ChemQuest 65

Solubility Equilibria

Name: _______________________________

Date: ________________

Hour: _____

Information: Solubility Rules

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

Soluble Ionic Compounds		**Important Exceptions**
Compounds containing	**NO_3^{-1}**	**None**
	$C_2H_3O_2^{-1}$	**None**
	Cl^{-1}	**Compounds of Ag^{+1}, Hg_2^{+2}, and Pb^{+2}**
	Br^{-1}	**Compounds of Ag^{+1}, Hg_2^{+2}, and Pb^{+2}**
	I^{-1}	**Compounds of Ag^{+1}, Hg_2^{+2}, and Pb^{+2}**
	SO_4^{-2}	**Compounds of Sr^{+2}, Ba^{+2}, Hg_2^{+2}, and Pb^{+2}**

Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	**S^{-2}**	**Compounds of NH_4^{+1}, Group 1 ions, and Ca^{+2}, Sr^{+2}, and Ba^{+2}**
	CO_3^{-2}	**Compounds of NH_4^{+1} and Group 1 ions**
	PO_4^{-3}	**Compounds of NH_4^{+1} and Group 1 ions**
	OH^{-1}	**Compounds of NH_4^{+1}, Group 1 ions, and Ca^{+2}, Sr^{+2}, and 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, $BaSO_4$ 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) $Pb(NO_3)_2$ B) $PbCl_2$ C) $PbSO_4$ D) Li_3PO_4 E) $AgC_2H_3O_2$

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: $BaCl_2$ (aq) + Na_2SO_4 (aq) → $BaSO_4$ (s) + 2 NaCl (aq). Aqueous ions are too small to filter, but a precipitate is not too small. Now, the $BaSO_4$ (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_{sp}

Let's consider a saturated solution of barium sulfate, $BaSO_4$. We would see a solid lump of undissolved $BaSO_4$ in the bottom of the container. There would be Ba^{+2} and SO_4^{-2} ions in the solution. We could write an equilibrium equation and an equilibrium constant for the situation:

$BaSO_4$ (s) ←→ Ba^{+2} (aq) + SO_4^{-2} (aq) $K_{sp} = [Ba^{+2}][SO_4^{-2}]$

Pure solids and pure liquids are never included in equilibrium constants

Here's another example for a saturated solution of $PbCl_2$:

notice

$PbCl_2$ (s) ←→ Pb^{+2} (aq) + 2 Cl^- (aq) $K_{sp} = [Pb^{+2}][Cl^-]^2$

Critical Thinking Questions

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

a) $Ag_2(CrO_4)$ b) CaF_2 c) $Ca_3(PO_4)_2$

4. $PbCl_2$ 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 $PbCl_2$, which is the moles dissolved per liter. (Hint: just change the 4.5g of $PbCl_2$ to moles of $PbCl_2$.)

   b) In part (a) you found the molar solubility of $PbCl_2$. Now use the molar solubility to calculate the equilibrium molarity of Pb^{+2} and of Cl^-. The following table may help:

Note: "x" is the molar solubility from part

	$PbCl_2$ (s) ↔	Pb^{+2} (aq) +	$2\,Cl^-$ (aq)
Initial:	Lots undissolved	0	0
Change:	-x	+x	+2x
Equilibrium:	Lots undissolved	________M	__________M

   c) You can now plug the equilibrium molarity values obtained in part (b) into the K_{sp} expression to find the value of K_{sp} for $PbCl_2$. Verify that $K_{sp} = 1.7x10^{-5}$.

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

5. The solubility of $Ni(OH)_2$ is $4.9x10^{-4}$ g/L. Following similar steps to the previous question, prove that the K_{sp} for $Ni(OH)_2$ is approximately $6x10^{-16}$.

<u>Information</u>: Writing K_{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_{sp} expressions in terms of "x" and then later we can solve for x.

Recall that for $PbCl_2$, the $K_{sp} = [Pb^{+2}][Cl^-]^2$. To write K_{sp} in terms of x we can write:

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

We can also write the K_{sp} in terms of x for $Ca_3(PO_4)_2$:

Note the equilibrium: $Ca_3(PO_4)_2 \leftrightarrow 3Ca^{+2} + 2PO_4^{-3}$…

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

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, oxylate)

   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 $3.6x10^{-8}$. 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 $3.6x10^{-8}$ 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 $8.4x10^{-12}$.

ChemQuest 67

What Affects Solubility?

Name: ______________________________
Date: ________________
Hour: _____

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:

$$XY \leftrightarrow X^+ + Y^-$$

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:

$$NH_3\ (aq) + H_2O\ (l) \leftrightarrow NH_4^+\ (aq) + OH^-\ (aq).$$

   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.)

A) $Fe(NO_3)_2$ B) $Mg(C_2H_3O_2)_2$ C) $Ba(NO_3)_2$ D) NaOH

4. Calculate the molar solubility (in mol/L) of $Mn(OH)_2$ in a solution of 0.015 M NaOH. The K_{sp} for $Mn(OH)_2$ is $1.6x10^{-13}$. The following table may be helpful:

	$Mn(OH)_2$ (s) $\leftrightarrow$	Mn^{+2} (aq) +	2 OH^- (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

$K_{sp} = [Mn^{+2}][OH^-]^2$ → $1.6x10^{-13} = (x)(0.015+2x)^2$ → "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 → $1.6x10^{-13} = (x)(0.015)^2$ Now solving for x is easier!

x = _______________ mol/L

5. What is the molar solubility of $Cr(OH)_3$ in a 0.021 M solution of $Ba(OH)_2$? K_{sp} for $Cr(OH)_3$ is $1.6x10^{-30}$.

6. The solubility of silver chromate (Ag_2CrO_4) in water is 0.0222 g/L. What is its solubility (in g/L) in 0.012 M $AgNO_3$? Hint: First calculate the K_{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.

<u>Information</u>: 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 H^+ and some do not:

- $HCl \rightarrow Cl^- + H^+$ The Cl^- does not affect pH because HCl is a "strong acid." With strong acids, a reverse reaction does not happen: Cl^- never combines with H^+.

- $HF \leftrightarrow F^- + H^+$ Here we see that F^- will affect the pH because it is the conjugate base of the "weak acid," HF. With "weak acids" a reverse reaction does occur: F^- is able to combine with H^+ to form HF.

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

- $OH^- + H^+ \rightarrow H_2O$ The OH^- ion loves to combine with H^+.

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

<u>Critical Thinking Questions</u>

7. What is the difference between a "strong" and a "weak acid?"

8. We saw in question 2c that the addition of Ni^{+2} ions affects the equilibrium of NH_3 because Ni^{+2} bonds with OH^- and effectively removes the 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:

$$Mg(OH)_2 \leftrightarrow Mg^{+2} + 2\ OH^-$$

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.