Chapter 16 – Cont.

AQUEOUS IONIC EQUILIBRIA

1

SOLUBILITY EQUILIBRIA

Carlsbad Caverns, NM. Limestone ($CaCO_3$) formations inside the cave results from subtle shifts in carbonate equilibria acting over millions of years.

http://www.traveleze.com/travel_planning/carlsbad.html

Big Gypsum, Thornhill Cave, Breckinridge County, KY

http://www.darklightimagery.net/gypsum.html

2

The Black Widow (Lynn Turner Case)

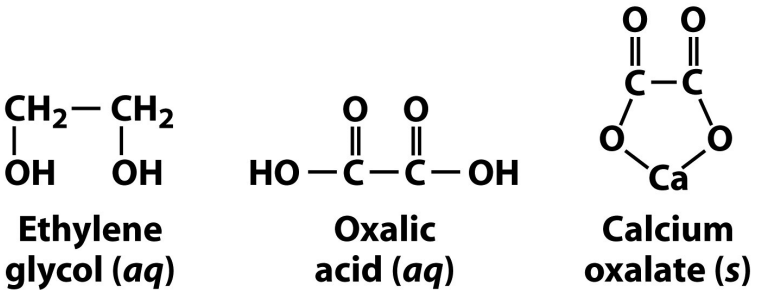
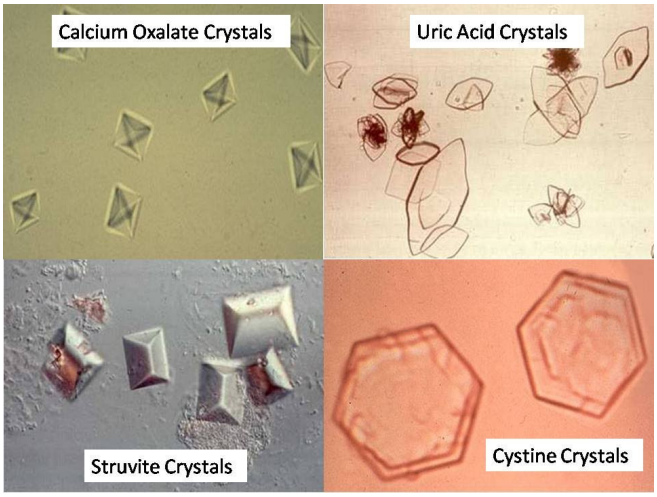


Figure 13-10
Investigating Chemistry, First Edition

Image available at Matthew E. Johll, " Investigating Chemistry: A Forensic Science Perspective." 1st ed. W.H. Freeman, New York: 2007.

3



Kidney stone types*:* calcium oxalate, calcium phosphate, struvite (magnesium ammonium phosphate), uric acid, and cystine.
Image available http://knol.google.com/k/kidney-stones

4

Solubility Product

Solubility product is the equilibrium constant for a reaction in which a solid dissolves into its constituent ions in solution

- The corresponding equilibrium constant is called **solubility product constant, K_{sp}**

Exercise: Write the K_{sp} expression for the reaction:

$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-_{(aq)}$$

Is this what you got?

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

- Table 16.2 (p. 747) lists K_{sp} values for various solids

5

Solubility Calculations

Significance of solubility product:

- The equation $K_{sp} = [Hg_2^{2+}][Cl^-]^2$

  indicates that *if solid Hg_2Cl_2 is placed in water, it will dissolve until the product of the ion concentrations (raised to a certain power) equals the solubility product for Hg_2Cl_2*

When a solution contains excess undissolved solid, it is said to be **saturated**.

6

Solubility Calculations – *Cont.*

Exercises: (Adapted from Silberberg's "Chemistry: The Molecular Nature of Matter and Change." 4th ed.)

(1) Calculate the solubility of **calcium hydroxide** (also known as *slaked lime*, a major component of plaster and cement) in water if the **K_{sp} is 6.5 x 10^{-6}**.

(2) When **lead (II) fluoride** is shaken with DI water at 25 ^{0}C, the solubility is found to be **0.64 g/L**. Calculate the K_{sp} of lead (II) fluoride.

7

1. Determining solubility from K_{sp}

Example: Calculate the solubility of **calcium hydroxide** (also known as *slaked lime*, a major component of plaster and cement) in water if the **K_{sp} is 6.5 x 10^{-6}**.

Exercise 1: Determining solubility from **K_{sp}**

unknown ↗ ↖ given

Which part of the K_{sp} expression is solubility? What is the unit of solubility?

Solubility is the value of **x** when you solve for x after setting up the ICE table. It is equal to the ***moles of the salt that dissolved per liter of solution***, so the unit is mol/L or M.

8

$$Ca(OH)_{2\,(s)} \Leftrightarrow Ca^{2+} + 2\,OH^-$$

I	**solid**	**0**	**0**
C	**solid**	+x	+2x
E	**solid**	x	2x

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

$6.5 \times 10^{-6} = (x)(2x)^2 = 4x^3$

$(6.5 \times 10^{-6})/4 = x^3$ **x =** solubility, ***S*** **$= 1.2 \times 10^{-2}$ M**

9

2. Determining solubility from K_{sp}

(2) When lead (II) fluoride is shaken with DI water at 25 ^{0}C, the solubility is found to be 0.64 g/L. Calculate the K_{sp} of lead (II) fluoride. MM PbF_2 = 245.20 g/mol

Exercise 2: Determining **K_{sp}** from solubility

unknown ↗ ↖ given

10

Answer: **(2) $K_{sp} = 7.0 \times 10^{-8}$**

11

The Reaction Quotient

The **reaction quotient, Q**, has the same form as the K_{sp}, except that the concentrations of the reactants and products are nonequilibrium concentrations.

- If **Q < K**, reaction will proceed in the forward direction (towards dissolution) until equilibrium is established
- If **Q = K** then the system is in equilibrium
- If **Q > K**, reaction will proceed in the reverse direction (towards precipitation) until equilibrium is established

Importance of Q

- ***Predicting the formation of a precipitate***. HOW? [Use the relationship between Q and K (subst. K_{sp}) above]

12

Exercise: (Adapted from Silberberg, p. 841) A common lab method for preparing a precipitate is to mix solutions containing the component ions. Does a precipitate form when 100. mL of 0.30 M $Ca(NO_3)_2$ is mixed with 200. mL of 0.060 M NaF?
$K_{sp\ (CaF2)} = 3.2 \times 10^{-11}$

Answer: **$[Ca^{2+}]_i = 0.10$ M; $[F^-]_i = 0.040$ M; $Q = 1.6 \times 10^{-4} > K_{sp}\ (CaCl_2) = 3.2 \times 10^{-11}$ so CaF_2 will ppt.**

13

The Common Ion Effect

The presence of a common ion decreases the solubility of slightly soluble salt (***common ion effect***)

Consider again the equilibrium for a saturated solution of mercury (I) chloride:

$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-_{(aq)}$$

Q. What happens to the equilibrium mixture when $NaCl_{(aq)}$ is added?

- At a given temperature, K_{sp} depends only on the product of the ions' concentration
- Thus, if $[Cl^-]$ goes up, $[Hg_2^{2+}]$ must go down to maintain the constant K_{sp}
  - In effect, the *solubility of Hg_2Cl_2 decreases*

14

The Common Ion Effect – *Cont.*

- Addition of Cl^- shifts the equilibrium to the left. This is explained by Le Chatelier's principle.

$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-_{(aq)}$$

Added Cl^-

- Added Cl^- combines with Hg_2^{2+} ions, forming more Hg_2Cl_2 precipitate (In effect, Hg_2Cl_2 becomes <u>less soluble</u>)
- The same result is obtained if we add a soluble Hg_2^{2+} salt, such as $Hg_2(NO_3)_2$

15

The Common Ion Effect – *Cont.*

Exercise: Problem 6-19. Find the solubility in g/L of $CaSO_4$ (FW 136.14) in (a) distilled water and (b) 0.50 M $CaCl_2$.

Answer: **(a) 0.67 g/L; (b) 0.0065 g/L**

WORK: Part (b) only

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{-}{}_{(aq)}$$

I	Solid		0.50 M	0
C	Solid		+ x	+ x
E	Solid		0.50 + x	x

$K_{sp} = [Ca^{2+}][SO_4^{2-}]$

$2.4 \times 10^{-5} = [0.50 + x][x] \approx 0.50x$ Assuming x << 0.50 M

$x = (4.8 \times 10^{-5}$ mol/L **dissolved $CaSO_4$** $)(136.14$ g $CaSO_4$/mol$) = 0.0065$ g/L **$CaSO_4$**

This value is << 0.50 M so the assumption is valid

16

Importance of Solubility Equilibria

❖ ***Separation of ions*** in a complex mixture. HOW?

➢ Selective precipitation using differences K_{sp}

Challenge: An aqueous solution consists of dissolved Ag^+, Pb^{2+} and Hg_2^{2+}. Can we separate them from each other by selective precipitation with Cl^-? If so, what is the order of precipitation?

What information do you need? K_{sp} of each chloride salt – Appendix F

K_{sp} values at 25 ^{0}C : AgCl = 1.8×10^{-10}; Hg_2Cl_2 = 1.2×10^{-18}; $PbCl_2$ = 1.7×10^{-5}

Answer: Yes, since their K_{sp}'s differ significantly. Hg_2Cl_2 will precipitate first (lowest K_{sp}), followed by AgCl. $PbCl_2$ will be the last to precipitate out.

NOTE: Don't forget to filter out each precipitate before the next one comes out of solution.

17