

# Solubility Equilibria

Name: \_\_\_\_\_

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## Information: Solubility Rules

You have previously learned about soluble and insoluble compounds. Recall the following solubility rules:

Soluble Ionic Compounds		Important Exceptions
Compounds containing	$\text{NO}_3^{-1}$	None
	$\text{C}_2\text{H}_3\text{O}_2^{-1}$	None
	$\text{Cl}^{-1}$	Compounds of $\text{Ag}^{+1}$ , $\text{Hg}_2^{+2}$ , and $\text{Pb}^{+2}$
	$\text{Br}^{-1}$	Compounds of $\text{Ag}^{+1}$ , $\text{Hg}_2^{+2}$ , and $\text{Pb}^{+2}$
	$\text{I}^{-1}$	Compounds of $\text{Ag}^{+1}$ , $\text{Hg}_2^{+2}$ , and $\text{Pb}^{+2}$
	$\text{SO}_4^{-2}$	Compounds of $\text{Sr}^{+2}$ , $\text{Ba}^{+2}$ , $\text{Hg}_2^{+2}$ , and $\text{Pb}^{+2}$

Insoluble Ionic Compounds		Important Exceptions
Compounds containing	$\text{S}^{-2}$	Compounds of $\text{NH}_4^{+1}$ , Group 1 ions, and $\text{Ca}^{+2}$ , $\text{Sr}^{+2}$ , and $\text{Ba}^{+2}$
	$\text{CO}_3^{-2}$	Compounds of $\text{NH}_4^{+1}$ and Group 1 ions
	$\text{PO}_4^{-3}$	Compounds of $\text{NH}_4^{+1}$ and Group 1 ions
	$\text{OH}^{-1}$	Compounds of $\text{NH}_4^{+1}$ , Group 1 ions, and $\text{Ca}^{+2}$ , $\text{Sr}^{+2}$ , and $\text{Ba}^{+2}$

You can use the experimentally discovered “solubility rules” to verify that silver acetate is soluble, but silver chloride is insoluble. Technically, “insoluble” should be defined as “very slightly soluble” or “barely” soluble. Many compounds are soluble to a very small degree. For example,  $\text{BaSO}_4$  is “insoluble” according to the solubility rules, but a very small amount of it dissolves—0.0024 grams will dissolve in one liter of water.

## Critical Thinking Questions

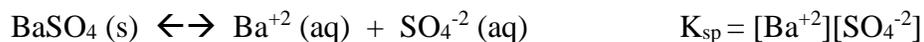
1. Which of the following compounds are “insoluble” according to the solubility rules?

- A)  $\text{Pb}(\text{NO}_3)_2$       B)  $\text{PbCl}_2$       C)  $\text{PbSO}_4$       D)  $\text{Li}_3\text{PO}_4$       E)  $\text{AgC}_2\text{H}_3\text{O}_2$

2. Let's say that the ground water is contaminated with barium ions caused by a barium chloride spill. We could add sodium sulfate to cause barium sulfate to precipitate according to the following balanced equation:  $\text{BaCl}_2 (\text{aq}) + \text{Na}_2\text{SO}_4 (\text{aq}) \rightarrow \text{BaSO}_4 (\text{s}) + 2 \text{NaCl} (\text{aq})$ . Aqueous ions are too small to filter, but a precipitate is not too small. Now, the  $\text{BaSO}_4 (\text{s})$  can be filtered out of the water. Does this procedure remove *all* of the barium ions from the water? Explain.

### Information: The Solubility Product Constant, $K_{\text{sp}}$

Let's consider a saturated solution of barium sulfate,  $\text{BaSO}_4$ . We would see a solid lump of undissolved  $\text{BaSO}_4$  in the bottom of the container. There would be  $\text{Ba}^{+2}$  and  $\text{SO}_4^{-2}$  ions in the solution. We could write an equilibrium equation and an equilibrium constant for the situation:



Pure solids and pure liquids are never included in equilibrium constants

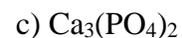
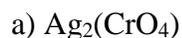
Here's another example for a saturated solution of  $\text{PbCl}_2$ :

notice



### Critical Thinking Questions

3. In the information section above two examples of solubility equilibrium equations were given along with their respective  $K_{\text{sp}}$  expressions. Write solubility equations and  $K_{\text{sp}}$  expressions for the following compounds:



4.  $\text{PbCl}_2$  dissolves very slightly in water. Its solubility is 4.5g/L. This means that in one liter 4.5 g will dissolve.

a) Calculate the *molar* solubility of  $\text{PbCl}_2$ , which is the moles dissolved per liter. (Hint: just change the 4.5g of  $\text{PbCl}_2$  to moles of  $\text{PbCl}_2$ .)

b) In part (a) you found the molar solubility of  $\text{PbCl}_2$ . Now use the molar solubility to calculate the equilibrium molarity of  $\text{Pb}^{+2}$  and of  $\text{Cl}^-$ . The following table may help:

Note: "x" is the molar solubility from part

	$\text{PbCl}_2 (\text{s}) \rightleftharpoons \text{Pb}^{+2} (\text{aq}) + 2 \text{Cl}^- (\text{aq})$
Initial:	Lots undissolved      0      0
Change:	$\rightarrow -x$ $+x$ $+2x$
Equilibrium:	Lots undissolved      _____M      _____M

c) You can now plug the equilibrium molarity values obtained in part (b) into the  $K_{\text{sp}}$  expression to find the value of  $K_{\text{sp}}$  for  $\text{PbCl}_2$ . Verify that  $K_{\text{sp}} = 1.7 \times 10^{-5}$ .

$$K_{\text{sp}} = [\text{Pb}^{+2}][\text{Cl}^-]^2 =$$

5. The solubility of  $\text{Ni}(\text{OH})_2$  is  $4.9 \times 10^{-4}$  g/L. Following similar steps to the previous question, prove that the  $K_{\text{sp}}$  for  $\text{Ni}(\text{OH})_2$  is approximately  $6 \times 10^{-16}$ .

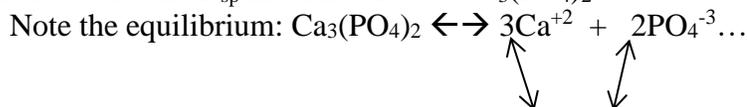
### Information: Writing $K_{\text{sp}}$ in terms of "x"

Look at question 4b and refresh your memory that "x" in the equilibrium problem is the molar solubility. In questions 4 and 5 you were given the solubility and then you calculated the molar solubility—see question 4a, for example. Sometimes we do not know what the molar solubility is. It is helpful to be able to write the  $K_{\text{sp}}$  expressions in terms of "x" and then later we can solve for x.

Recall that for  $\text{PbCl}_2$ , the  $K_{\text{sp}} = [\text{Pb}^{+2}][\text{Cl}^-]^2$ . To write  $K_{\text{sp}}$  in terms of x we can write:

$$K_{\text{sp}} = [\text{Pb}^{+2}][\text{Cl}^-]^2 \rightarrow K_{\text{sp}} = (x)(2x)^2 \rightarrow K_{\text{sp}} = (x)(4x^2) \rightarrow K_{\text{sp}} = 4x^3$$

We can also write the  $K_{\text{sp}}$  in terms of x for  $\text{Ca}_3(\text{PO}_4)_2$ :



$$K_{sp} = [Ca^{+2}]^3[PO_4^{-3}]^2 \rightarrow K_{sp} = (3x)^3(2x)^2 \rightarrow K_{sp} = (27x^3)(4x^2) \rightarrow K_{sp} = 108x^5$$

Make sure you understand the above examples before proceeding! ☺

### **Critical Thinking Questions**

6. Write  $K_{sp}$  expressions in terms of  $x$  for the following substances:
  - a) Zinc oxalate,  $ZnC_2O_4$  (note:  $C_2O_4^{2-}$  is the polyatomic ion, oxalate)
  
  - b) Chromium(III) hydroxide,  $Cr(OH)_3$
  
  - c) Manganese(IV) hydroxide,  $Mn(OH)_4$
  
7. In questions 4 and 5 you learned how to calculate the  $K_{sp}$  after being given the solubility of a substance. Now, given the  $K_{sp}$  you should be able to calculate the solubility. The  $K_{sp}$  of  $PbF_2$  is  $3.6 \times 10^{-8}$ . Find the solubility in g/L. You can follow these steps...
  - a) Write the  $K_{sp}$  expression in terms of  $x$ .
  
  - b) Substitute in the value of  $3.6 \times 10^{-8}$  for the  $K_{sp}$  and then solve for  $x$ . You should get a value for  $x$  of 0.00208 mol/L.
  
  - c) Convert your answer from part (b) into grams by multiplying it by the molar mass of  $PbF_2$  obtained from the periodic table. Check your answer: your solubility should be 0.51 g/L.
  
8. Follow the same reasoning as question 7 and calculate the molar solubility and the solubility in g/L for silver carbonate,  $Ag_2CO_3$ . The  $K_{sp}$  for  $Ag_2CO_3$  is  $8.4 \times 10^{-12}$ .

# What Affects Solubility?

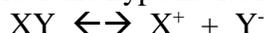
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## Information: LeChatelier's Principle Review

Recall that LeChatelier's Principle states that when an equilibrium is stressed, it will adjust to relieve the stress. For example, consider the hypothetical equilibrium:



If  $X^+$  ions are added to the above equilibrium, the equilibrium will shift to the *left* to get rid of the ions you added. If  $X^+$  ions are removed from the equilibrium, the equilibrium will shift to the *right* to produce more  $X^+$  ions to take the place of the ones that were removed.

## Critical Thinking Questions

1. Consider the equilibrium of the weak base, ammonia,  $NH_3$ :



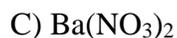
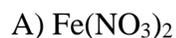
- a) If  $NH_4Cl(s)$  were added to the container of ammonia, the equilibrium would shift. Which direction would it shift?
- b) If  $NaCl$  were added to the equilibrium, the equilibrium would not shift. Why not?
2. Question 1 was basically review. Now comes some new concepts based on solubility.

- a) According to the solubility rules label each of the following as soluble or insoluble:

\_\_\_\_\_  $Ni(OH)_2$ \_\_\_\_\_  $Ni(NO_3)_2$ 

- b) If a solution of  $Ni(NO_3)_2$  were added to the ammonia equilibrium from question 1 the  $NO_3^-$  ions would have no effect. Explain.
- c) Perhaps surprisingly, the  $Ni^{+2}$  ions would affect the ammonia equilibrium. The  $Ni^{+2}$  ions would bond with the  $OH^-$  ions and create an insoluble solid,  $Ni(OH)_2$ .  $OH^-$  would be removed from the equilibrium and form a solid and sink to the bottom of the beaker. Which way will the ammonia equilibrium shift when the  $OH^-$  is removed—right or left?

3. Which of the following substances would cause a shift in the ammonia equilibrium? If the equilibrium shifts, indicate which direction it would shift. (Hint: consult the solubility rules.)



4. Calculate the molar solubility (in mol/L) of  $\text{Mn}(\text{OH})_2$  in a solution of 0.015 M  $\text{NaOH}$ . The  $K_{\text{sp}}$  for  $\text{Mn}(\text{OH})_2$  is  $1.6 \times 10^{-13}$ . The following table may be helpful:

	$\text{Mn}(\text{OH})_2 (\text{s})$	$\leftrightarrow$	$\text{Mn}^{2+} (\text{aq})$	+	$2 \text{OH}^- (\text{aq})$
Initial:	N/A		0		0.015 M
Change:	N/A		+ x		+ 2x
Equilibrium:	N/A		x		$0.015 + 2x$

Make sure you understand why the initial

Make sure you understand why

$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^-]^2 \rightarrow 1.6 \times 10^{-13} = (x)(0.015 + 2x)^2 \rightarrow$  "x" is the molar solubility; solve for x

\*\*\*note: we can assume that x will be very small—so small, that we can make our math easier!

$(0.015 + 2x)$  will be just about equal to 0.015 because  $2x$  is very tiny compared to 0.015!

Our equation becomes  $\rightarrow 1.6 \times 10^{-13} = (x)(0.015)^2$  Now solving for x is easier!

x = \_\_\_\_\_ mol/L

5. What is the molar solubility of  $\text{Cr}(\text{OH})_3$  in a 0.021 M solution of  $\text{Ba}(\text{OH})_2$ ?  $K_{\text{sp}}$  for  $\text{Cr}(\text{OH})_3$  is  $1.6 \times 10^{-30}$ .

6. The solubility of silver chromate ( $\text{Ag}_2\text{CrO}_4$ ) in water is 0.0222 g/L. What is its solubility (in g/L) in 0.012 M  $\text{AgNO}_3$ ? Hint: First calculate the  $K_{\text{sp}}$  for silver chromate as you learned in the previous ChemQuest; then do a second calculation similar to the previous question, except you will need to convert your final answer from mol/L to g/L.

### **Information: How pH Affects Solubility**

We have previously learned that some ions can affect the pH and others cannot. In the following examples, please take note of the fact that some ions readily combine with  $\text{H}^+$  and some do not:

- $\text{HCl} \rightarrow \text{Cl}^- + \text{H}^+$  The  $\text{Cl}^-$  does not affect pH because HCl is a “strong acid.” With strong acids, a reverse reaction does not happen:  $\text{Cl}^-$  never combines with  $\text{H}^+$ .
- $\text{HF} \leftrightarrow \text{F}^- + \text{H}^+$  Here we see that  $\text{F}^-$  will affect the pH because it is the conjugate base of the “weak acid,” HF. With “weak acids” a reverse reaction does occur:  $\text{F}^-$  is able to combine with  $\text{H}^+$  to form HF.

The above two examples are typical of strong and weak acids. One more equation is important to remember:

- $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$  The  $\text{OH}^-$  ion loves to combine with  $\text{H}^+$ .

Make sure you understand the chemistry behind the above reactions before moving on.

### **Critical Thinking Questions**

7. What is the difference between a “strong” and a “weak acid?”
8. We saw in question 2c that the addition of  $\text{Ni}^{+2}$  ions affects the equilibrium of  $\text{NH}_3$  because  $\text{Ni}^{+2}$  bonds with  $\text{OH}^-$  and effectively removes the  $\text{OH}^-$  from solution. The equilibrium shifts to the right because of this. Review question 2c for a moment to refresh your memory... Consider the following solubility equilibrium with the slightly soluble compound magnesium hydroxide:



- a) Adding an acid such as HCl is just like adding  $H^+$  ions. Use the reasoning in the information section to explain why adding  $H^+$  will affect the solubility of magnesium hydroxide.
- b) Is  $Mg(OH)_2$  more soluble or is it less soluble in acidic solution?
9. The solubility of AgCl is unaffected by the presence of an acid, but the solubility of AgF is affected. Explain why and also compare the solubility of AgF in pure water and in acidic solution.