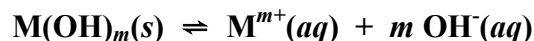


**ALE 18. pH Dependent Solubility**(Reference: 19.3 Silberberg 5<sup>th</sup> edition)

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.



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

$$K_{\text{sp}} = [\text{M}^{m+}][\text{OH}^-]^m$$

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-]$$

$$\text{pH} = -\log[\text{H}^+]$$

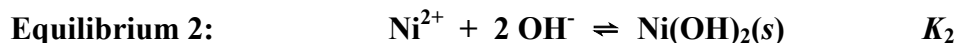
**Exercises**

1. The  $K_{\text{sp}}$  of  $\text{Ni(OH)}_2$  is  $2.8 \times 10^{-16}$ . What is the pH of a saturated  $\text{Ni(OH)}_2(\text{aq})$  solution?  
(Hint: When you set up the law of mass action, consider what stoichiometric relationship exists between  $[\text{Ni}^{2+}]_{\text{eq}}$  and  $[\text{OH}^-]_{\text{eq}}$ .)
  
2. Due to the high solubility of salts such as nickel(II) nitrate, it is very easy to make a 0.1 M  $\text{Ni}^{2+}(\text{aq})$  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  $\text{Ni}^{2+}(\text{aq})$  solution. If one wants to prepare a 0.1 M  $\text{Ni}^{2+}(\text{aq})$  solution and prevent the nickel(II) hydroxide from precipitating, what must the maximum pH of the solution be?

### The Model: Simultaneous Equilibria

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



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

#### Key Questions

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- 3 a. Finish the law of mass action for Equilibrium 1:  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^-$   
 $K_1 =$
- 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.  
 $K_3 =$
- 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:  $\text{Ni}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Ni}(\text{OH})_2(s)$   
 $K_2 =$
- 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.  
 $K_4 =$
- 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 ( $K_{\text{net}}$ ) determined? Circle your choice.
- |  |  |
|--|--|
| i. $K_{\text{net}} = K_I + K_{II}$                 | v. $K_{\text{net}} = K_I \cdot K_{II}$                                     |
| ii. $K_{\text{net}} = \sqrt{(K_I)^2 + (K_{II})^2}$ | vi. $K_{\text{net}} = K_I / K_{II}$  |
| iii. $K_{\text{net}} =  K_I - K_{II} $             | vii. $K_{\text{net}} = K_{II} / K_I$                                       |
| iv. $K_{\text{net}} = \sqrt{K_I \cdot K_{II}}$     | viii. $K_{\text{net}}$ is either $K_I$ or $K_{II}$ , whichever is smallest |

### Exercise

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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  $\text{Ni}^{2+}(\text{aq})$  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

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8. The  $K_{a1}$  and  $K_{a2}$  of  $\text{H}_2\text{S}$  are  $9.5 \times 10^{-8}$  and  $1 \times 10^{-19}$ , respectively. What is  $K_{a,\text{total}}$  for the following reversible reaction?



(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.



- b. What is the  $K_{\text{net}}$  of eqn 1 (the reversible reaction in Question 9a) in terms of  $K_{\text{a,total}}$  of  $\text{H}_2\text{S}$  and the  $K_{\text{sp}}$  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  $K_{\text{net}}$  of eqn 1 have in order for the forward reaction to proceed more than the reverse reaction?)

Metal Sulfide	$K_{\text{sp}}$
HgS	$6.4 \times 10^{-53}$
CuS	$1.3 \times 10^{-36}$
PbS	$9.0 \times 10^{-29}$

Metal Sulfide	$K_{\text{sp}}$
ZnS	$2.9 \times 10^{-25}$
FeS	$1.6 \times 10^{-19}$
MnS	$4.7 \times 10^{-14}$

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.
- $\text{CaF}_2$  vs.  $\text{CaCl}_2$
  - $\text{CuBr}_2$  vs.  $\text{Ca}_3(\text{PO}_4)_2$
  - $\text{AgCl}$  vs.  $\text{Cu}(\text{OH})_2$

### Exercise

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11. Consider iron (II) sulfide, which has a moderate solubility in an acidified solution of hydrogen sulfide. If the concentration of  $\text{H}_2\text{S}$  is maintained at  $1.0\text{ M}$ , what must the pH of the solution be reduced to in order for the solution to allow an aqueous  $\text{Fe}^{2+}$  concentration of  $0.10\text{ M}$ ?