrow \qquad [Mg^{2+}][F^-]^2 = K_{sp\ MgF_2}$$

and $\qquad [Sr^{2+}][F^-]^2 = K_{sp\ SrF_2}$

Note that : $\qquad [F^-] = 2\left([Mg^{2+}] + [Sr^{2+}]\right)$

[This is an Electrical charge neutrality equation]

$$[F^-] = 2\left(\frac{K_{sp\ MgF_2}}{[F^-]^2} + \frac{K_{sp\ SrF_2}}{[F^-]^2}\right)$$

$$\Rightarrow \qquad [F^-] = \sqrt[3]{2\left(K_{sp\ MgF_2} + K_{sp\ SrF_2}\right)}$$

$$= 2.62 \times 10^{-3}\ M$$