CHAPTER 17: SOLUBILITY AND COMPLEX ION EQUILIBRIA

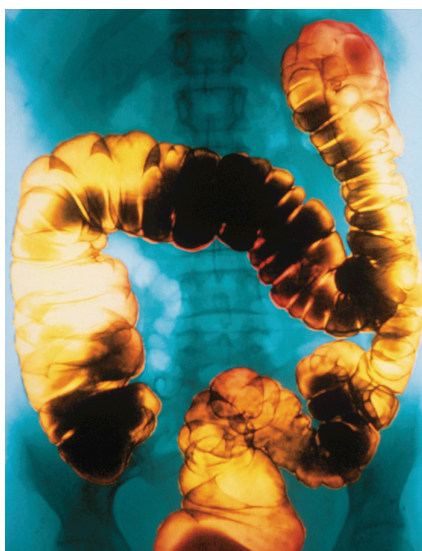## Part One: Solubility Equilibria

A. K_{sp}, the Solubility Product Constant. (Section 17.1)

    1. Review the solubility rules. (Table 4.1)

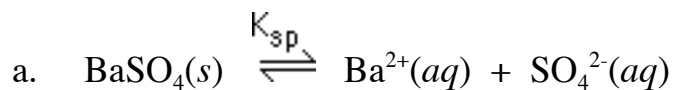   2. Insoluble and slightly soluble compounds are important in nature and commercially.

        a.

        b.

        c.

   3. Solubility behavior expressed mathematically by special equilib. constant = K_{sp}.

        a. $BaSO_4(s) \overset{K_{sp}}{\rightleftharpoons} Ba^{2+}(aq) + SO_4^{2-}(aq)$

        b. $Ca_3(PO_4)_2 \rightleftharpoons 3\,Ca^{2+} + 2\,PO_4^{3-}$

4. Note - in __all__ saturated aqueous solutions of $BaSO_4$, no matter what other materials are present:

5. Table of K_{sp} in Table 17.1.

6. <u>Solubility</u> = moles of a compound which dissolve in a liter of solution. Directly related to but not equal to K_{sp}.

B. Finding K_{sp}. (Section 17.1)

    1. Usually determined by conductivity experiment.

    2. Example: Found that 6.93×10^{-3} g of $CaCO_3$ can dissolve in 1.00 L of water. What is K_{sp} of $CaCO_3$?

    3. Example: The molar solubility of $PbBr_2$ is 1.16×10^{-2} moles/Liter. What is K_{sp}?

$$PbBr_2 (s) \quad \overset{K_{sp}}{\rightleftharpoons} \quad Pb^{2+}(aq) \quad + \quad 2\,Br^{-}(aq)$$
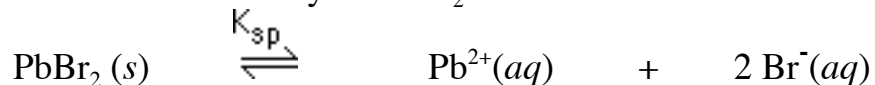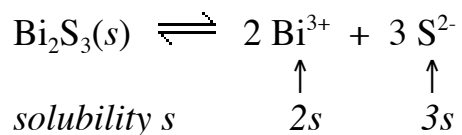
4. For Bi_2S_3 with molar solubility = s

C. Finding the Solubility from K_{sp}. (Section 17.1)

1. Example: Calculate the molar solubility of AgCl and the concentrations $[Ag^+]$ and $[Cl^-]$ in a saturated aqueous solution of AgCl. The $K_{sp} = 1.8 \times 10^{-10}$.

2. Example: Calculate the molar solubility of Bi_2S_3, and $[Bi^{3+}]$ and $[S^{2-}]$ concentrations. The $K_{sp} = 1.6 \times 10^{-72}$.

$$Bi_2S_3(s) \rightleftharpoons 2\ Bi^{3+} + 3\ S^{2-}$$

$$\textit{solubility s} \qquad 2s \qquad 3s$$

$$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3$$

D. The Common Ion Effect in Solubility Calculations. (Section 17.2)

1. Previously showed that in saturated solution of AgCl:

$$[Cl^-] = [Ag^+] = 1.3 \times 10^{-5} \text{ M} = \sqrt{K_{sp}}$$

2. Calculate the solubility of AgCl and the concentration of ionic species present in a 2.0 M NaCl solution saturated with AgCl. K_{sp} of AgCl is 1.8×10^{-10}.

Here Cl^- ion is present from two sources: NaCl and AgCl.

Part Two: Uses of the Solubility Product Principle

A. Predicting if Precipitation Will Occur. (Section 17.3)

  1. Precipitation will occur whenever the ion concentration product for a compound exceeds the K_{sp} of that compound.

  For example, when $[Ag^+][Cl^-] > K_{sp}$

  2. The solution is unstable, and precipitate of AgCl will occur until:

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

  3. Example: The following reagents are added to water and the final volume is adjusted to 1.00 L. What, if any, compounds will precipitate?

1.0 g NaOH	$\div$	40.0 g/mol	=	$2.5 \times 10^{-2}\ M$
1.0 g Na_2CO_3	$\div$	106.0 g/mol	=	$9.4 \times 10^{-3}\ M$
1.0 g $CaCl_2$	$\div$	110.9 g/mol	=	$9.0 \times 10^{-3}\ M$
1.0 g $PbNO_3$	$\div$	269.2 g/mol	=	$3.7 \times 10^{-3}\ M$

  (Hint: Don't expect any Na^+ or NO_3^- salts to precipitate due to their high solubility.)

$Ca(OH)_2$? $\quad [Ca^{2+}][OH^-]^2 \quad = (9.0 \times 10^{-3})(2.5 \times 10^{-2})^2$
$\qquad\qquad\qquad\qquad\qquad\qquad = 5.62 \times 10^{-6} < K_{sp} = 7.9 \times 10^{-6}\ NO!$

$CaCO_3$? $\quad [Ca^{2+}][CO_3^-] \quad = (9.0 \times 10^{-3})(9.4 \times 10^{-3})$
$\qquad\qquad\qquad\qquad\qquad\qquad = 8.46 \times 10^{-5} > K_{sp} = 4.8 \times 10^{-6}\ YES!$

$Pb(OH)_2$? $\quad [Pb^{2+}][OH^-]^2 \quad = (3.7 \times 10^{-3})(2.5 \times 10^{-2})^2$
$\qquad\qquad\qquad\qquad\qquad\qquad = 2.3 \times 10^{-6} > K_{sp} = 2.8 \times 10^{-16}\ YES!$

$PbCO_3$? $\quad [Pb^{2+}][CO_3^-] \quad = (3.7 \times 10^{-3})(9.4 \times 10^{-3})$
$\qquad\qquad\qquad\qquad\qquad\qquad = 3.5 \times 10^{-5} > K_{sp} = 1.5 \times 10^{-13}\ YES!$

$PbCl_2$? $\quad [Pb^{2+}][Cl^-]^2 \quad = (3.7 \times 10^{-3})(2 \times 9.0 \times 10^{-3})^2$
$\qquad\qquad\qquad\qquad\qquad\qquad = 1.1 \times 10^{-6} < K_{sp} = 1.7 \times 10^{-5}\ NO!$

$Pb(OH)_2$ will precipitate <u>first</u>, because its ion product is the greatest relative to its K_{sp}.

B. Predicting Concentration Required to Cause Precipitation. (Section 17.3)

1. Example: A solution is 0.100 M Na_2CO_3. Then, calcium ions are added by another source. At what concentration of Ca^{2+} ion will precipitation of $CaCO_3$ occur? K_{sp} of $CaCO_3$ is 4.8×10^{-9}.

2. Part 2: How many grams of $CaCl_2$ would need to be added to 500 mL of 0.100 M Na_2CO_3 to start forming this precipitate?

   precipitate when $[Ca^{2+}] = 4.8 \times 10^{-8} M$ (moles/Liter)

   OR: $= 2.4 \times 10^{-8}$ moles in 500 mL

   2.4×10^{-8} moles $\times$ 110.9 g/mol $= 2.66 \times 10^{-6}$ grams $CaCl_2$

C. Fractional Precipitation (Section 17.3)

1. May wish to precipitate some ions from solution but leave others.

2. Example: Have solution: 0.10 M Cu^+
   0.10 M Ag^+
   0.10 M Au^+

   Slowly add NaCl to the solution. Which will precipitate first: CuCl, AgCl, or AuCl? At what $[Cl^-]$ will these each begin to precipitate?

   Given: K_{sp} of CuCl $= 1.9 \times 10^{-7}$
   K_{sp} of AgCl $= 1.8 \times 10^{-10}$
   K_{sp} of AuCl $= 2.0 \times 10^{-13}$

3. What will $[Au^+]$ be when AgCl just begins to precipitate?

$[Au^+][Cl^-] = 2.0 \times 10^{-13}$

$\uparrow$

$1.8 \times 10^{-9}\ M$ to precipitate AgCl

$[Au^+] \times 1.8 \times 10^{-9} = 2.0 \times 10^{-13}$
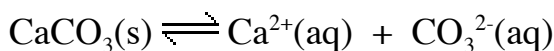
$[Au^+] = 1.3 \times 10^{-4}\ M$
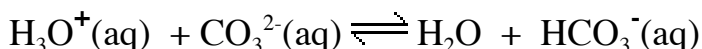
(remember, $[Au^+]$ was originally $0.10\ M$)

D. Effect of pH on Solubility (Section 17.4)

1. Example: Limestone/Marble tends to dissolve in acidic conditions.

2. Solubility equilibrium for $CaCO_3(s)$

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq)\ +\ CO_3^{2-}(aq)$

3. This equilibrium is affected by addition of strong acid:

$H_3O^+(aq)\ +\ CO_3^{2-}(aq) \rightleftharpoons H_2O\ +\ HCO_3^-(aq)$

4. This reaction removes carbonate ion, shifting the solubility equilibrium to the right, causing more $CaCO_3(s)$ to go into solution.

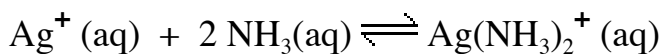**Part Four: Complex-Ion Equilibria**

A. Complex-Ion Formation. (Section 17.5)

1. Some metal ions in solution can bind varying numbers of molecules or molecular ions.

2. Example: Ag^+ ion and ammonia molecules:

$Ag^+(aq)\ +\ NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq)$
$Ag(NH_3)^+(aq)\ +\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
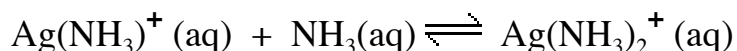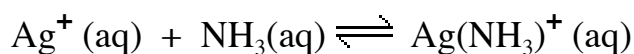
3. The combined complexation reaction is then:

$$Ag^+ (aq) \ + \ 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+ (aq)$$

4. This equilibrium is governed by the **formation constant**, or **stability constant**, K_f.

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

TABLE 17.2

Formation Constants of Complex Ions at 25°C

Complex Ion	K_f
$Ag(CN)_2^-$	5.6×10^{18}
$Ag(NH_3)_2^+$	1.7×10^7
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}
$Cd(NH_3)_4^{2+}$	1.0×10^7
$Cu(CN)_2^-$	1.0×10^{16}
$Cu(NH_3)_4^{2+}$	4.8×10^{12}
$Fe(CN)_6^{4-}$	1.0×10^{35}
$Fe(CN)_6^{3-}$	9.1×10^{41}
$Ni(CN)_4^{2-}$	1.0×10^{31}
$Ni(NH_3)_6^{2+}$	5.6×10^8
$Zn(NH_3)_4^{2+}$	2.9×10^9
$Zn(OH)_4^{2-}$	2.8×10^{15}

5. The **dissociation constant** K_d is simply the reciprocal of K_f.

6. Calculations with this equilibrium. (See text Section 17.5)

7. Formation of complex ions can have important effects on solubility of ions in solution. (See lab manual - Experiments #21-26)