

## Solubility Equilibria II

### Precipitation or not?

- We now know how to calculate the amount of substance that will dissolve.
- If we mix two solutions does anything precipitate from the combination?
- How can we calculate this?
  - First determine the new concentrations after dilution.
  - Then calculate  $Q_{sp}$  and compare it to  $K_{sp}$ .

### $Q_{sp}$ vs. $K_{sp}$

- $Q_{sp} > K_{sp}$ 
  - In this case the concentrations of the ions are too high so a solid will precipitate to reduce the concentrations.
- $Q_{sp} = K_{sp}$ 
  - This is just at equilibrium so nothing occurs
- $Q_{sp} < K_{sp}$ 
  - The concentrations of the ions are too low to reach equilibrium and there is no solid present to make more. Nothing occurs.

### Example

- A solution contains  $1.5 \times 10^{-4}$  M Hydrochloric acid and  $1.2 \times 10^{-3}$  M Lead(II) Nitrate. Is there a precipitate from this solution?
  - Determine the equilibrium
    - $PbCl_2 \rightleftharpoons Pb^{2+} + 2 Cl^-$
  - Find  $Q_{sp}$   
 $Q_{sp} = [Pb^{2+}][Cl^-]^2 = (1.2 \times 10^{-3})(1.5 \times 10^{-4})^2 = 2.7 \times 10^{-11}$

### Answer

- Compare  $Q_{sp}$  to  $K_{sp}$   
 $2.7 \times 10^{-11} < 1.6 \times 10^{-5} = K_{sp}$
- There will be no precipitate from this solution.

### Fractional precipitation

- If we have a mixture of ions, we can select an ion that will precipitate both of them.
- We select the ion based on the  $K_{sp}$ 's of the respective compounds that would form.
- We can calculate the concentration range of ion to add that will precipitate one of them but not the other.

### Example

- A mixture is 0.10 M  $\text{Ag}^+$  and 0.10 M  $\text{Cu}^{2+}$ . What range of chromate ion concentration will precipitate one ion but not the other?
  - Look at the equilibria
    - $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$   $K_{sp} = 1.1 \times 10^{-12}$
    - $\text{CuCrO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{CrO}_4^{2-}$   $K_{sp} = 3.5 \times 10^{-6}$

### Answer

- Calculate the  $[\text{CrO}_4^{2-}]$  to precipitate each of the metals.
$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12} \quad K_{sp} = [\text{Cu}^{2+}] [\text{CrO}_4^{2-}] = 3.5 \times 10^{-6}$$
$$[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{1.1 \times 10^{-12}}{(0.10)^2} = 1.1 \times 10^{-10} \quad [\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Cu}^{2+}]} = \frac{3.5 \times 10^{-6}}{(0.10)} = 3.5 \times 10^{-5}$$
- This means that the silver will precipitate first when the chromate gets up to  $1.1 \times 10^{-10}$  M.
- Copper starts to precipitate when the chromate gets up to  $3.5 \times 10^{-5}$  M

### pH dependence of solubility

- If the anion of the solid is the conjugate base of a weak acid, the presence of an acid can “remove” the ion from solution.
- This can cause more of the solid to dissolve. The solid is more soluble in an acidic solution.

### pH dependence of solubility

- Qualitative example
  - $\text{SrCO}_3 \rightleftharpoons \text{Sr}^{2+} + \text{CO}_3^{2-}$
  - If we add hydrogen ion (acid) the following equilibrium occurs
    - $\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$
  - The net effect is that the carbonate ions are removed from the solution.
  - This results in more  $\text{SrCO}_3$  being dissolved.

### Complex Ions

### Formation of Complex Ions

- Metals can react with Lewis bases to form complex ions
  - $\text{M}^{n+} + y \text{L}^m \rightleftharpoons \text{ML}_y^{(n-ym)}$
  - This is an equilibrium and as such has an equilibrium constant,  $K_f$ , which is called the formation constant.
  - Formation constants are generally large ( $>10^7$ ).

## Complex Ion Formation

- $K_f$ , for the previous general equilibrium is

$$K_f = \frac{[ML_y^{(n-ym)}]}{[M^{n+}][L^{m-}]^y}$$

- Because  $K_f$  is large, we will solve the equilibrium by assuming the reaction goes to completion and then to equilibrium.

## Example

- The Iron(II) ion forms a complex ion with 6 cyanide ions.  $K_f = 1.0 \times 10^{35}$  for the reaction  $Fe^{2+} + 6 CN^- \rightleftharpoons Fe(CN)_6^{4-}$ . What is the equilibrium concentration of  $Fe^{2+}$  if the solution starts with  $[Fe^{2+}] = 0.10$  M and  $[CN^-] = 1.00$  M?

## Answer

- Setup ICE table including the completion step

	$Fe^{2+}$	$CN^-$	$Fe(CN)_6^{4-}$
I	0.10	1.00	0
Comp	-0.10	-0.60	+0.10
C	+x	+6x	-x
E	x	0.40+6x	0.10-x

## Answer

- Solve the equilibrium

$$K_f = \frac{[Fe(CN)_6^{4-}]}{[Fe^{2+}][CN^-]^6} = 1.0 \times 10^{35} = \frac{(0.10 - x)}{(x)(0.40 + 6x)^6} \approx \frac{(0.10)}{x(0.40)^6}$$

$$x = \frac{0.10}{(1.0 \times 10^{35})(0.40)^6} = 2.4 \times 10^{-34} \text{ M}$$

The assumptions are valid. The equilibrium concentration of  $Fe^{2+}$  is  $2.4 \times 10^{-34}$  M.

This concentration is so low that there is far less than 1 ion in 1 L of solution.

## Amphoteric Hydroxides

- A substance is **amphoteric** if it reacts with both acids and bases.
- An amphoteric hydroxide is a slightly soluble metal hydroxide that will do just that.
- Example –  $Zn(OH)_2$

## $Zn(OH)_2$

- $Zn(OH)_2$  will react with acids as expected
  - $Zn(OH)_2 + 2 H^+ \rightarrow Zn^{2+} + H_2O$
- It will also react with bases to form a soluble complex ion
  - $Zn(OH)_2 + 2 OH^- \rightarrow Zn^{2-} + 2 H_2O$
- Several other metals hydroxides such as those of  $Al^{3+}$ ,  $Cr^{3+}$ , and  $Pb^{2+}$  also do this.

## Solubility and complex ions

- Amphoteric hydroxides give us a prime example of how the formation of a complex ion can affect the solubility of a slightly soluble compound.
- We have also seen this in the lab when we did Cation B and we'll see it again in Cation C.

## Calculations involving complex ions and solubility

- These problems generally ask if there is a precipitate formed for the solubility of the salt in a solution that forms a complex ion with the cation.
- When we are dealing with both equilibria, the easiest method of solving the problem is to add the relevant equilibria together.
- We can do this because the  $K_f$  is generally large so we assume that all of the metal ion ends up in the complex ion.

## Calculations involving complex ions and solubility

- We will do one of two things
  - find Q and compare it to the overall K
  - setup the ICE table and solve the overall equilibrium
  - If we are asked for the equilibrium concentration of the metal ion, we will plug it back into the relevant equilibrium expression.

## Example

- Will a precipitate form from a solution that contains 0.0010 M  $\text{Ni}^{2+}$ , 1.00 M  $\text{OH}^-$ , and 1.00 M  $\text{CN}^-$ ?
- The equilibria are
  - $\text{Ni}(\text{OH})_2 \rightleftharpoons \text{Ni}^{2+} + 2 \text{OH}^- \quad K_{\text{sp}} = 2.0 \times 10^{-15}$
  - $\text{Ni}^{2+} + 4 \text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-} \quad K_f = 1.0 \times 10^{31}$
  - $\text{Ni}(\text{OH})_2 + 4 \text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-} + 2 \text{OH}^- \quad K = 2.0 \times 10^{16}$

## Answer

- Find Q
 
$$Q = \frac{[\text{Ni}(\text{CN})_4^{2-}][\text{OH}^-]^2}{[\text{CN}^-]^4} = \frac{(0.0010)(1.00)^2}{(1.00)^4} = 0.0010$$
- Compare Q to K
  - $Q = 0.0010 < 1.0 \times 10^{16} = K$
  - Q is less than K so we aren't yet at equilibrium so there is no precipitate.

## Example

- What is the molar solubility of Silver Carbonate in 1.00 M  $\text{NH}_3$ ?
- Find equilibria
  - $\text{Ag}_2\text{CO}_3 \rightleftharpoons 2 \text{Ag}^+ + \text{CO}_3^{2-} \quad K_{\text{sp}} = 1.4 \times 10^{-11}$
  - $2 \text{Ag}^+ + 4 \text{NH}_3 \rightleftharpoons 2 \text{Ag}(\text{NH}_3)_2^+ \quad K_f = 1.7 \times 10^{17}$
  - $\text{Ag}_2\text{CO}_3 + 4 \text{NH}_3 \rightleftharpoons 2 \text{Ag}(\text{NH}_3)_2^+ + \text{CO}_3^{2-} \quad K = 2.4 \times 10^6$

[ Answer ]

- Set up ICE table

	$\text{NH}_3$	$\text{Ag}(\text{NH}_3)_2^+$	$\text{CO}_3^{2-}$
I	1.00	0	0
cp	0.00	0.50	0.50
C	+4x	-2x	-x
E	4x	0.50-2x	0.50-x

[ Answer ]

- Solve the equilibrium

$$K = 2.4 \times 10^6 = \frac{[\text{Ag}(\text{NH}_3)_2^+]^2 [\text{CO}_3^{2-}]}{[\text{NH}_3]^4} = \frac{(0.50-2x)^2 (0.50-x)}{(4x)^4} \approx \frac{(0.50)^3}{(4x)^4}$$

$$x = \sqrt[4]{\frac{(0.50)^3}{4^4 (2.4 \times 10^6)}} = 3.8 \times 10^{-3}$$

- The assumption here is valid. 0.50-x is the concentration of carbonate which is the molar solubility. The molar solubility is 0.50 M