

# Chapter 15

## (pg. 618-633)

### Solubility and Simultaneous Equilibria

#### Solubility Product ( $K_{sp}$ )

*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  $\text{Mg}_3(\text{AsO}_4)_2$   $K_{sp} = 2.1 \times 10^{-20}$  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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## Solubility Product Constant

### 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  $Ag_2CrO_4$ . ( $1.1 \times 10^{-12}$ )

### 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  $MgF_2$  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.  $BaCrO_4$  ( $1.4 \times 10^{-5} M$ )      b.  $Mg(OH)_2$  ( $1.2 \times 10^{-11} M$ )      c.  $Ag_2SO_3$  ( $1.6 \times 10^{-5} M$ )
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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## Solubility Product Constant

### 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  $\text{BaF}_2$  ( $K_{\text{sp}} = 1.8 \times 10^{-7}$ ). When added to the saturated barium fluoride solution, which of the following salts will affect the solubility of  $\text{BaF}_2$  in water?

NaF                  NaCl                   $\text{BaCl}_2$                   KF                   $\text{KNO}_3$                    $\text{Ba}(\text{NO}_3)_2$

Calculate the molar solubility of  $\text{BaF}_2$  in pure water and in 0.30 M KF. In which is the  $\text{BaF}_2$  most soluble, pure water or 0.30 M KF?

#### Examples:

- Calculate the molar solubility of  $\text{PbCrO}_4$  ( $K_{\text{sp}} = 1.8 \times 10^{-14}$ ) in:
  - Pure water ( $1.3 \times 10^{-7}$  M)
  - $1.0 \times 10^{-3}$  M  $\text{K}_2\text{CrO}_4$  ( $1.8 \times 10^{-11}$ )
- Calculate the molar solubility at 25 °C of  $\text{MgF}_2$  ( $K_{\text{sp}} = 6.6 \times 10^{-9}$ ) in:
  - 0.10 M NaF ( $6.6 \times 10^{-7}$  M)
  - 0.10 M  $\text{MgCl}_2$  ( $1.3 \times 10^{-4}$  M)

### 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  $\text{CaF}_2$  ( $K_{\text{sp}} = 3.9 \times 10^{-11}$ ) in aqueous solution?

*Metal hydroxides also contain the conjugate base of a weak acid (i.e.  $\text{OH}^-$  is the conjugate base of the weak acid  $\text{H}_2\text{O}$ ) and will INCREASE in solubility as strong acid is added!!*

**Q** Explain how addition of strong acid affects the solubility of  $\text{Fe}(\text{OH})_3$  ( $K_{\text{sp}} = 1.6 \times 10^{-39}$ )

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

AgCl                   $\text{PbI}_2$                    $\text{Al}(\text{OH})_3$                   MnS                   $\text{Hg}_2\text{Br}_2$   
  
ZnCO<sub>3</sub>                   $\text{Ni}(\text{OH})_2$                    $\text{Ca}_3(\text{PO}_4)_2$                   AgOH                   $\text{Mg}(\text{OH})_2$

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## Solubility Product Constant

### 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  $\text{AgNO}_3$  and  $\text{K}_2\text{SO}_4$  are mixed?

**Answer:** It depends on.....

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

- 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  $\text{Na}_2\text{CO}_3$ ?
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  $\text{K}_2\text{SO}_4$ ?
3. Will a precipitate form if 100. mL of 0.0250 M  $\text{BaCl}_2$  is mixed with 250. mL of 0.00100 M  $\text{Hg}_2(\text{NO}_3)_2$ ?

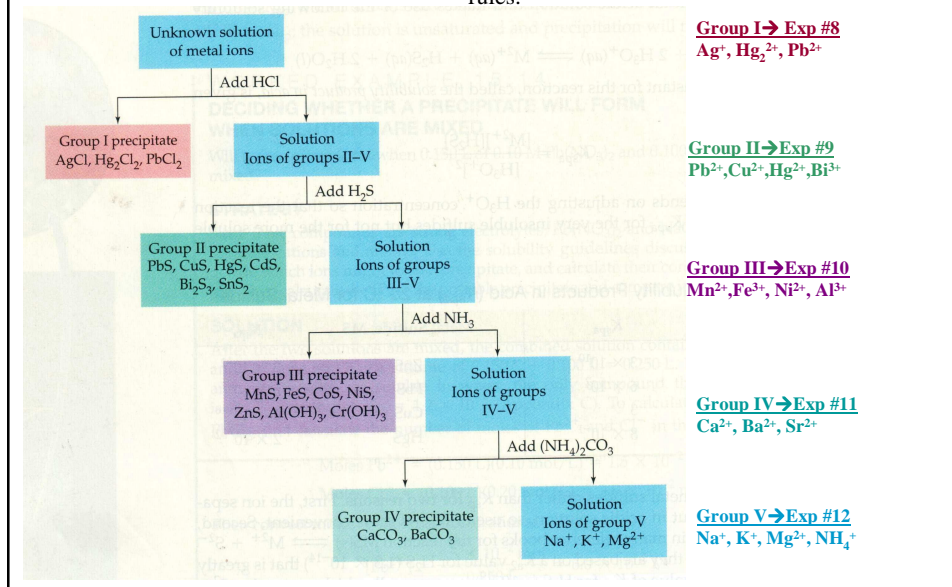
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## Solubility Product Constant

### 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  $\text{PbCl}_2$ ,  $\text{AgCl}$ , and  $\text{Hg}_2\text{Cl}_2$  are low.  $K_{sp}$  values for most other metal chlorides are high.

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

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## Solubility Product Constant

### 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  $K_{\text{spa}}$  values (Group II)

**High pH conditions:**  $IP_{\text{spa}} > K_{\text{spa}}$  for metal sulfides with high and low  $K_{\text{spa}}$  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	$K_{\text{spa}}$	Sulfide	$K_{\text{spa}}$
PbS	$3 \times 10^{-7}$	MnS	$3 \times 10^{10}$
CuS	$6 \times 10^{-16}$	FeS	$6 \times 10^2$
HgS	$2 \times 10^{-32}$	NiS	0.8
		ZnS	0.03

1. A solution with a  $\text{pH}=0.52$  and  $\text{H}_2\text{S}$  concentration of  $0.10 \text{ M}$  is  $0.0010 \text{ M}$  in each of the cations  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ . Under these Group II conditions, which metal cations will precipitate as the sulfide?
2. A solution is  $0.0010 \text{ M}$  in each of the seven metal cations shown in the table above. If the  $\text{H}_2\text{S}$  concentration is  $0.10 \text{ M}$ , what pH is needed to precipitate all seven of the metal cations?

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## Solubility Product Constant

### Other Examples: Precipitation and Separation

- A solution is 0.500 M in each of the ions  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  and has a pH of 4.00. Solid NaOH is added to precipitate the hydroxides.  $K_{\text{sp}}(\text{Ni}(\text{OH})_2) = 2 \times 10^{-15}$ ;  $K_{\text{sp}}(\text{Cr}(\text{OH})_3) = 6.3 \times 10^{-31}$ 
  - 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  $\text{Cr}^{3+}$  as possible without precipitating the  $\text{Ni}^{2+}$ ?
- A solution is 0.0050 M in  $\text{Sn}^{2+}$  and  $\text{Al}^{3+}$  and has a pH = 1.00. Solid NaOH is added to make the solution more basic. Which of these metal cations will precipitate first?  
 $\text{Sn}(\text{OH})_2$  ( $K_{\text{sp}} = 3 \times 10^{-27}$ )  $\text{Al}(\text{OH})_3$  ( $K_{\text{sp}} = 2.0 \times 10^{-32}$ )
- A solution is  $1.0 \times 10^{-3}$  M in each of the metal cations  $\text{Cu}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ , and  $\text{Ag}^+$ . Solid NaBr is added to this solution. In what order will the bromides precipitate?  
 $\text{CuBr}$  ( $K_{\text{sp}} = 6.3 \times 10^{-9}$ )       $\text{AgBr}$  ( $K_{\text{sp}} = 5.4 \times 10^{-13}$ )  
 $\text{PbBr}_2$  ( $K_{\text{sp}} = 6.6 \times 10^{-6}$ )       $\text{Hg}_2\text{Br}_2$  ( $K_{\text{sp}} = 6.4 \times 10^{-23}$ )

### 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:**  $\text{CuCO}_3$  is insoluble with  $K_{\text{sp}} = 2.5 \times 10^{-10}$ . However addition of ammonia increases the solubility of this salt and causes  $\text{CuCO}_3$  to dissolve. Explain. Hint:  $\text{Cu}(\text{II})$  forms the soluble ammonia complex ion  $\text{Cu}(\text{NH}_3)_4^{+2}$   $K_f = 1.1 \times 10^{13}$ .

**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  $\text{AgBr}$  ( $K_{\text{sp}} = 5.4 \times 10^{-13}$ ) at 25 °C in:
- Pure water
  - 0.75 M  $\text{NH}_3$

