Exam Review
M, 5-6PM
BUR 106

CH 302 – Unit 3 Review 3

POLYPROTICS, INTRODUCTION TO KSP

Question

pK_{a_1} $H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$

pK_{a_2} $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

What is the dominant species of sulfurous acid (H_2SO_3) at the following pH values:

$pK_{a1} = 1.82$ $pK_{a2} = 7.00$

pH = 4 HSO_3^-

pH = 9 SO_3^{2-}

pH = 7 HSO_3^-, SO_3^{2-}

pH = 0.7 H_2SO_3

0-1.82	H_2SO_3
1.82 - 7.00	HSO_3^-
7.00 - 14	SO_3^{2-}

What is the dominant species if 35 g Na_2SO_3 is placed in 233 mL deionized water? What is the pH?

Question

Now consider a different molecule, phenolphthalein. This molecule has only one acidic proton with a $pK_a = 8.2$. When phenolphthalein is protonated, it is clear. When it is deprotonated, it is pink. What is the color at the following pH values?

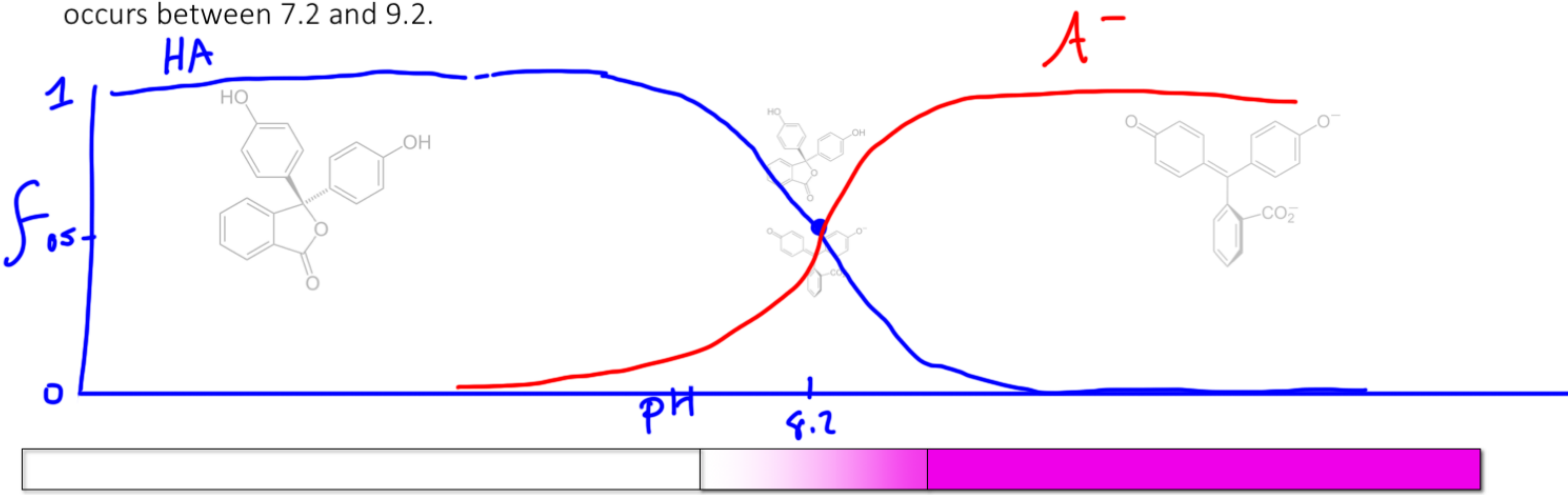
pH = 4 Clear

pH = 12 pink

pH = 8.2 pink-clear

Dominant Species: Indicators

What is the color of a phenolphthalein solution at pH 4, 12, and 8.2? The color change of phenolphthalein occurs between 7.2 and 9.2.



FYI: this is a great indicator for titration curves of weak acids, where the pH at equivalence point is around 8.2

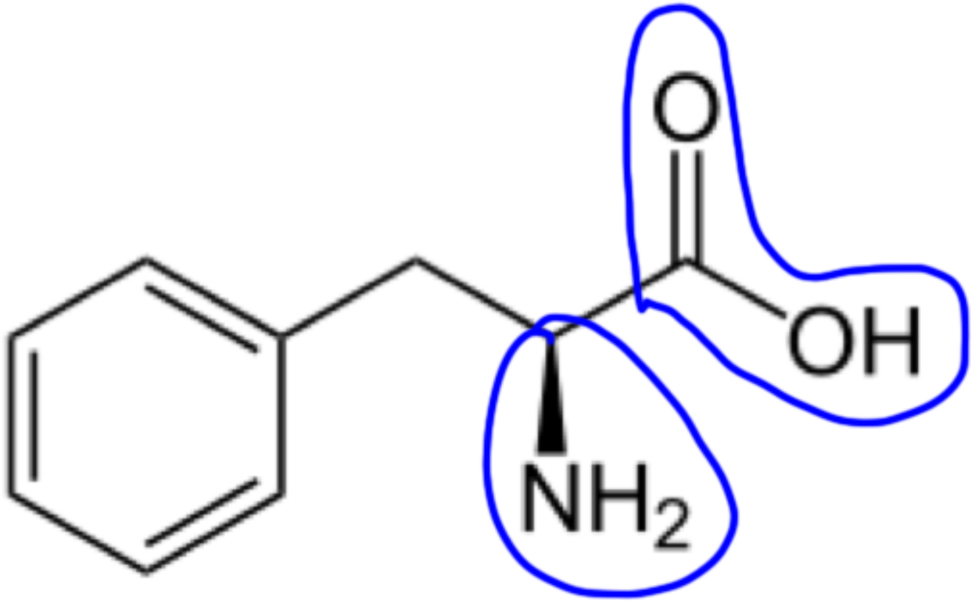
Big-ass Molecule

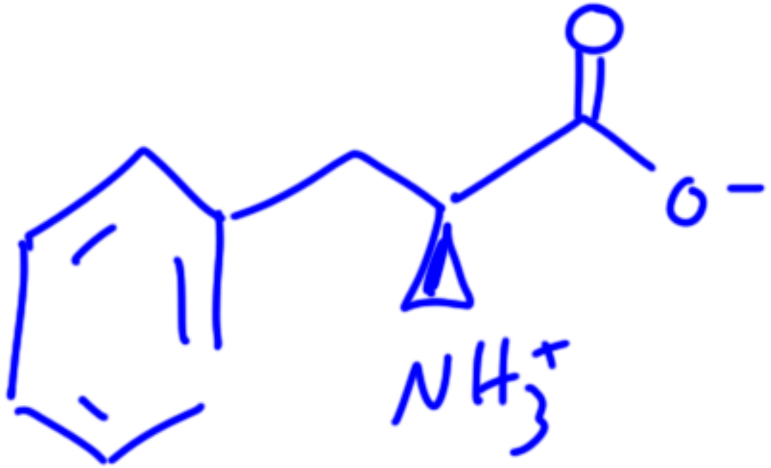
pKa1 $R-COOH \rightleftharpoons H^+ + R-COO^-$

pKa2 $R-NH_3^+ \rightleftharpoons H^+ + R-NH_2$

Consider the molecule below, which is the big-ass molecule phenylaline. This molecule has two functional groups that participate in acid/base chemistry with pKa's of 2.18 and 9.09. Draw this molecule at physiological pH (pH = 7.35)

deprotonated protonated





Solubility Equilibria, K_{sp}

K_{SP} IS A UNIQUE FORM OF EQUILIBRIUM THAT QUANTIFIES THE DISSOLUTION OF A SOLID SALT INTO ITS AQUEOUS PRODUCTS.

WE MOSTLY FOCUS ON SPARINGLY SOLUBLE SALTS

K_{sp} , Q_{sp} , and Saturation - Definitions

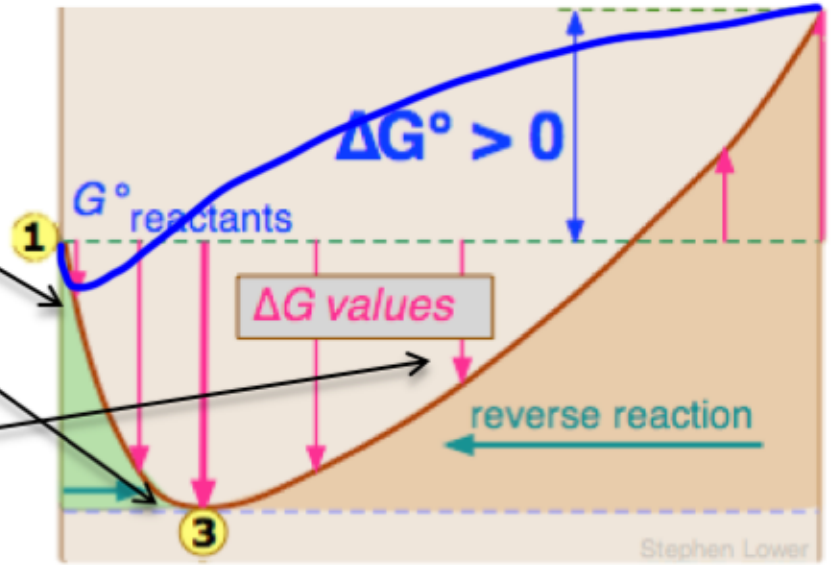
- **Solubility Product (K_{sp}):** K_{sp} is a constant that represents the product of all ion concentrations at equilibrium specific to a given salt. **This is the K of the salt dissolution reaction.**
- **Molar Solubility:** Solved from K_{sp}, molar solubility represents the maximum amount of solute that can dissolve for a reaction in terms of Molarity (M). This term is represented by the "x" in K_{sp} calculations. **This is your best measurement of the solubility of a salt.**
- **Common Ion Effect:** When an ion is already present in solution, the molar solubility of a salt containing that ion significantly decreases.
- **Reaction Quotient Solubility Product (Q_{sp}):** Q_{sp} is a variable that is calculated by the product of all ion concentrations typically **at a point away from equilibrium**. Solved in the same way as K_{sp}, Q_{sp} uses experimental values rather than equilibrium values.
- **Saturation:** when the maximum amount of ions are present in solution ($K_{sp} = Q_{sp}$)
  - Saturation is an equilibrium position where Q = K.
  - Dissolution: when $Q_{sp} < K_{sp}$ and your reaction moves forward (solid becomes ions)
  - Precipitation: when $Q_{sp} > K_{sp}$ and your reaction moves backward (ions become solid)

NOT equilibrium

Saturation: Q_{sp} vs. K_{sp}

- K_{sp} represents the ion product of a saturated solution in terms of molar solubility (x). You can think of it as a measurement of the maximum saturation capacity of a solution.
- Q_{sp} represents the ion product of the actual concentrations of ions at any given time. You can control these concentrations experimentally. **You can think of Q_{sp} like a starting point**
- Remember: K_{sp} is a fixed value ; Q_{sp} is defined by the your actual concentrations in your experiment. **Therefore, your value of Q_{sp} in relationship to K_{sp} will describe what happens:**

1. $Q_{sp} < K_{sp}$ (unsaturated) ; more solid can dissolve if added to the solution
2. $Q_{sp} = K_{sp}$ (saturated) ; your reaction is at equilibrium
3. $Q_{sp} > K_{sp}$ (over saturated) ; precipitation occurs until $Q_{sp} = K_{sp}$



K_{sp} to Molar Solubility

What is the molar solubility of Li_3PO_4? The K_{sp} of Li_3PO_4 is 3.2×10^{-9}.

R	$Li_3PO_{4(s)} \rightleftharpoons$	$3Li^+_{(aq)}$ +	$PO_{4(aq)}^{3-}$
I	a lot	0	0
C	$-x$	$+3x$	$+x$
E		$3x$	x

$$K_{sp} = [Li^+]^3[PO_4^{3-}]$$

$$K_{sp} = \underline{(3x)^3 x} = 27x^4$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$\underline{x = 3.3 \cdot 10^{-3}}M$$

K_{sp} is the "Solubility Product," which is a constant unique to a particular compound that represents the product of ion concentrations that are present at equilibrium

x represents the "Molar Solubility," which is a direct measurement of solubility. Molar solubility is the concentration of a solute that dissolves in molarity (M) for a reaction.

Solubility Equilibrium Overview

R	$A_2B_3(s)$	$\rightleftharpoons 2A^+(aq)$	$+ 3B^-(aq)$
I	a chunk	0	0
C	$-X$	$+2X$	$+3X$
E		$2X$	$3X$

ALL SALT RATIOS

1:1	$K_{sp} = x^2$
1:2	$K_{sp} = 4x^3$
1:3	$K_{sp} = 27x^4$
2:3	$K_{sp} = 108x^5$

Question

Solve for x

Cannot rely on Ksp

Rank the following molecules according to their molar solubility (lowest molar solubility to highest molar solubility)

1:1

$AlPO_4$, $K_{sp} = 9.8 \times 10^{-21}$ $= x^2$ $x = \sqrt{9.8 \times 10^{-21}} = 9.9 \times 10^{-11}$

1:3

$Ba(IO)_3$, $K_{sp} = 4.0 \times 10^{-9}$ $= 27x^4$ $x = \sqrt[4]{\frac{4.0 \times 10^{-9}}{27}} = 3.5 \times 10^{-3}$

1:1

CuCl, $K_{sp} = 1.7 \times 10^{-7}$ $= x^2$ $x = \sqrt{1.7 \times 10^{-7}} = 4.1 \times 10^{-4}$

$AlPO_4 < CuCl < Ba(10)_3$

K_{sp} Question Types

There are three main scenarios of solubility equilibria:

1. You add a chunk of a sparingly soluble salt to deionized water and calculate the molar solubility from the K_{sp} and stoichiometry (or vice versa).
    - $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3$
    - x is your molar solubility
2. You add a chunk of a sparingly soluble salt to a a solution with a common ion already in solution
    - $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(0.05M - 2x)^2 = 4x^3$
    - x is still your molar solubility, but much lower than in the previous example
3. You mix two aqueous solutions to perform a double displacement precipitation reaction
    - $Q_{sp} = [Pb^{2+}][I^-]^2$
    - If $Q > K$, a precipitate forms

K_{sp} Scenario One

1. You add a chunk of a sparingly soluble salt to deionized water and calculate the molar solubility from the K_{sp} and stoichiometry (or vice versa).

What is the molar solubility of PbI_2? The K_{sp} of $PbI_2 = 9.8 \times 10^{-9}$.

- $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3$
- x is your molar solubility

$$x = \sqrt[3]{\frac{9.8 \times 10^{-9}}{4}} = 0.0013$$

PbI_2

$$K_{sp} = \underset{x}{\underset{\downarrow}{[Pb^{2+}]}}\underset{(2x)^2}{\underset{\downarrow}{[I^-]^2}}$$

R	$PbI_{2(s)} \rightleftharpoons$	$Pb^{2+}_{(aq)}$	$+2I^-_{(aq)}$
I	chunk	0	0
C	$\boxed{-x}$	$+x$	$+2x$
E	chunk $-x$	x	$2x$

$-x \rightarrow$ molar solubility

$2x \rightarrow 0.0026$

K_{sp} Scenario Two: Common Ion Effect

2. You add a chunk of a sparingly soluble salt to a a solution with a common ion already in solution.

$NaI \rightarrow Na^+ + I^-$

100%

Consider adding PbI_2 to a 0.05 M solution of NaI. What is the molar solubility of PbI_2? The K_{sp} of PbI_2 = 9.8×10^{-9}.

- $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(0.05\ M - 2x)^2 = 4x^3$
- x is still your molar solubility, but much lower than in the previous example

R	PbI_2	$\rightleftharpoons$	Pb^{2+}	$+ 2I^-$
I	chunk		0	0.05
C	$-x$		$+x$	$+2x$
				$0.05 + 2x$

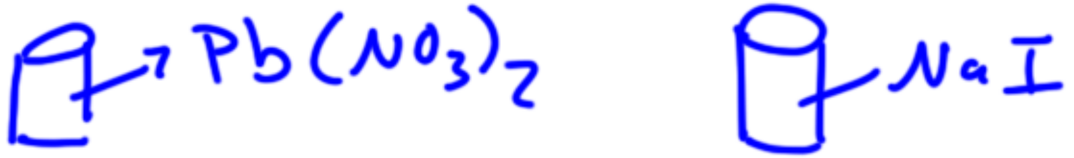
E $\quad x \quad 0.05+2x$

$$K_{sp} = (x)(0.05\cancel{+2x})^2$$

$$x = \frac{9.8\times10^{-9}}{0.05^2} = 3.9\times10^{-6}$$

K_{sp} Scenario Three: Precipitation Reaction

3. You mix two aqueous solutions to perform a double displacement precipitation reaction.



= 200mL

Consider adding 100 mL 0.03 M $Pb(NO_3)_2$ to 100 mL 0.05 NaI.

What is the value of Q_{sp}? What precipitate, if any, forms?

$Q_{sp} = [Pb^{2+}][I^-]^2$

$K_{sp} = 9.8 \times 10^{-9}$

$$Pb(\cancel{NO_3})_2(aq) + 2\cancel{Na}I(aq) \rightleftharpoons PbI_2(s) + 2\cancel{NaNO_3}(aq)$$

$$Q_{sp} = [Pb^{2+}][I^-]^2$$

given

$C_1V_1 = C_2V_2$

Soluble
1) Na^+
2) K^+

$(3)NO_3$

$[Pb^{2+}] = \frac{0.1L \times 0.03M}{0.2L} = 0.015M$

$[I^-] = \frac{0.1L \times 0.05M}{0.2L} = 0.025M$

$\boxed{PbI_2 \rightleftharpoons Pb^{2+} + 2I^-}$

$Q_{sp} = (0.015)(0.025)^2$

$= 9.4 \times 10^{-6}$

$Q > K$, PbI_2 ppt forms!

Preview Slides for Exam Review

K_{SP} WALKTHROUGHS

K_{sp} to Molar Solubility

What is the molar solubility of Li_3PO_4? The K_{sp} of Li_3PO_4 is 3.2×10^{-9}.

$$K_{sp} = [Li^{+}]^{3}[PO_4^{3-}]$$

K_{sp} is the “Solubility Product,” which is a constant unique to a particular compound that represents the product of ion concentrations that are present at equilibrium

$$K_{sp} = (3x)^{3}x = 27x^{4}$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

x represents the “Molar Solubility,” which is a direct measurement of solubility. Molar solubility is the concentration of a solute that dissolves in molarity (M) for a reaction.

$$x = 3.3 \cdot 10^{-3} M$$

K_{sp} and the common ion effect

What is the apparent molar solubility of Li_3PO_4 when added to a 0.5M solution of LiCl? The K_{sp} of Li_3PO_4 is 3.2 x 10^{-9}.

$$K_{sp} = [Li^+]^3[PO_4^{3-}]$$

$$K_{sp} = (0.5)^3 x$$

K_{sp} remains constant (because it is a constant). Therefore, you should predict that the presence of a common ion decreases the overall "apparent" molar solubility of your compound.

$$x = \frac{K_{sp}}{(0.5)^3} = \frac{K_{sp}}{.125}$$

Notice how the molar solubility here is much less than that of the last problem we solved.

$$x = 2.56 \cdot 10^{-8} M$$

K_{sp} vs. Q_{sp}

What happens when you mix 135mL 0.2M lithium nitrate and 250mL 0.1M potassium phosphate? The K_{sp} of Li_3PO_4 is 3.2 x 10^{-9}.

Here you are given "starting point" concentrations of lithium and phosphate ions. Therefore, your ion product will be Q_{sp}.

$$Q_{sp} = [Li^{+}]^{3}[PO_4^{3-}]$$

$$Q_{sp} = (0.07M)^{3}(0.065M) = 2.2 \cdot 10^{-5}$$

$$Q_{sp} > K_{sp}$$

You have oversaturated your solution. The reaction will run backwards until equilibrium is reached, **resulting in a solid Li_3PO_4 precipitate.**

K_{sp} Solubility Comparison

Which of the following salts is more soluble?

Li_3PO_4 ($K_{sp} = 3.2 \times 10^{-9}$) **or** **$Fe(OH)_2$ ($K_{sp} = 8 \times 10^{-16}$)**

K_{sp} Solubility Comparison

Which of the following salts is more soluble?

Li_3PO_4 (K_{sp} = 3.2 x 10^{-9})

$$K_{sp} = (3x)^3 x = 27x^4$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$x = 3.3 \cdot 10^{-3} M$$

or

$Fe(OH)_2$ (K_{sp} = 8 x 10^{-16})

$$K_{sp} = (x)(2x)^2 = 4x^3$$

$$\sqrt[3]{\frac{K_{sp}}{4}} = x$$

$$x = 1.2 \cdot 10^{-4} M$$