Name ______________________________Chem 163 Section: ______ **Team Number:** ______

ALE 18. pH Dependent Solubility

(Reference: 19.3 Silb*erberg 5th edition*)

How can an acid be used to dissolve an "insoluble" species?

The Model: Insoluble Metal Hydroxides as Weak Bases

When placed in water, "insoluble" metal hydroxides are weak bases.

$$\mathbf{M(OH)}_{m}(s) \rightleftharpoons \mathbf{M}^{m+}(aq) + m\ \mathbf{OH}^{-}(aq)$$

The solubility product constant of the metal hydroxide determines how great the concentration of hydroxide ion (and therefore the pH) will be.

$K_{sp} = [M^{m+}][OH^{-}]^{m}$ $\qquad$ $K_w = [H^+][OH^-]$ $\qquad$ $pH = -\log[H^+]$

Exercises

1. The K_{sp} of $Ni(OH)_2$ is 2.8×10^{-16}. What is the pH of a saturated $Ni(OH)_2(aq)$ solution? (*Hint*: When you set up the law of mass action, consider what stoichiometric relationship exists between $[Ni^{2+}]_{eq}$ and $[OH^-]_{eq}$.)

2. Due to the high solubility of salts such as nickel(II) nitrate, it is very easy to make a 0.1 *M* $Ni^{2+}(aq)$ solution. However, since nickel(II) hydroxide has such a small solubility product, the solid tends to precipitate out of solution soon after the original salt is dissolved. To prevent the nickel(II) hydroxide from precipitating, one can add a couple of drops of strong acid to the $Ni^{2+}(aq)$ solution. If one wants to prepare a 0.1 *M* $Ni^{2+}(aq)$ solution and prevent the nickel(II) hydroxide from precipitating, what must the maximum pH of the solution be?

The Model: Simultaneous Equilibria

To form the nickel(II) hydroxide precipitate, we can think of the Ni^{2+} ions as abstracting OH^- ions out of what naturally is present in water. Here, we consider the process of simultaneous equilibria occurring in solution.

Equilibrium 1: $\mathbf{H_2O(\mathit{l}) \rightleftharpoons H^+ + OH^-}$ $\boldsymbol{K_1}$

Equilibrium 2: $\mathbf{Ni^{2+} + 2\ OH^- \rightleftharpoons Ni(OH)_2(\mathit{s})}$ $\boldsymbol{K_2}$

So that Equilibrium 1 produces as much hydroxide as Equilibrium 2 consumes, Equilibrium 1 is multiplied through by two.

Key Questions

3 a. Finish the law of mass action for Equilibrium 1: $\mathbf{H_2O(\mathit{l}) \rightleftharpoons H^+ + OH^-}$

$\boldsymbol{K_1} =$

b. What is the numerical value of K_1?

c. Let Equilibrium 3 be the resultant reversible chemical equation when Equilibrium 1 is multiplied through by two. Write Equilibrium 3 below.

d. Finish the law of mass action for Equilibrium 3.

$\boldsymbol{K_3} =$

e. Compare the law of mass action for Equilibrium 3 to the law of mass action for Equilibrium 1. What is the numerical value of K_3?

4 a. Finish the law of mass action for Equilibrium 2: $\mathbf{Ni^{2+} + 2\ OH^- \rightleftharpoons Ni(OH)_2(\mathit{s})}$

$\boldsymbol{K_2} =$

b. What is the numerical value of K_2? (Revisit Exercise #1.)

5 a. Let Equilibrium 4 be the algebraic sum of Equilibrium 2 and Equilibrium 3. Write Equilibrium 4.

b. Finish the law of mass action for Equilibrium 4.

$\boldsymbol{K_4} =$

c. Compare the law of mass action for Equilibrium 4 to the laws of mass action for Equilibria 2 and 3. How is K_4 related to K_2 and K_3? What is the numerical value of K_4?

6. When equilibria with constants K_I and K_{II} are algebraically added together, how is the value of the resultant reversible reaction's equilibrium constant (K_{net}) determined? *Circle your choice*.

i. $K_{net} = K_I + K_{II}$	v. $K_{net} = K_I \cdot K_{II}$
ii. $K_{net} = \sqrt{(K_I)^2 + (K_{II})^2}$	vi. $K_{net} = K_I / K_{II}$
iii. $K_{net} = \| K_I - K_{II} \|$	vii. $K_{net} = K_{II} / K_I$
iv. $K_{net} = \sqrt{K_I \cdot K_{II}}$	viii. K_{net} is either K_I or K_{II}, whichever is smallest

Exercise

7. Use Equilibrium 4 (law of mass action in Question 5b and value of K_4 in Question 5c) to determine at what pH (or lower) must a 0.1 *M* $Ni^{2+}(aq)$ solution be maintained in order to prevent the nickel(II) hydroxide from precipitating. (Compare this answer to the one you obtained in Exercise #2.)

Key Questions

8. The K_{a1} and K_{a2} of H_2S are 9.5×10^{-8} and 1×10^{-19}, respectively. What is $K_{a,total}$ for the following reversible reaction?

$$\mathbf{H_2S(\mathit{aq}) \rightleftharpoons 2\,H^+(\mathit{aq}) + S^{2-}(\mathit{aq})}$$

(*Hint*: What are the reversible reactions governed by K_{a1} and K_{a2}? And how are these reactions related to the above "net" reversible reaction? See Question 6.)

9 a. Metal sulfides are notoriously insoluble in water. Complete and balance the reversible reaction showing a metal (II) sulfide dissolving in a strong acid to yield aqueous hydrogen sulfide and metal cations.

$$MS(s) + \_\_\_\_\_\_\_\_\_\_ \rightleftharpoons H_2S(aq) + \_\_\_\_\_\_\_\_\_\_ \qquad \mathbf{(1)}$$

b. What is the K_{net} of eqn **1** (the reversible reaction in Question 9a) in terms of $K_{a,total}$ of H_2S and the K_{sp} of the metal sulfide? (*Hint*: How can you add the reversible reaction in Question 8 to the reversible dissolution of solid MS to yield eqn **1**?)

c. Which of the following could one use an acidified hydrogen sulfide solution to dissolve? *Explain*. (There may be more than one! *Hint*: Compared to a value of 1, what value must the K_{net} of eqn **1** have in order for the forward reaction to proceed more than the reverse reaction?)

Metal Sulfide	K_{sp}
HgS	6.4×10^{-53}
CuS	1.3×10^{-36}
PbS	9.0×10^{-29}

Metal Sulfide	K_{sp}
ZnS	2.9×10^{-25}
FeS	1.6×10^{-19}
MnS	4.7×10^{-14}

10. Circle the member of each pair below that has a solubility that is affected by pH and then write the appropriate equations to explain why.

a. CaF_2 vs. $CaCl_2$

b. $CuBr_2$ vs. $Ca_3(PO_4)_2$

c. AgCl vs. $Cu(OH)_2$

Exercise

11. Consider iron (II) sulfide, which has a moderate solubility in an acidified solution of hydrogen sulfide. If the concentration of H_2S is maintained at 1.0 *M*, what must the pH of the solution be reduced to in order for the solution to allow an aqueous Fe^{2+} concentration of 0.10 *M*?