Name ______________________________**Chem 163 Section**: ______ **Team Number:** ______

ALE 17. Equilibria of Slightly Soluble Compounds

(Reference: 19.3 Silberberg *5th edition*)

How is the solubility of a salt related to its solubility product constant?

Model: the dissolution of magnesium hydroxide in water

When solid $Mg(OH)_2$ dissolves in water the chemical reaction is:

$$\mathbf{Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\ OH^{-}_{(aq)}} \qquad \textbf{(1)}$$

Table 1. The results after equilibrium has been established of adding solid $Mg(OH)_2$ to 10.0 L H_2O.

Total amount of $Mg(OH)_2$ added		**Equilibrium Concentrations**		**Mass of $Mg(OH)_2$ that does not dissolve (g)**
(g)	**(moles)**	$[Mg^{2+}]$ (*M*)	$[OH^-]$ (*M*)	
0.00963	1.65 x 10^{-4}	1.65 x 10^{-5}	3.30 x 10^{-5}	0.00000
0.04815	8.26 x 10^{-4}	8.26 x 10^{-5}	1.65 x 10^{-4}	0.00000
0.09590	1.64 x 10^{-3}	1.64 x 10^{-4}	3.29 x 10^{-4}	0.00000
0.09630	1.65 x 10^{-3}	1.65 x 10^{-4}	3.30 x 10^{-4}	0.00000
0.09700	1.66 x 10^{-3}	1.65 x 10^{-4}	3.30 x 10^{-4}	0.00070
0.10000	1.71 x 10^{-3}	1.65 x 10^{-4}	3.30 x 10^{-4}	0.00370
0.15000	2.57 x 10^{-3}	1.65 x 10^{-4}	3.30 x 10^{-4}	0.05370
0.20000	3.43 x 10^{-3}	1.65 x 10^{-4}	3.30 x 10^{-4}	0.10370

Key Questions

1. When 8.26 x 10^{-4} moles of $Mg(OH)_2$ are added ….
   a. why is $[Mg^{2+}]$ = 8.26 x 10^{-5} M?

   b. why is $[OH^-]$ = 1.65 x 10^{-4} M?

2. When 0.20000 grams of $Mg(OH)_2$ are added, how many grams dissolve? ____________________

3. When 0.09700 grams of $Mg(OH)_2$ are added, how many grams dissolve? ____________________

4. According to the table, what is the maximum number of moles of $Mg(OH)_2$ that can be dissolved in **10.0 L H_2O**? ________________

5. Based on your answer to the previous question…
   a. what is the maximum number of *moles* of $Mg(OH)_2$ that can be dissolved in **1.00 L H_2O**? ___________________

   b. what is the maximum *mass* of $Mg(OH)_2$ that can be dissolved in **1.00 L H_2O**? ______________

6. Based on your answers to questions 5a, what is the maximum value for the expression $[Mg^{2+}] [OH^-]^2$? (As you will see in question 9, below, this value is called the **solubility product** and is abbreviated, $\boldsymbol{K_{sp}}$.)

$$K_{sp} = [Mg^{2+}] [OH^-]^2 = \underline{\hspace{8cm}}$$

7. Is it possible for the value of $[Mg^{2+}] [OH^-]^2$ to be less than the answer you gave to the previous question? *Explain*. (As you will see on page 5, this value is called the **ion product** and is abbreviated, $\boldsymbol{Q_{sp}}$.)

The Model: The Solubility Product Expression

Once equilibrium is established between a solid and the associated aqueous species, the solution is said to be **saturated**. For $Mg(OH)_2$, we say the **solubility** of magnesium hydroxide is 9.63 x 10^{-3} g/L or that the solubility of magnesium hydroxide is 1.65 x 10^{-3} M.

By convention, if a saturated solution of an ionic compound is greater than about 0.1 M, we say that the compound is **soluble**. If the saturated solution is less than about 0.001 M, the compound is said to be **insoluble**. Intermediate cases are said to be moderately or **slightly soluble**. Experimental evidence has shown that essentially all compounds containing the nitrate ion, NO_3^-, and also all those containing the sodium ion, Na^+, are soluble in water.

Silver chloride is so insoluble in water that a saturated solution contains only 0.002 g of AgCl per liter of water. Hence if a mere 1.000 g AgCl were added to a liter of water the following equilibrium would be present between the 0.998 g of undissolved AgCl and the 0.002 g of ions in solution:

$$\mathbf{AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}} \qquad \textbf{(2)}$$

Key Questions

8. Complete the equilibrium expression for the equilibrium in eqn 2. *Hint*: remember that it is a heterogeneous equilibrium!

$$K_c =$$

9. Since this equilibrium constant is proportional to the solubility of the salt, it is called the **solubility product equilibrium constant** for the reaction, or $\boldsymbol{K_{sp}}$. Write the K_{sp} expression for silver chloride.

$$K_{sp} =$$

10. The $\boldsymbol{K_{sp}}$ expression for a salt is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium. Write the K_{sp} expression for the following ionic compounds.

a. Calcium fluoride: K_{sp} =

b. Magnesium phosphate: K_{sp} =

c. Iron (III) hydroxide: K_{sp} =

d. Mercury (I) iodide: K_{sp} =
Hint: remember that the Mercury (I) ion is "di-ionic"

Model: The Relationship Between K_{sp} And the Solubility of a Salt

K_{sp} is called the **solubility product** because it is literally the product of the solubilities of the ions in moles per liter. The solubility product of a salt can therefore be calculated from its solubility, or vice versa. Like all equilibrium constants, *a given K_{sp} value depends only on the temperature, not on the individual ion concentrations*.

Photographic films are based on the sensitivity of silver bromide to light. When light hits a crystal of AgBr, a small fraction of the Ag^+ ions are reduced to silver metal. The rest of the Ag^+ ions in these crystals are reduced to silver metal when the film is developed. AgBr crystals that do not absorb light are then removed from the film to "fix" the image. Can the silver bromide be removed by simply washing the film in water? Let's see by calculating the solubility of AgBr in water in grams per liter.

Key Questions

11. Let's calculate the **solubility of AgBr in water in grams per liter**, to see whether AgBr can be removed by simply washing the film. The K_{sp} for silver bromide is 5.0×10^{-13} at 25 °C.

    a. Start by writing the balanced chemical equation for the equilibrium and the corresponding K_{sp} expression:

    $AgBr_{(s)} \rightleftharpoons$ $\quad\quad\quad$ **K_{sp} =** 5.0×10^{-13} =

    b. What is the relationship between $[Ag^+]$ and $[Br^-]$ if there is no other source of silver or bromide ions in the solution?

    c. Calculate the $[Ag^+]$ and $[Br^-]$ in **moles per liter**. *Show your work using correct sig. figs.& circle your answer.*

    d. Calculate the solubility of silver bromide in **grams AgBr per liter**. *Show your work dimensional analysis and sig. figs.—circle your answer.*

    e. Based on your response to part d, above, is it practical to try to wash the unexposed AgBr off photographic film with water? *Explain*.

Exercises

12. For an ionic compound with ions in a 1:1 ratio (e.g. $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$), $\boldsymbol{K_{sp} = x^2}$

    What is the K_{sp} expression in terms of x for $Al(OH)_3$? $\boldsymbol{K_{sp}}$ **=**

    What is the K_{sp} expression in terms of x for Al_2S_3? $\boldsymbol{K_{sp}}$ **=**

13. a. Calcium fluoride has been studied as possible source of fluoride ion for use in toothpaste. As the first step toward evaluating its use as a fluoridating agent, write the balanced chemical equation that describes the relationship between the solubility of solid CaF_2 and the equilibrium concentrations of the Ca^{2+} and F^- ions in a saturated aqueous solution.

    b. Calculate the solubility of calcium fluoride in **grams per liter**. Comment on the potential of CaF_2 to act as a fluoridating agent. (CaF_2: $K_{sp} = 4.0 \times 10^{-11}$)

14. Calculate the solubility in *grams per liter* of ***mercury (I) iodide*** ($K_{sp} = 4.7 \times 10^{-29}$) in order to decide whether it is accurately labeled when described as an insoluble salt. *Hint*: See question 10d! *Circle your answer.*

15. The solubility of calcium sulfate at 30 ^oC is 0.209 g/100mL solution. Calculate the K_{sp} of calcium sulfate. *Circle your answer.*

Model: Using K_{sp} As A Measure Of the Solubility of a Salt

The K_a for an acid is proportional to the strength of the acid. Hence, we can immediately conclude that formic acid ($HCOOH$, $K_a = 1.8 \times 10^{-4}$) is a stronger acid than acetic acid (CH_3COOH, $K_a = 1.8 \times 10^{-5}$). The same can be said about values of K_b: Methylamine (CH_3NH_2, $K_b = 4.8 \times 10^{-4}$) is a stronger base than ammonia (NH_3, $K_b = 1.8 \times 10^{-5}$).

Unfortunately, there is no simple way to predict the relative solubilities of salts from their K_{sp}'s if the salts produce different numbers of positive and negative ions when they dissolve in water.

Key Questions

16. Which salt, $CaCO_3$ ($K_{sp} = 2.8 \times 10^{-9}$) or Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$) is more soluble in water in units of moles per liter? *Hint*: This question requires a calculation—calculate the molar solubility of each salt!

17. A list of K_{sp} values like that on page A-13 in Appendix C in your textbook can be used to compare the solubility of silver chloride, $AgCl$, directly with that of silver bromide, $AgBr$, but not with that of silver chromate, Ag_2CrO_4. Explain

18. Compare the K_{sp} values on page A-13 in Appendix C in your textbook to determine which of the following is more soluble in water? *Circle your response and write the formula and K_{sp} value below each compound*.

    a. Strontium sulfate or barium chromate

    b. Calcium carbonate or copper (II) carbonate

    c. Barium iodate or silver chromate

Model: The Role of the Ion Product (Q_{sp}) Predicting the Formation of a Precipitate

As you discovered in Key Question #7, when a solution is *not saturated* the product of the concentrations of the ions dissolved in solution is *less* than the value for the K_{sp}. In this case, the product of the concentration of the ions is called the **ion product, Q_{sp}**.

One of the most useful applications of K_{sp} and Q_{sp} is to predict whether a precipitate will form when two solutions are mixed.

Key Question

19. If the ions of a slightly soluble substance are brought together, three types of situations are possible. Match the statement below that best corresponds with the three situations involving Q_{sp} and K_{sp}. (*Circle your choices*.)

    i.) $\boldsymbol{Q_{sp} = K_{sp}}$: *a, b or c*? ii.) $\boldsymbol{Q_{sp} < K_{sp}}$ *a, b or c*? iii.) $\boldsymbol{Q_{sp} > K_{sp}}$ *a, b or c*?

    a. *No precipitate forms*: The solution is unsaturated and the system not at equilibrium. To establish equilibrium Q_{sp} must increase to the value of K_{sp}, which means the concentrations of ions in solution are insufficient to produce a saturated solution.

    b. *Precipitate is present*: The solution is saturated and an equilibrium exists between dissolved and undissolved solute.

    c. *More precipitate will form*: The system is not at equilibrium and more precipitate must form to attain equilibrium. To establish equilibrium, the value of Q_{sp} must decrease to the value of Ksp, which means the concentrations of ions must be decreased. To do so ions combine to give solid.

Exercises

20. For $BaSO_4$, $K_{sp} = 1.1 \times 10^{-10}$. If you mix 200. mL of 1.0×10^{-4} M $Ba(NO_3)_2$ and 500. mL of 8.0×10^{-2} M H_2SO_4, what will be observed?
    a) A precipitate forms because $Q_{sp} > K_{sp}$
    b) No precipitate forms because $Q_{sp} = K_{sp}$
    c) No precipitate forms because $Q_{sp} > K_{sp}$
    d) A precipitate forms because $Q_{sp} < K_{sp}$
    e) No precipitate forms because $Q_{sp} < K_{sp}$

21. Does any solid lead (II) chloride, $PbCl_2$, form when 3.5 mg NaCl is dissolved in 0.250 L of 0.12 *M* $Pb(NO_3)_2$?

22. Suppose 0.0085 mol of $CaSO_4$ is dissolved in 100.0 mL of distilled water at 60ºC. Will a precipitate form when it is cooled to 25ºC if the $K_{sp} = 2.4 \times 10^{-5}$ at 25ºC?

23. A saturated solution of $Ca(OH)_2$, has a pH of 12.40. What is the K_{sp} for $Ca(OH)_2$?

a) 2.5×10^{-2} b) 1.3×10^{-2} c) 8.0×10^{-6} d) 2.0×10^{-6} e) 4.0×10^{-13}

24. Calculate the molar solubility of AgCl in a 0.10 M solution of NaCl. K_{sp} of AgCl is 1.8×10^{-10}

a) 1.3×10^{-5} M b) 5.5×10^{8} M c) 1.8×10^{-9} M d) 4.2×10^{-5} M e) 4.8×10^{-4} M

25. The solubility of salts can be affected by other equilibria. Addition of all of the following will affect the solubility of $FeCO_3$ *EXCEPT*:

a) $NaHCO_3$ b) NaCl c) H_2CO_3 d) Na_2CO_3 e) HCl

26. A kidney stone is mainly composed of Mg^{2+}, Ca^{2+}, $C_2O_4^{2-}$, and PO_4^{3-}. The cation-anion pair with the smallest solubility product is calcium phosphate. Assuming that a 0.044 g kidney stone is made up of calcium phosphate, how many liters of pure water would the stone have to be placed in for it to completely dissolve? *Hints*: Write the K_{sp} expression for calcium phosphate. Determine the *molar mass* of calcium phosphate. Determine the number of moles calcium ions and phosphate ions there are in 0.044 g of calcium phosphate. Let *V* represent the volume of the solution in liters. Look up the K_{sp} of calcium phosphate in your textbook. Substitute the value of the K_{sp} of calcium phosphate, the numbers of moles of calcium and phosphate ions, and the algebraic expression for the volume of the solution into K_{sp} expression. Solve for the volume.