

Chapter 15

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Solubility and Simultaneous Equilibria

Solubility Product Constant (K_{sp})

Equilibrium constant for dissolution reaction.

The product of molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficients in the equilibrium equation

- * **Small amounts** of a sparingly soluble salt (considered insoluble using solubility rules) dissolve in water and exist in the aqueous phase as dissociated ions.

- * At equilibrium, the ion concentrations remain _____ because the rate at which the solid dissolves to give the aqueous ions _____ the rate at which ions crystallize to reform the solid salt.

Q For $Mg_3(AsO_4)_2$ $K_{sp} = 2.1 \times 10^{-20}$ What is the equilibrium specified by this K_{sp} value?

- * The numerical value of K_{sp} gives information about the _____ of the salt.

Q What do high K_{sp} values specify? low K_{sp} values?

- * The value of K_{sp} depends only on _____.

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Use of Solubility to Calculate K_{sp}

1. A saturated solution of $PbCl_2$ has $[Pb^{2+}] = 1.44 \times 10^{-2} M$. What is the solubility product constant for $PbCl_2$?
2. A saturated solution of $Ca_3(PO_4)_2$ has $[Ca^{2+}] = 3.43 \times 10^{-7} M$. Calculate K_{sp} , $[PO_4^{3-}]$, and the molar solubility of calcium phosphate in water.
3. A saturated solution of Ag_2CrO_4 prepared by dissolving solid Ag_2CrO_4 in water had $[CrO_4^{2-}] = 6.5 \times 10^{-5} M$. Calculate K_{sp} for Ag_2CrO_4 . (1.1×10^{-12})

Use of K_{sp} to Calculate Solubility

Solubility is the maximum amount of ionic compound that dissolves per volume of solution (mol/L; g/L; g/100 ml)

Molar solubility – max number of moles of compound that dissolves in 1 L of solution (i.e. to give a saturated solution)

– defined for a **saturated solution**, so we can use the equilibrium law to find it.

1. Calculate the solubility of MgF_2 ($K_{sp}=7.4 \times 10^{-11}$) in water at 25 °C in units of mol/L and g/L.
2. Calculate the solubility of $Mg_3(AsO_4)_2$ ($K_{sp} = 2.1 \times 10^{-20}$) in units of g/100 mL. What is the concentration of magnesium and arsenate ions in a saturated solution of magnesium arsenate?
3. Use the values of K_{sp} to calculate the molar solubility of the following compounds.
a. $BaCrO_4$ b. $Mg(OH)_2$ c. Ag_2SO_3
4. Which has the greater molar solubility: $AgCl$ with $K_{sp} = 1.8 \times 10^{-10}$ or Ag_2CrO_4 with $K_{sp} = 1.1 \times 10^{-12}$? (Ag_2CrO_4)
Which has the greater solubility in grams per liter? (Ag_2CrO_4)

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Factors Affecting Solubility

Common Ion Effect

Addition of a strong electrolyte with an ion in common with a salt DECREASES the solubility of the salt.

Q Consider a saturated solution of BaF_2 ($K_{\text{sp}} = 1.8 \times 10^{-7}$). When added to the saturated barium fluoride solution, which of the following salts will affect the solubility of BaF_2 in water?

NaF NaCl BaCl_2 KF KNO_3 $\text{Ba}(\text{NO}_3)_2$

Calculate the molar solubility of BaF_2 in pure water and in 0.30 M KF. In which is the BaF_2 most soluble, pure water or 0.30 M KF?

Examples:

- Calculate the molar solubility of PbCrO_4 ($K_{\text{sp}} = 2.8 \times 10^{-13}$) in:
 - Pure water
 - 1.0×10^{-3} M K_2CrO_4
- Calculate the molar solubility at 25 °C of MgF_2 ($K_{\text{sp}} = 7.4 \times 10^{-11}$) in:
 - 0.10 M NaF
 - 0.10 M MgCl_2

Factors Affecting Solubility

pH of Solution

Addition of a strong acid to a saturated solution of salt that contains conjugate base of WEAK ACID will INCREASE the solubility of the salt.

Q Explain how addition of HCl (or lowering of pH) affects the solubility of CaF_2 ($K_{\text{sp}} = 1.5 \times 10^{-10}$) in aqueous solution?

Metal hydroxides also contain the conjugate base of a weak acid (i.e. OH^- is the conjugate base of the weak acid H_2O) and will INCREASE in solubility as strong acid is added!!

Q Explain how addition of strong acid affects the solubility of $\text{Fe}(\text{OH})_3$ ($K_{\text{sp}} = 2.6 \times 10^{-39}$)

Q Which of the following compounds are more soluble in acidic solution than in pure water?

AgCl PbI_2 $\text{Al}(\text{OH})_3$ MnS Hg_2Br_2

 ZnCO_3 $\text{Ni}(\text{OH})_2$ $\text{Ca}_3(\text{PO}_4)_2$ AgOH $\text{Mg}(\text{OH})_2$

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Examples

1. Calculate the molar solubility and pH of a solution saturated with $\text{Mg}(\text{OH})_2$. $K_{\text{sp}}(\text{Mg}(\text{OH})_2) = 5.6 \times 10^{-12}$.
2. Calculate the molar solubility of $\text{Mg}(\text{OH})_2$ in water buffered at a pH of 8.00.

Precipitation of Ionic Compounds

Question: Will a precipitate form if aqueous solutions of AgNO_3 and K_2SO_4 are mixed?

Answer: It depends on.....

To decide if a precipitate will form, calculate the value of the ion product (IP or Q_{sp}).

- 1.
- 2.
- 3.

If

- * $\text{IP} > K_{\text{sp}}$, then solution is _____ and precipitate _____ form.
- * $\text{IP} < K_{\text{sp}}$, then solution is _____ and precipitate _____ form.
- * $\text{IP} = K_{\text{sp}}$, then solution is _____ and precipitate _____ form.

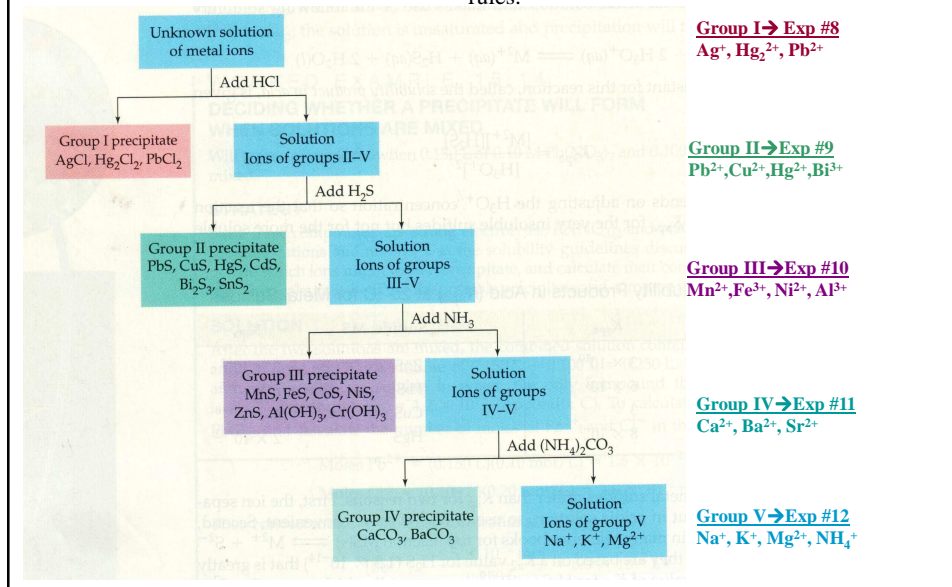
Examples:

1. Will a precipitate form if 100. mL of 0.075 M $\text{Mg}(\text{NO}_3)_2$ is mixed with 200. mL of 0.010 M Na_2CO_3 ?
2. Will a precipitate form if 500. mL of 0.050 M $\text{Ag}_2\text{C}_2\text{O}_4$ is mixed with 300. mL of 0.010 M K_2SO_4 ?
3. Will a precipitate form if 100. mL of 0.0250 M BaCl_2 is mixed with 250. mL of 0.00100 M $\text{Hg}_2(\text{NO}_3)_2$?

Qualitative Analysis Scheme

A procedure for separating and identifying metal cations present in an unknown solution

Group based separation into five groups is by differences in K_{sp} values and NOT by solubility rules.



Separation of Group I from Groups II-V

Based upon differences in K_{sp} values for the metal chlorides. K_{sp} values for PbCl_2 , AgCl , and Hg_2Cl_2 are low. K_{sp} values for most other metal chlorides are high.

- A solution is 0.0015 M in each of the cations Ag^+ , Pb^{2+} , and Hg_2^{2+} . What concentration of chloride ion must be used to precipitate as much of the Hg_2^{2+} (as Hg_2Cl_2) as possible without precipitating the chlorides of Ag^+ and Pb^{2+} ? ($K_{sp}(\text{Hg}_2\text{Cl}_2) = 1.4 \times 10^{-18}$, $K_{sp}(\text{PbCl}_2) = 1.2 \times 10^{-5}$; $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$)
- Consider the question above. What concentration of Cl^- is needed to precipitate as much of the Ag^+ and Hg_2^{2+} as possible without precipitating the Pb^{2+} ? What is the concentration of Hg_2^{2+} ions in the solution at this concentration of Cl^- ? At this Cl^- concentration, has most of the Hg_2^{2+} been precipitated from solution?

More Selective Precipitation

Separation of Group II (acid insoluble) from Group III (base insoluble) cations

Mixtures of metal cations, M^{2+} , can be separated into two groups by the selective precipitation of metal sulfides, MS

Group II Metal Sulfides: Insoluble at low pH ($\text{pH} < 1$) and at high pH (acid insoluble sulfides)

Group III Metal Sulfides: Soluble at low pH but insoluble at high pH ($\text{pH} > 8$) (base insoluble sulfides)

The equilibrium set up by a metal sulfide (MS(s)) in aqueous solution at different pH values is:

Low pH conditions: $IP_{\text{spa}} > K_{\text{spa}}$ only for metal sulfides with low K_{spa} values (Group II)

High pH conditions: $IP_{\text{spa}} > K_{\text{spa}}$ for metal sulfides with high and low K_{spa} values (Groups II and III)

Solubility of metal sulfide or whether or not a metal sulfide will precipitate from solution depends on the pH of the solution!!

Sulfide	K_{spa}	Sulfide	K_{spa}
PbS	3×10^{-7}	MnS	3×10^{10}
CuS	6×10^{-16}	FeS	6×10^2
HgS	2×10^{-32}	NiS	0.8
		ZnS	0.03

1. A solution with a $\text{pH}=0.52$ and H_2S concentration of 0.10 M is 0.0010 M in each of the cations Pb^{2+} , Hg^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} . Under these Group II conditions, which metal cations will precipitate as the sulfide?
2. A solution is 0.0010 M in each of the seven metal cations shown in the table above. If the H_2S concentration is 0.10 M , what pH is needed to precipitate all seven of the metal cations?

Other Examples: Precipitation and Separation

- A solution is 0.500 M in each of the ions Ni^{2+} and Cr^{3+} and has a pH of 4.00. Solid NaOH is added to precipitate the hydroxides. $K_{\text{sp}}(\text{Ni}(\text{OH})_2) = 5.5 \times 10^{-16}$; $K_{\text{sp}}(\text{Cr}(\text{OH})_3) = 6.7 \times 10^{-31}$
 - Before NaOH is added, will either ion be precipitated as the hydroxide?
 - Can these two ions be separated from each other by adjusting pH of the solution?
 - What pH is needed to precipitate as much of the Cr^{3+} as possible without precipitating the Ni^{2+} ?
- A solution is 0.0050 M in Sn^{2+} and Al^{3+} and has a pH = 1.00. Solid NaOH is added to make the solution more basic. Which of these metal cations will precipitate first?
 $\text{Sn}(\text{OH})_2$ ($K_{\text{sp}} = 5.4 \times 10^{-27}$) $\text{Al}(\text{OH})_3$ ($K_{\text{sp}} = 1.9 \times 10^{-33}$)
- A solution is 1.0×10^{-3} M in each of the metal cations Cu^+ , Pb^{2+} , Hg_2^{2+} , and Ag^+ . Solid NaBr is added to this solution. In what order will the bromides precipitate?
 CuBr ($K_{\text{sp}} = 6.3 \times 10^{-9}$) AgBr ($K_{\text{sp}} = 5.4 \times 10^{-13}$)
 PbBr_2 ($K_{\text{sp}} = 6.6 \times 10^{-6}$) Hg_2Br_2 ($K_{\text{sp}} = 6.4 \times 10^{-23}$)

Formation of Metal Complex Ions or Coordination Compounds

If metal cation of salt forms a soluble metal complex ion, addition of ligand will increase the solubility of the salt.

Metal Complex Ion....Definition: _____.

Ligand: _____.

Formation of a metal complex ion is an example of _____ chemistry.

Example: CuCO_3 is insoluble with $K_{\text{sp}} = 2.5 \times 10^{-10}$. However addition of ammonia increases the solubility of this salt and causes CuCO_3 to dissolve. Explain. Hint: $\text{Cu}(\text{II})$ forms the soluble ammonia complex ion $\text{Cu}(\text{NH}_3)_4^{+2}$ $K_f = 5.6 \times 10^{11}$.

Example: Silver chloride ($K_{\text{sp}} = 1.8 \times 10^{-10}$) is insoluble in water and in acid, but dissolves in an excess of aqueous ammonia. Explain. Hint: Silver(I) forms the soluble complex ion $\text{Ag}(\text{NH}_3)_2^+$ $K_f = 1.7 \times 10^7$.

- Q.** Calculate the molar solubility of AgBr ($K_{\text{sp}} = 5.4 \times 10^{-13}$) at 25 °C in:
- Pure water
 - 0.75 M NH_3

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Sample Questions

1. A solution is 0.60 M in $[\text{Cu}(\text{NH}_3)_4]^{2+}$. $K_f = 5.6 \times 10^{11}$. Calculate the concentration of free Cu^{2+} and NH_3 in this solution.

2. Calculate the solubility of $\text{Cu}(\text{OH})_2$ in a solution of 1.2 M NH_3 .
 $K_{\text{sp}}(\text{Cu}(\text{OH})_2) = 1.6 \times 10^{-19}$; $K_f([\text{Cu}(\text{NH}_3)_4]^{2+}) = 5.6 \times 10^{11}$.

3. Calculate the equilibrium concentrations of Ni^{2+} and NH_3 in the solution when 0.050 mol $\text{Ni}(\text{NO}_3)_2$ are added to 1000. ml of 1.0 M NH_3 . $K_f([\text{Ni}(\text{NH}_3)_6]^{2+}) = 2.0 \times 10^8$.

4. The complex ion $[\text{Ag}(\text{NH}_3)_2]^+$, $K_f = 1.7 \times 10^7$, is formed from a solution that is 0.10 M Ag^+ and 1.0 M NH_3 . After the complex is formed, the solution is made of 0.030 M in NaCl . Will any AgCl precipitate? $K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$.