

Objectives

At the end of this unit the student will be able to :

- 1- Write the K_{sp} expression for the ionization of any salts.
 - 2- Calculate K_{sp} from solubility and vice versa.
 - 3- Tell if a precipitate will form when mixing solutions .
 - 4- predict whether it is possible to separate metal ions by the precipitation of its hydroxides or salts .
 - 5- predict whether a complexing agent will dissolve the metal precipitate or not .
 - 6- Understand the concept of common ion effect .
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Introduction



The concept of solubility product is very useful in explaining many phenomena. Various fields in which it can be used are:-

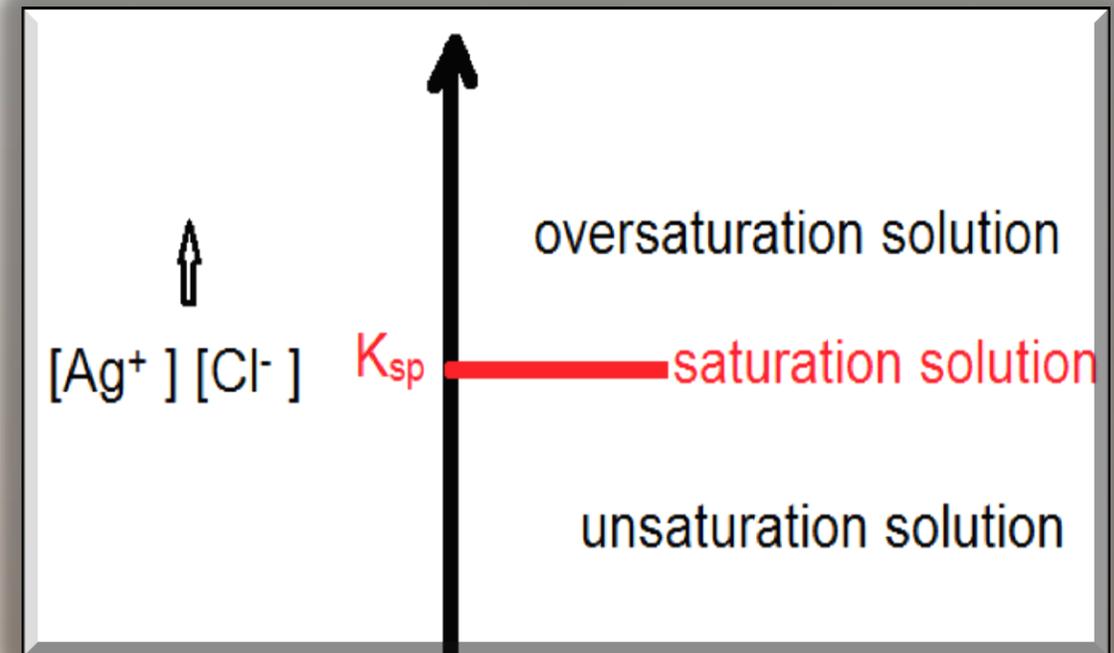
1. Calculation of solubility: If we know the solubility product of a meagerly soluble salt like AgCl we can calculate the solubility of the salt and vice versa.
2. In predicting the precipitation in reactions: If we know the solubility product of a salt, we can find whether on mixing the solution of its ions, precipitation will occur or not.
3. In inorganic qualitative analysis:

The concept of solubility product and common ion effect play a vital role in the separation of basic radicals i.e. cations into different groups of qualitative analysis.

4. Purification of sodium chloride: Sodium Chloride obtained from sea water or lakes is always impure. It can be purified on the basis of common ion effect .

The Solubility Product Concept

When adding Cl^- solution to a beaker containing Ag^+ solution, the product of $[\text{Cl}^-] \times [\text{Ag}^+]$ in the beaker solution will increase until reaching what so called solubility product constant (K_{sp}) of the compound AgCl . Before reaching K_{sp} the beaker solution is called unsaturated when reaching K_{sp} the solution is called saturated and in both states no precipitation occurs. But when the product of $[\text{Cl}^-] \times [\text{Ag}^+]$ exceeds the value of K_{sp} , the solution is called oversaturated and the precipitation of AgCl may occurs.

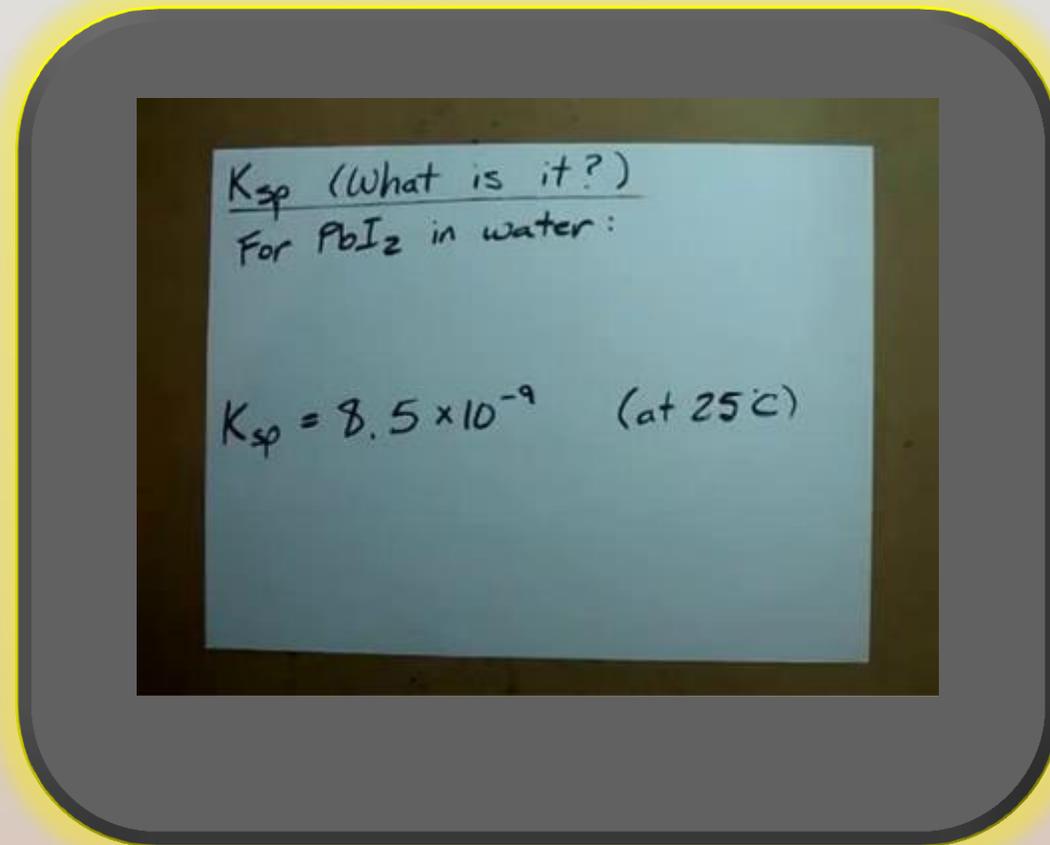


The Solubility Product Concept

The state of oversaturation is temporary (less than one second) because Cl^- and Ag^+ will react to form the precipitate AgCl

and the $[\text{Cl}^-]$ and $[\text{Ag}^+]$ will go back to the saturation state .So when you see a solution of AgCl with a solid in it you will know that the product of $[\text{Cl}^-] \times [\text{Ag}^+]$ dissolving in solution is equal to the K_{sp} of AgCl . What we said about AgCl applies to all salts .

To write the expression of K_{sp} for any salt you should first write the dissociation equation , for example the dissociation equation for the salt Al_2S_3 is :



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The Solubility Product Concept

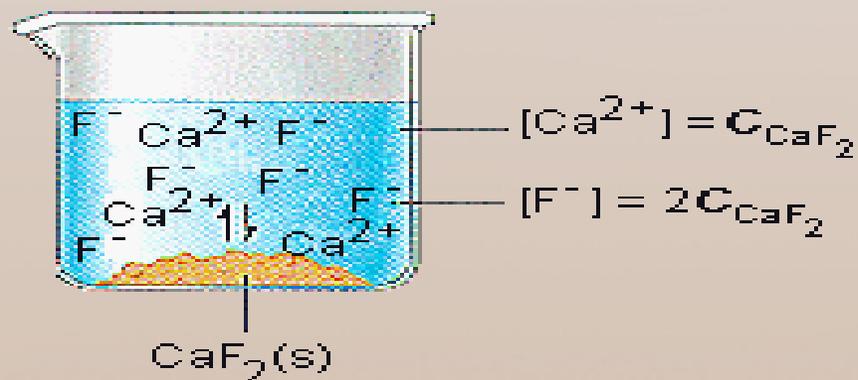


The K_{sp} expression for Al_2S_3 is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in its balanced dissociation equation thus :

$$K_{sp} = [\text{Al}^{3+}]^2[\text{S}^{2-}]^3$$

and do the same with any other salt e.g for CaF_2 , $K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$ and so on .

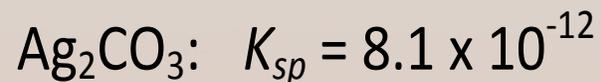
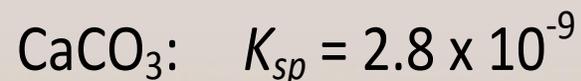
Saturated solution of CaF_2



The Solubility Product Concept

The higher the value of K_{sp} the more soluble the salt .

Example ; Which one of the following salts is more soluble in water ?



Solution : Since the value of K_{sp} for CaCO_3 is higher than that of Ag_2CO_3 then the first is more soluble than the later . :

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Solubility Equilibrium

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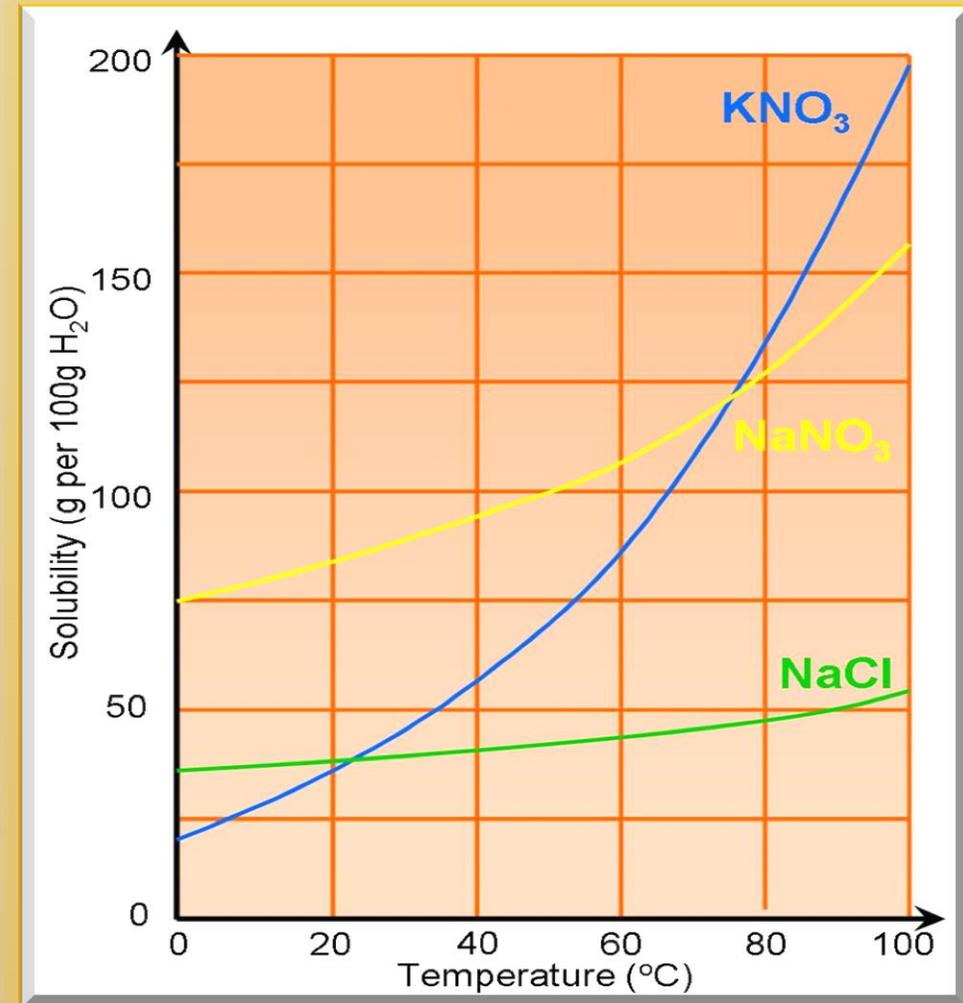
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Factors Affecting Solubility (Temperature)

Effect of temperature on solubility :

Generally in most cases solubility increases with the rise in temperature. However we must follow two behaviors : In endothermic process solubility increases with the increase in temperature and vice versa.

In exothermic process solubility decrease with the increase in temperature. Gases are more soluble in cold solvent than in hot solvent



Factors Affecting Solubility (Solvent)

Effect of solvent on solubility :

Solubility of a solute in a solvent purely depends on the nature of both solute and solvent. A polar solute dissolved in polar solvent. A polar solute has low solubility or insoluble in a non-polar solvent . For this reason if you want to decrease the solubility of an inorganic salt (polar salt) in water you mix the water with an organic solvent (non polar) .

Predicting precipitation

Determining whether a precipitate will, or will not form when two solutions are combined :

Example : 25.0 mL of 0.002 M K_2CrO_4 are mixed with 75.0 mL of 0.000125 M $\text{Pb}(\text{NO}_3)_2$.

Will a precipitate of PbCrO_4 form. K_{sp} of $\text{PbCrO}_4 = 1.8 \times 10^{-14}$?

Solution : The term Q is called the ion product (or the trial K_{sp}) for the solution mixture after the mixing of the solutions and before the reaction of the ions at any state (unsaturation , saturation or supersaturation) . So we will calculate Q using the dilution equation :

$$C_1 V_1 = C_2 V_2$$

The concentration of CrO_4^{2-} in the mixture and before the reaction

$$= (0.002 \text{ M} \times 25 \text{ mL}) / 100 \text{ mL} = 0.0005 \text{ M}$$

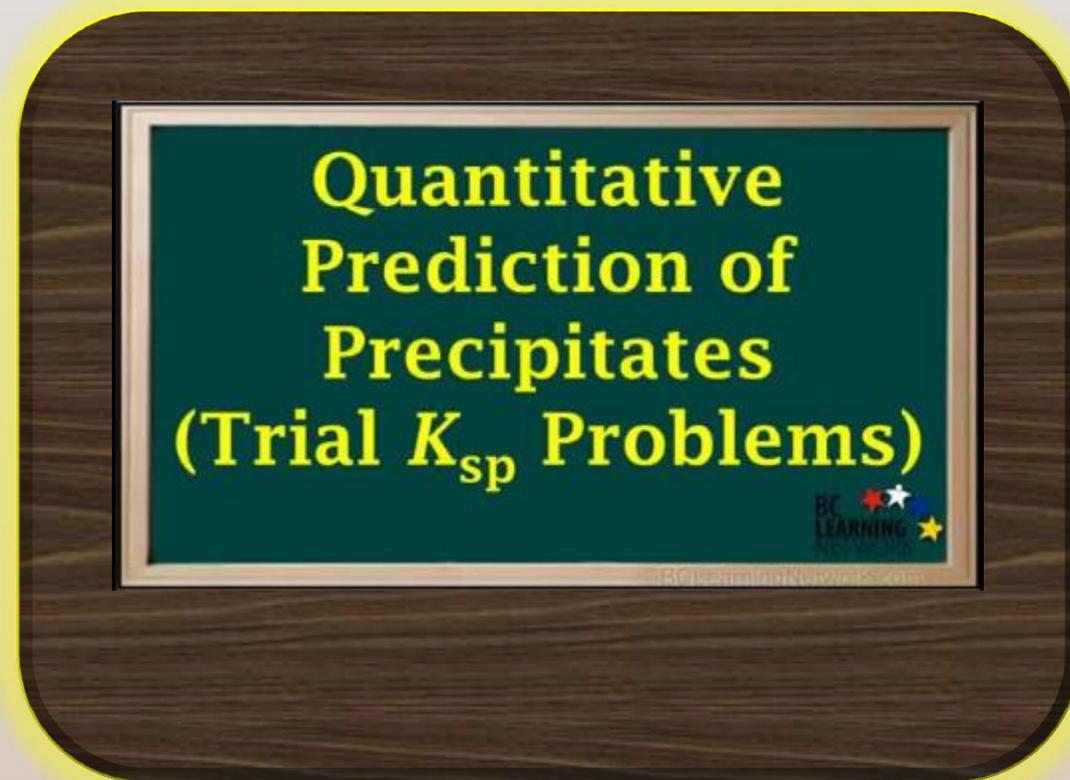
Similar calculation for Pb^{2+} yield $[\text{Pb}^{2+}] = (0.000125 \text{ M} \times 75 \text{ mL}) / 100 \text{ mL} = 0.0000934 \text{ M}$

$$Q = [\text{CrO}_4^{2-}] [\text{Pb}^{2+}] = 0.0005 \times 0.0000934 = 4.69 \times 10^{-8}$$

Predicting Precipitation

Q is greater than K_{sp} so a precipitate of lead(II) chromate will form. If $Q \leq K_{sp}$ the solution will be either saturated (if equal) or unsaturated (if less than) and in both states there will be no precipitation .

$Q < K_{sp}$	Unsaturated solution
$Q = K_{sp}$	Saturate solution
$Q > K_{sp}$	Oversaturate solution



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Calculating K_{sp} From Solubility

What is the solubility of a salt ? It is the maximum amount (moles , mmoles , g ...etc) of this salt that can be dissolved in a certain volume of solution (L , 50 mL , 500 mL ...ect.). The molar solubility is the solubility in moles of a salt in liter of a solution .

Calculating K_{sp} of a salt from it's Solubility : From the definition of K_{sp} and molar solubility one can calculate the K_{sp} of a salt from it's molar solubility or vice versa .

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K_{sp} Concept

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Calculating K_{sp} From Solubility

Example : Calculate the solubility product constant for $PbCl_2$ (mw= 278.1) , if 50.0 mL of a saturated solution of $PbCl_2$ was found to contain 0.2207 g of $PbCl_2$ dissolved in it (i.e.solubility in 0.2207g / 50 mL) ?

Solution : First we write the K_{sp} expression :

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

Second we convert the solubility in 0.2207 g / 50 mL to molar solubility thus :

$$\text{Molar Solubility of } PbCl_2 = \frac{0.2207 \text{ (g)}}{278.1} \times \frac{1000}{50 \text{ (mL)} \times 10^{-3} \text{ (L)}} = 0.0159 \text{ moles / L}$$

Third, create an "ICE" table .:

Calculating K_{sp} From Solubility

	PbCl_2 (s)	\longrightarrow	Pb^{2+} (aq)	2Cl^{-} (aq)
Initial Concentration (I)	0.0159 moles/L		0	0
Complete dissolution (C)	0		+ 0.0159 M	+ 0.0318 M

Fourth, substitute these concentrations into the equilibrium expression and solve for K_{sp} :

Calculating Solubility from K_{sp}

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = [0.0159][0.0318]^2 = 1.61 \times 10^{-5}$$

Calculating the Solubility of a salt from its K_{sp} :

Example : Estimate the molar solubility of Ag_2CrO_4 in pure water if the solubility product constant for silver chromate is 1.1×10^{-12} ?

Solution :



$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

Let "x" be the number of moles of silver chromate that dissolves in one liter of solution (its molar solubility).

Calculating Solubility from K_{sp}

Make an "ICE" chart :



Substitute into the K_{sp} expression and solve for x.

$$1.1 \times 10^{-12} = [2x]^2[x]$$

$$\text{Molar solubility of } Ag_2CrO_4 = x = 6.50 \times 10^{-5} \text{ M}$$

Effect of the Common Ion on Solubility

Effect of the common ion on solubility : The solubility of an ionic compound decreases in the presence of a common ion. A common ion is any ion in the solution that is common to the ionic compound being dissolved. For example, the chloride ion in a sodium chloride solution is common to the chloride in silver chloride. The presence of a common ion must be taken into account when determining the solubility of an ionic compound. To do this, simply use the concentration of the common ion as the initial concentration.

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Common ion effect

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Common ion effect

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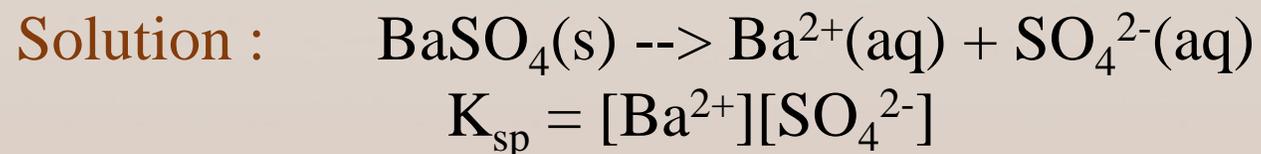
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Common ion effect

Effect of the Common Ion on Solubility

Example: Estimate the molar solubility of barium sulfate in a 0.02 M sodium sulfate solution. The solubility product constant for barium sulfate is 1.1×10^{-10} ?



Let "x" represent the barium sulfate that dissolves in the sodium sulfate solution expressed in moles per liter
Make an "ICE" chart..



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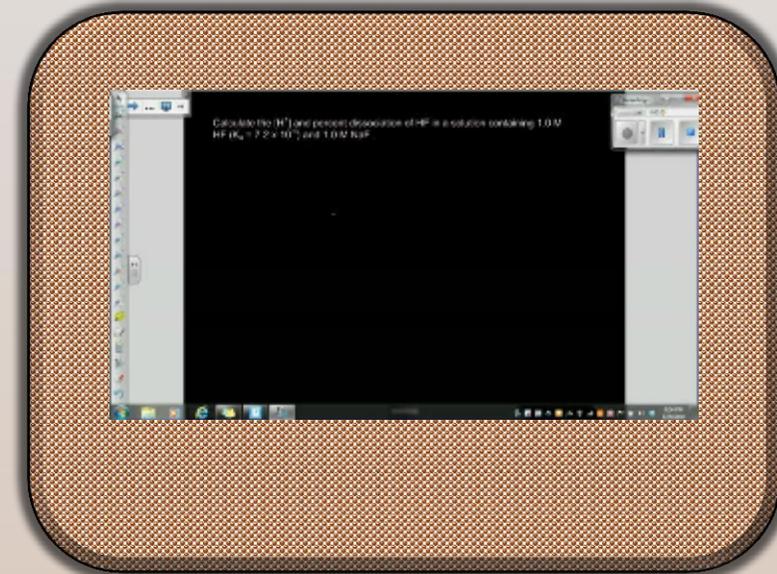
Effect of the Common Ion on Solubility

	BaSO ₄ (s)	Ba ²⁺ (aq)	SO ₄ ²⁻ (aq)
Initial (before dissolution) (I)	x	0	0.020 M (from Na ₂ SO ₄)
Complete dissolution (C)	0	x	0.02 M + x

Substitute into the equilibrium expression and solve for x. We will make the assumption that since x is going to be very small (the solubility is reduced in the presence of a common ion), the term "0.020 + x" is the same as "0.020." (You can leave x in the term and use the quadratic equation but it will not improve the significance of your answer.) :

$$1.1 \times 10^{-10} = [x][0.020 + x] = [x][0.020]$$

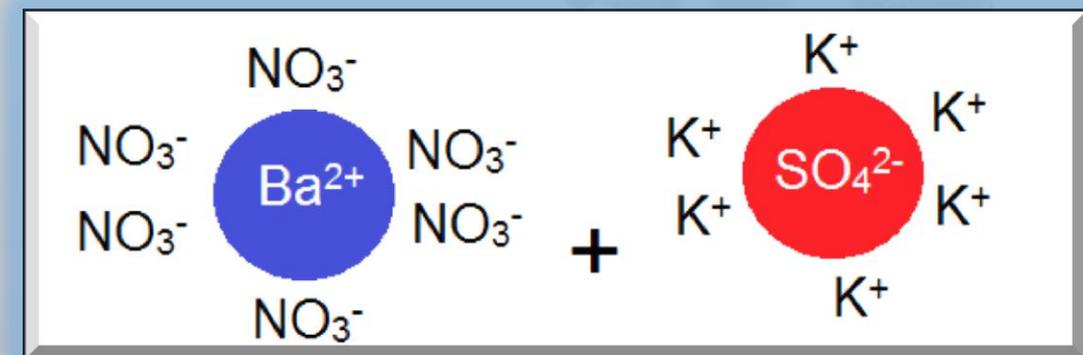
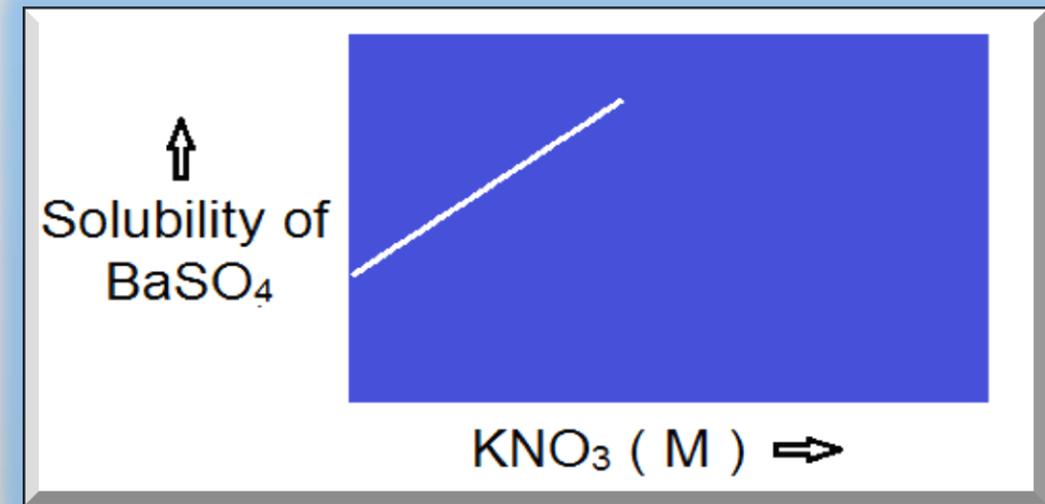
$$x = 5.5 \times 10^{-9} \text{ M}$$



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Effect Of Ionic Strength On Solubility

Salt effect (ionic strength): Having an opposing effect on the K_{sp} value compared to the common ion effect, uncommon ions increase the K_{sp} value. Uncommon ions are those that are different from those involved in K_{sp} equilibrium. The figures on your right show the effect of KNO_3 on the solubility of $BaSO_4$. As you see K^+ ions surround SO_4^{2-} and NO_3^- ions surround Ba^{2+} ions. Therefore, Ba^{2+} ions will have difficulty reacting with SO_4^{2-} to form the precipitate $BaSO_4$.



Effect of pH on Solubility

Effect of pH on Solubility : Many weakly soluble ionic compounds have solubility which depend on the pH of the solution e.g metal hydroxides and the salts of weak acids .

1- Effect of pH on metal hydroxides :

Example : Zinc hydroxide $\text{Zn}(\text{OH})_2$ has $K_{sp} = 4.5 \times 10^{-17}$
In pure water calculate its molar solubility ?

Solution : Assume the molar solubility = x

	$\text{Zn}(\text{OH})_2(\text{s})$	$\text{Zn}^{2+}(\text{aq})$	$+2 \text{OH}^{-}(\text{aq})$
I	x	0	0
C	0	x	2x



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Effect of pH on Solubility

$$K_{sp} = 4.5 \times 10^{-17} = x(2x)^2.$$

$$x = (4.5 \times 10^{-17} / 4)^{1/3} = 2.2 \times 10^{-6} \text{ M}.$$

the resulting pH is : $[\text{OH}^-] = 2x = 4.4 \times 10^{-6} \text{ M}$ therefore

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \\ &= 14 - (-\log(4.4 \times 10^{-6})) \\ &= 8.64 \end{aligned}$$

Therefore the pH of a saturated solution of $\text{Zn}(\text{OH})_2$ equal to 8.64 .

If $\text{pH} < 8.64$ (more acidic) then $[\text{OH}^-]$ decreases (reaction shifts right to try to produce more OH^-). Solubility increases.



Effect of pH on Solubility

if $\text{pH} > 8.64$ (more basic) then $[\text{OH}^-]$ increases (reaction shifts left to try to use more OH^-). Solubility decreases.

Example : At what pH the $\text{Zn}(\text{OH})_2$ will start to precipitate (pH_S) and at what pH the precipitation is complete (pH_C) from a solution containing 0.1 M Zn^{2+} ?

Solution : $\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn}(\text{OH})_2$

(I) 0.1 ? 0

$$K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^-]^2 = (0.1)(?)^2$$

Effect of pH on Solubility

$$(?)^2 = [OH^-]^2 = \frac{K_{sp}}{(0.1)}, [OH^-] = \sqrt{\frac{4.5 \times 10^{-17}}{(0.1)}} = 2.1 \times 10^{-8} \text{ M}$$

$$pOH_s = -\log 2.1 \times 10^{-8} = 7.67, \quad pH_s = 14 - 7.67 = 6.33$$

Since the precipitation of Zn^{2+} or any other metal ion is not complete 100 % so let us assume that the precipitation is complete when its concentration is reduced 10000 times that means C is reduced to $C \times 10^{-4}$. This applies to all metal ion precipitation. Therefore will repeat the same previous calculation but instead of 0.1 M we will use 0.1×10^{-4} :

$$[OH] = \sqrt{\frac{4.5 \times 10^{-17}}{0.1 \times 10^{-4}}} = 2.1 \times 10^{-6} \text{ M}$$

$$pOH_c = -\log 2.1 \times 10^{-6} = 5.67, \quad pH_c = 14 - 5.67 = 8.33$$

Effect of pH on Solubility

The precipitation of $\text{Zn}(\text{OH})_2$ will start at $\text{pH} = 6.33$ and will be complete at $\text{pH} = 8.33$.

Example :A solution containing 0.1 M Ca^{2+} and 0.02 M Mg^{2+} . Is it possible to separate one of these ions by precipitating it as hydroxide while keeping the other in solution ?

$$K_{\text{sp}} [\text{Ca}(\text{OH})_2] = 5.5 \times 10^{-6} \quad , \quad K_{\text{sp}} [\text{Mg}(\text{OH})_2] = 5 \times 10^{-12}$$

Effect of pH on Solubility

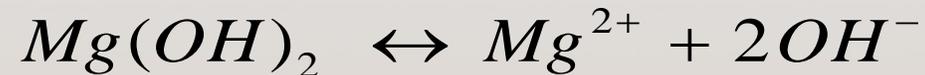
Solution : when you add OH^- to the solution , the metal ion with the smallest K_{sp} will precipitate first because it requires less amount of OH^- compared with the one with higher K_{sp} value . Therefore , $\text{Mg}(\text{OH})_2$ will precipitate first .

The pH at which the metal hydroxide precipitate is direct proportional to its K_{sp}

$$\text{pH} \propto K_{\text{SP}}$$

Now we will calculate the pH_s at which the precipitation of $\text{Mg}(\text{OH})_2$ is complete thus :

Effect of pH on Solubility



$$K_{sp} = [Mg^{2+}][OH^{-}]^2$$

$$[OH^{-}] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}}$$

$$[OH^{-}] = \sqrt{\frac{5 \times 10^{-12}}{0.02 \times 10^{-4}}} = 1.58 \times 10^{-3} \text{ M}$$

$$\therefore pOH = -\log 1.58 \times 10^{-3} = 2.8$$

$$\therefore pH_c = 14 - 2.8 = 11.2$$

Effect of pH on Solubility

Then we calculate the pH_s at which the precipitation of $Ca(OH)_2$ will start thus :

$$[OH^-] = \sqrt{\frac{5.5 \times 10^{-6}}{0.1}} = 7.4 \times 10^{-3} \text{ M}$$

$$\therefore pOH = -\log 7.4 \times 10^{-3} = 2.12$$

$$\therefore pH_s = 14 - 2.12 = 11.88$$

So it is possible to keep the pH of the solution in the range $11.8 > pH > 11.2$ to separate Mg^{2+} by precipitating it as $Mg(OH)_2$ while keeping Ca^{2+} in the solution . Note that the pH

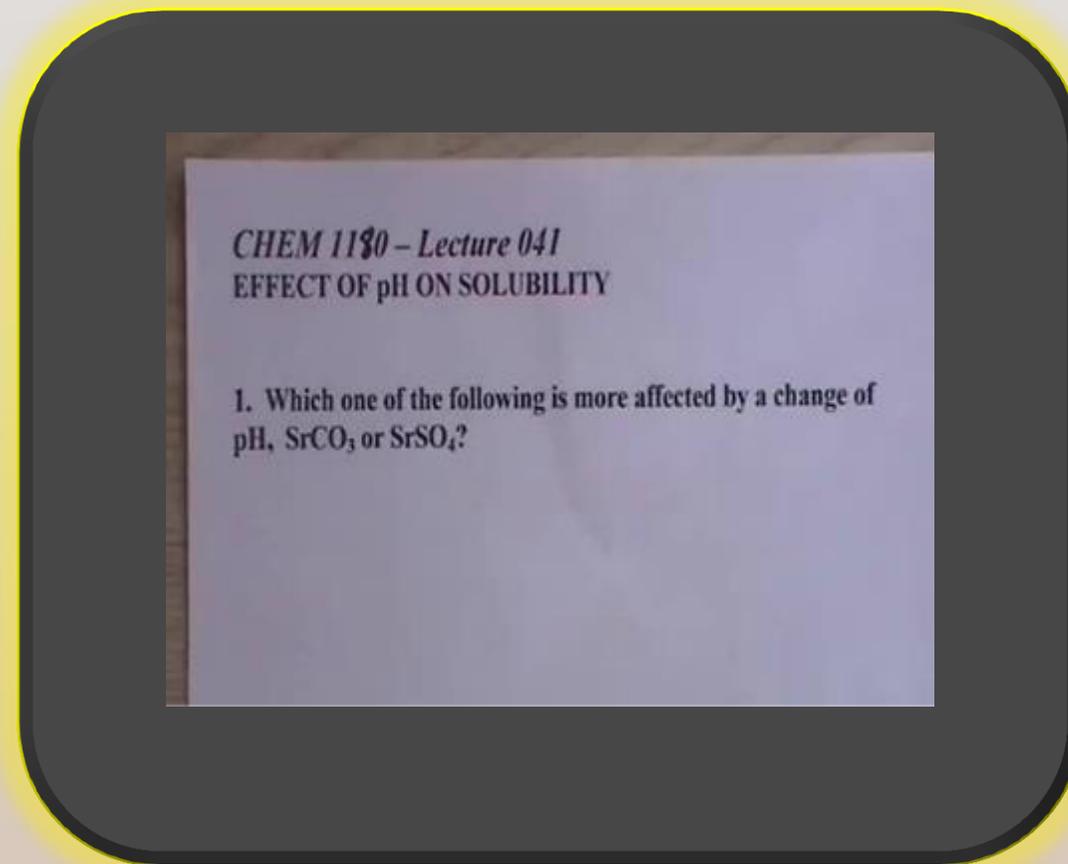
Effect of pH on Solubility

should not reach 11.8 otherwise the $\text{Ca}(\text{OH})_2$ will precipitate . On the other hand the pH should exceed 11.2 in order for the precipitation of $\text{Mg}(\text{OH})_2$ to be complete . Note also that if $\text{Ca}(\text{OH})_2$ starts to precipitate at $\text{pH} \leq 11.2$, then the two metal ions can not be separated and both will precipitate at the same time .

1- Effect of pH on salts of weak acids : For the salt of weak acid (e.g sulphides , carbonates , oxalates and phosphates) the smaller the value of K_{sp} the lower the pH at which the salt precipitates ($\text{pH} \propto K_{\text{SP}}$) exactly the same as metal hydroxides .

Effect of pH on Solubility

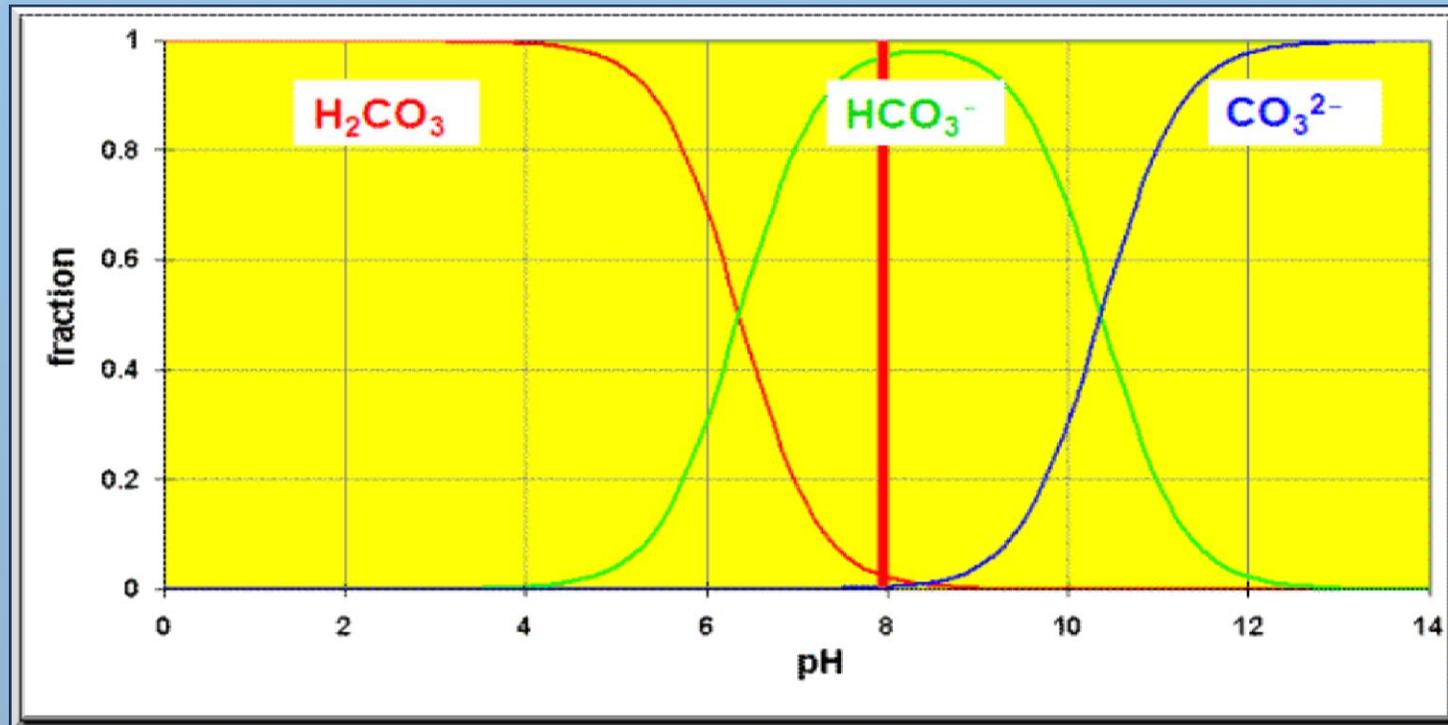
That means the salt with smaller K_{sp} will precipitate in more acidic medium whereas the one with larger K_{sp} will precipitate in less acidic medium. Take for example the precipitation of Ca^{2+} as CaCO_3 . At low pH, CO_3^{2-} will be turned to HCO_3^- or may be to H_2CO_3 (see the diagram below at $\text{pH} \leq 8$) while at $\text{pH} \geq 13$ all the carbonic acid species are present as CO_3^{2-} . Therefore CaCO_3 will precipitate in basic medium and will dissolve in acidic medium.



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Effect of pH on Solubility



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Effect of pH on Solubility

Example : Which one will precipitate in more acidic medium CaCO_3 ($K_{sp} = 4.8 \times 10^{-9}$) or MgCO_3 ($K_{sp} = 1 \times 10^{-5}$) ?

Solution : Of course , CaCO_3 because it has the lowest K_{sp}

Example : You have a solution containing 0.1 M Ti^+ and 0.05 M Cd^{2+} . Is it possible to separate these two ions by precipitating one of them as sulphide ?

$$K_{sp} (\text{CdS}) = 2 \times 10^{-28} \quad , \quad K_{sp} (\text{Ti}_2\text{S}) = 2 \times 10^{-22}$$

Solution : When you add S^{2-} to the solution , CdS will precipitate first because it has smallest K_{sp} .

$$K_{sp} = 2 \times 10^{-28} = [\text{Cd}^{2+}][\text{S}^{2-}] = (0.05 \times 10^{-4}) \times [\text{S}^{2-}]$$

$$[\text{S}^{2-}] = 4 \times 10^{-23} \text{ M}$$

Effect of pH on Solubility

This means that the precipitation of CdS will be complete when the concentration of $[S^{2-}]$ reaches $4 \times 10^{-23} \text{ M}$. Now we calculate the $[S^{2-}]$ at which Ti_2S starts to precipitate :

$$K_{sp} = 2 \times 10^{-22} = [Ti^+]^2 [S^{2-}] = (0.1)^2 \times [S^{2-}]$$

$$[S^{2-}] = 2 \times 10^{-20} \text{ M}$$

According to these results it is possible to precipitate CdS while keeping Ti^+ in solution if you control the concentration of S^{2-} in solution to be in the range :

$$2 \times 10^{-20} \text{ M} > [S^{2-}] > 4 \times 10^{-23} \text{ M}$$

$[S^{2-}]$ should be more than $4 \times 10^{-23} \text{ M}$ to obtain complete precipitation of CdS but not to reach to $2 \times 10^{-20} \text{ M}$ to avoid precipitation of Ti_2S . It is possible to control $[S^{2-}]$ through controlling the pH (see reference 1).

Effect of pH on Solubility

Note that the pH has no effect on the solubility of the strong acids salts e.g. Cl^- , Br^- , SO_4^{2-} ..etc because the concentration of these conjugated bases is the same wither in acidic or basic medium . However , metal ions can be separated by these anions according to their K_{sp} values as the hydroxides or the salts of weak acids .

<http://www.youtube.com/watch?v=3KrPFz2Dzw8#t=1061>

FRACTIONAL PRECIPITATION

Know the definition of Fractional Precipitation.

1. A solution contains $\overset{\text{Mg}^{2+}}{0.200 \text{ M}}$ $\overset{\text{Ca}^{2+}}{\text{Ca}(\text{NO}_3)_2}$, $\overset{\text{Cd}^{2+}}{0.200 \text{ M}}$ $\text{Cd}(\text{NO}_3)_2$ and 0.200 M $\text{Mg}(\text{NO}_3)_2$. If solid sodium oxalate is added to the solution slowly, what is the order in which the ions fall out of solution? When the second ion begins to precipitate, what percentage of the first ion is left in solution? When the third ion begins to precipitate, what percentages of the first and second ion are left in solution?

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Complex Ions and Solubility

Complex Ions and Solubility : Because we can use complexation reactions to 'tie up' metal ions in water, we can use these to increase the solubility of metal ion salts. For example, silver chloride is weakly soluble in water but quite readily dissolves in concentrated ammonia. The effect of complexing agent on the solubility of metal salts is governed by two factors: the value of K_{sp} of the salt and the value of K_f of the complex between the metal ion and the complexing agent.

CP68C - Ionic Equilibrium - Complex formation and solubility - Problems

Prob: Use values of K_{sp} for AgI and K_f for $\text{Ag}(\text{CN})_2^-$ to (a) calculate the molar solubility of AgI in pure water, (b) calculate the equilibrium constant for the reaction

$$\text{AgI}(s) + 2 \text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq) + \text{I}^-(aq)$$

(c) Determine the molar solubility of AgI in a 0.100 M NaCN solution.

Ans: $K_f(\text{Ag}(\text{CN})_2^-) = 1 \times 10^{21}$, $K_{sp}(\text{AgI}) = 8.3 \times 10^{-17}$
 (a) 9.1×10^{-9} mol (b) $K = K_{sp} \times K_f = 8 \times 10^4$ (c) 0.0500 mol AgI/L

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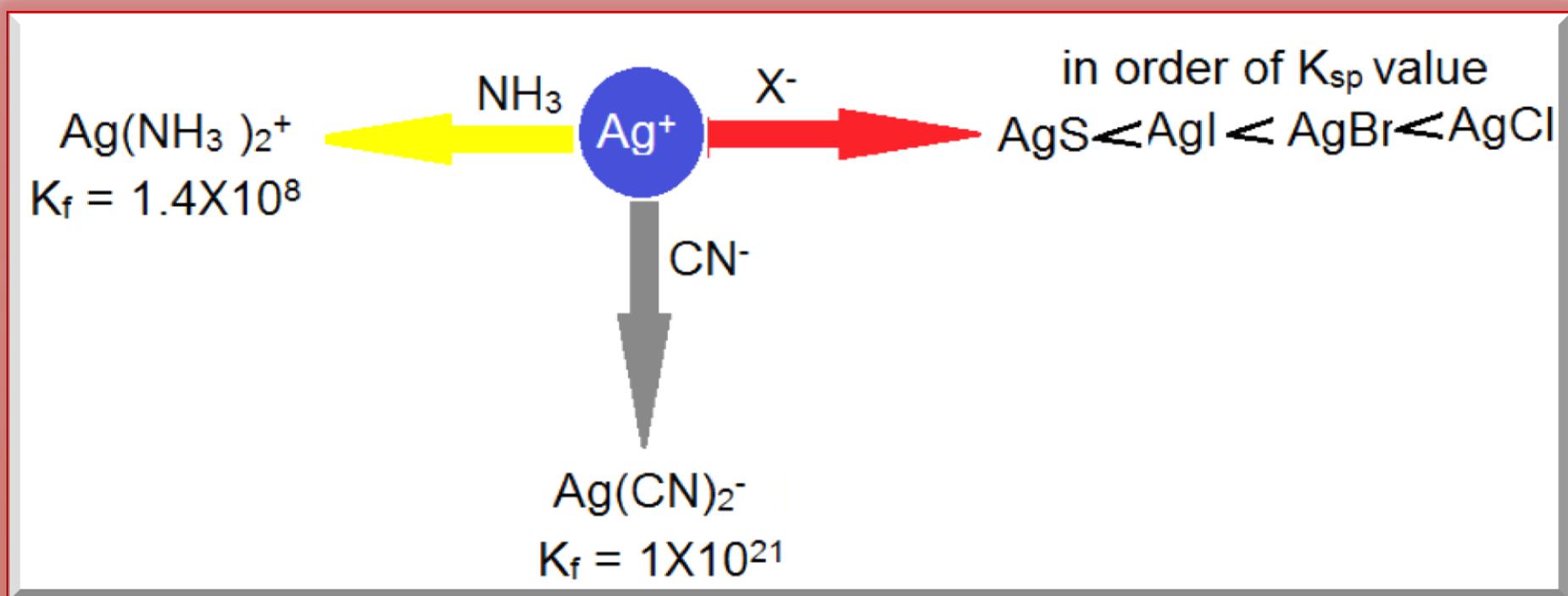
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Complex Ions and Solubility

Let us take the effect of ammonia NH_3 and cyanide CN^- as complexing agents on the precipitation of silver halides as an example. Practically NH_3 dissolves only AgCl which has relatively large K_{sp} value because the value of K_{f} for $\text{Ag}(\text{NH}_3)_2^+$ is small. Where as CN^- dissolves all silver halides because the value of K_{f} for $\text{Ag}(\text{CN})_2^-$ is large. However CN^- can not dissolve silver sulphide because its K_{sp} value is very small (see the following figure) .

Complex Ions and Solubility

To summarize the larger the K_{sp} value of the salt and the value of K_f of the metal complex the more the effect of the complexing agent on dissolving the salt and vice versa .



General Rules For Solubility In Water

There are rules that determine whether a compound is soluble in water or not. They are as follows:

1. All common salts of the Group 1 elements and the ammonium ion are soluble.
 2. All common acetates and nitrates are soluble.
 3. All binary compounds of Group 17 (except Fluorine) are soluble except with silver, mercury and lead.
 4. Sulfates are soluble except with calcium, strontium, barium, silver, mercury and lead.
 5. Carbonates, Hydroxides, Oxides and Phosphates are insoluble except as in rule one.
- 

Summary

In this unit we investigated , the concept of solubility product constant , its importance in analytical chemistry , how to calculate K_{sp} from solubility and vice versa , how to predict the precipitation when two solutions are mixed together and the factors affecting the solubility such as , temperature , common ion , ionic strength , pH and the complex formation . We have drawn the attention to the separation of metal ions by stepwise precipitation as hydroxides or acid salts . We have used graphics, pictures and videos to illustrate the concepts and fundamentals of this unity .

Tutorial

EXERCISE 1 : The K_{sp} for AgCl is 1.8×10^{-10} . What is its molar solubility ?

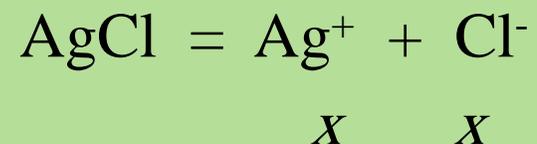
Your answer :

**Our answer
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Tutorial

Answer 1 :

Let x be the molar solubility, then



$$\text{Molar solubility of AgCl} = x = (1.8 \times 10^{-10})^{1/2} = 1.3 \times 10^{-5} \text{ M}$$

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Exercise 2 : The K_{sp} for $\text{Cr}(\text{OH})_3$ is 1.2×10^{-15} . What is the molar solubility of $\text{Cr}(\text{OH})_3$ in water?

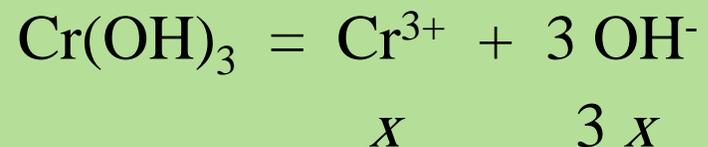
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next slide

Tutorial

Answer 2 :

Let x be the molar solubility of $\text{Cr}(\text{OH})_3$, then you have



Thus,

$$x(3x)^3 = 1.2 \times 10^{-15}$$

$$\text{Molar solubility} = x = 8.2 \times 10^{-5} \text{ M}$$

Tutorial

Exercise 3 : Very careful experiment indicates that the molar solubility of Bi_2S_3 is $1.8 \times 10^{-15} \text{ M}$, what value of K_{sp} does this compound have?

Your answer :

**Our answer
next slide**

Tutorial

Answer 3 : If the molar solubility of Bi_2S_3 is 1.8×10^{-15} , then



$$3.6 \times 10^{-15} \quad 5.4 \times 10^{-15}$$

$$\begin{aligned} K_{\text{sp}} &= (3.6 \times 10^{-15})^2 (5.4 \times 10^{-15})^3 \\ &= 2.0 \times 10^{-72} \end{aligned}$$



Tutorial

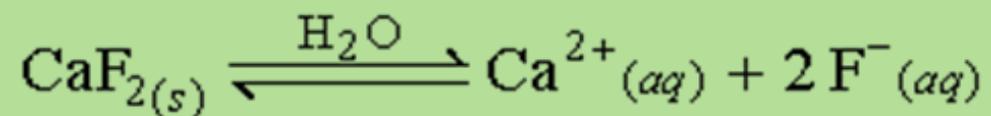
Exercise 4 : Calculate the solubility of CaF_2 (mw = 78.1) in g/L ($K_{sp} = 4.0 \times 10^{-8}$) ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 4 :



The reasons why we do not involve $[\text{H}_2\text{O}]$ and solids in the equilibrium expression is that its concentrations remains unchanged .

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = 4.0 \times 10^{-8}$$

Solubility of $\text{CaF}_2 = [\text{Ca}^{2+}] = x$ and $[\text{F}^{-}] = 2x$

$$\begin{aligned} K_{sp} = 4.0 \times 10^{-8} &= (x)(2x)^2, \quad x = 2.2 \times 10^{-3} \text{ moles / L} \\ &= 2.2 \times 10^{-3} \times 78.1 = 0.017 \text{ g CaF}_2 / \text{L} \end{aligned}$$

Tutorial

Exercise 5 : A solution is prepared by mixing equal volumes of 0.01M MgCl_2 , and 0.02M $\text{Na}_2\text{C}_2\text{O}_4$ at 18°C . Would MgC_2O_4 precipitate out? K_{sp} of MgC_2O_4 at $18^\circ\text{C} = 8.57 \times 10^{-5}$.

Your answer :

**Our answer
next slide**

Tutorial

Answer 5 : When mixed, the total volume gets doubled and hence the effective concentrations of the ions would be half of the initial concentration, i.e., in solution

$$[\text{Mg}^{2+}] = (0.01/2) = 0.005 \text{ mol/L}$$
$$[\text{C}_2\text{O}_4^{2-}] = (0.02/2) = 0.01 \text{ mol/L}$$
$$Q = 0.005 \times 0.01 = 5 \times 10^{-5} \quad , \quad Q < K_{\text{sp}} \quad , \quad \text{so precipitation do not take place .}$$

Tutorial

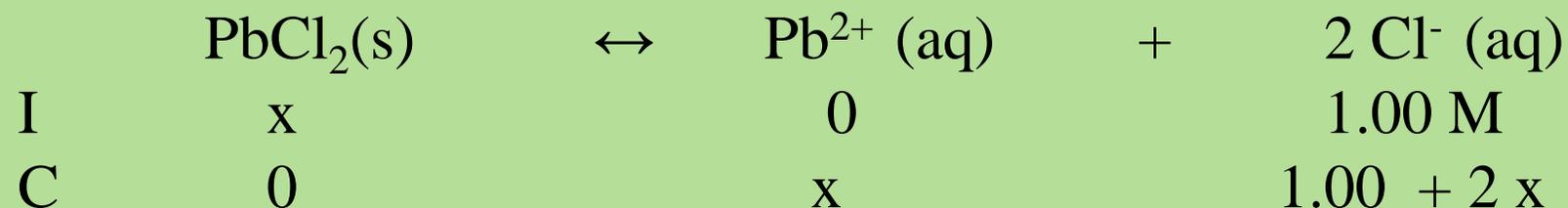
Exercise 6 : What is the molar solubility of PbCl_2 in 1.00 M HCl ? $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$

Your answer :

**Our answer
next slide**

Tutorial

Answer 6 : Let us assume the molar solubility equal to x :



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = 1.7 \times 10^{-5}.$$

$$x(1.00 + 2x)^2 \approx x(1.00)^2 = 1.7 \times 10^{-5}, \quad x = 1.7 \times 10^{-5}\text{ M}$$

In the absence of the common ion : $1.7 \times 10^{-5} = (x)(2x)^2$, $x = 1.6 \times 10^{-2}$

So The solubility is significantly reduced due to *common ion effect*.

Tutorial

Exercise 7 : Calculate the pH_s at which $\text{Fe}(\text{OH})_3$ starts to precipitate and the pH_C at which the precipitation is complete from a solution of 0.1 M Fe^{3+} ? K_{sp} for $\text{Fe}(\text{OH})_3 = 4 \times 10^{-38}$.

Your answer :

Our answer
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Tutorial

$$\text{Answer 7 : } K_{sp} = [Fe^{2+}][OH^{-}]^3$$

$$[OH^{-}] = \sqrt[3]{\frac{K_{sp}}{[Fe^{3+}]}} = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7.4 \times 10^{-13}$$

$$\therefore [H^{+}] = \frac{1 \times 10^{-14}}{7.4 \times 10^{-13}} = 0.0135 \text{ M} \therefore pH_s \approx 1.9$$

$$[OH^{-}] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1 \times 10^{-4}}} = 1.6 \times 10^{-11}$$

$$\therefore [H^{+}] = \frac{1 \times 10^{-14}}{1.6 \times 10^{-11}} = 6.25 \times 10^{-4} \therefore pH_c = 3.2$$

Tutorial

Exercise 8 : You have a solution containing 0.1 M Mn^{2+} and 0.2 M Fe^{3+} . Is it possible to separate the two ions by precipitation of one of them as hydroxide while keeping the other in solution ? $K_{\text{sp}} \text{Mn(OH)}_2 = 2 \times 10^{-13}$, $K_{\text{sp}} \text{Fe(OH)}_3 = 4 \times 10^{-38}$

Your answer :

**Our answer
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Tutorial

Answer 8 : First we calculate the pH_C at which the precipitation of $Fe(OH)_3$ is complete :

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.2 \times 10^{-4}}} = 1.3 \times 10^{-11} \therefore [H^+] = 7.7 \times 10^{-4} \therefore pH_C = 3.1$$

Second we calculate the pH_S at which the precipitation of $Mn(OH)_2$ starts :

$$K_{sp} = [Mn^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mn^{2+}]}} = \sqrt{\frac{2 \times 10^{-13}}{0.1}} = 1.4 \times 10^{-6} \therefore [H^+] = 7.1 \times 10^{-9} \therefore pH_S = 8.2$$

Tutorial

The results of the above calculations indicate that it is possible to precipitate $\text{Fe}(\text{OH})_3$ while keeping Mn^{2+} in solution by controlling the pH to be in the range : $8.2 > \text{pH} > 3.1$

على الراغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابراهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التالية :

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