Solubility Equi ⇌ librium K_{sp}

Chapter 17
Sections 17.4−17.6

Precipitation Reactions

- Earlier in this course, we considered precipitation reactions

  ✓ zinc nitrate reacts with sodium hydroxide

    ‣ $Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_{2(ppt)} + 2NaNO_3$

  ✓ zinc ions react with hydroxide ions. (Nitrate and sodium ions would be spectator ions.)

    ‣ $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_{2(ppt)}$

  ✓ For this reaction, we worked solution stoichiometry problems and assumed all of the precipitation ions would end up on the bottom (considering any limiting reactant issues)

  ✓ The problems, you may recall looked like this….

Write the overall (molecular) and the net ionic equation for the reaction of zinc nitrate with sodium hydroxide.

- Remember from unit B these types of questions:
- 100. ml of 0.03 M zinc nitrate was combined with 100. ml of 0.04 M sodium hydroxide.
  - Which ions remain in solution after the precipitation? Order those ions from least to highest concentration.
  - Calculate the mass of precipitate on the bottom.
  - Calculate the molarity of each ion remaining in solution

100. ml of 0.03 M zinc nitrate was combined with 100. ml of 0.04 M sodium hydroxide.
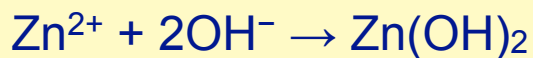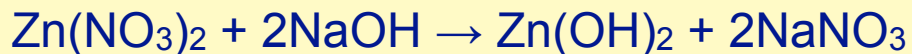
$Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$

- Which ions remain in solution after the precipitation? Order those ions from least to highest concentration. $OH^- < Zn^{2+} < Na^+ < NO_3^-$

$$0.03M \times 100ml = 3mmoleZn(NO_3)_2 \qquad 3mmoleZn^{2+}, only\ 2mmole\ Usedup$$

$$0.04M \times 100ml = 4mmoleNaOH \qquad 4mmoleOH^-\ Limits$$

$$6mmoleNO_3^-allLeftOver \qquad 4mmoleNa^+allLeftOver \qquad 1mmoleZn^{2+}leftOver$$

- Calculate the mass of precipitate on the bottom.

$$0.002moleZn(OH)_2\left(\frac{99.43g}{1mol}\right) = 0.199gZn(OH)_2\ precipitate$$

- Calculate the molarity of each ion remaining in solution. Up til now we would consider no OH^- left in solution, however.....

$$\frac{6mmole}{200ml} = 0.03MofNO_3^- \qquad \frac{4mmole}{200ml} = 0.02MofNa^+ \qquad \frac{1mmole}{200ml} = 0.005MofZn^{2+}$$

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Precipitation Reactions

- The *real truth* is that an equilibrium is set up between the undissolved precipitate and very small quantities of the ions remaining in solution.

- As we've just said, earlier in this course, we had considered precipitation reactions to be all precipitated out

  ‣ $Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_{2(ppt)}$

- but the *real story* is that an equilibrium is reached between the undissolved salts and the ions.
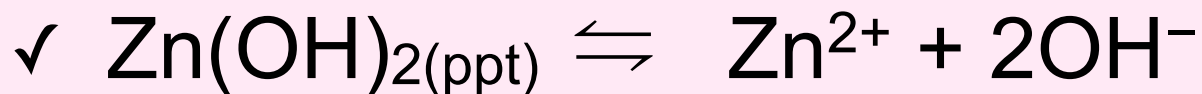
- so we can write and equilibrium expression:

$$K = \frac{1}{[Zn^{2+}][OH^-]^2}$$

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Solubility Equilibrium

- Having an equlilibrium expression that is a reciprocal is cumbersome and inconvenient

$$K = \frac{1}{[Zn^{2+}][OH^-]^2}$$

- We can rewrite the reaction for zinc hydroxide in equilibrium with zinc ions and hydroxide ions

  ✓ $Zn(OH)_{2(ppt)} \rightleftharpoons Zn^{2+} + 2OH^-$

  ✓ and for this reaction we can write the equilibrium expression:
  $$K_{sp} = [Zn^{2+}][OH^-]^2$$

- We call this the solubility-product constant

Two days ago I put 6 g of calcium hydroxide in 3.5 L of water, as you can see it's not all dissolving. $Ca(OH)_2 \rightleftharpoons Ca^{+2} + 2OH^-$

- Write a equilibrium expression for this reaction.
  - ✓ $K = [Ca^{2+}] [OH^-]^2$
- We call this K_{sp}
  - ✓ The solubility-product constant
- If you knew that in this "saturated" solution, the concentration of the dissolved calcium hydroxide is 0.0117 M, calculate the K_{sp}

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  - ✓ The solubility-product constant
- If you knew that in this "saturated" solution, the concentration of the dissolved calcium hydroxide is 0.0117 M, calculate the K_{sp}
  - ✓ $K_{sp} = [0.0117][0.0234]^2 = 6.41 \times 10^{-6}$

Vocabulary

- As long as there is some solid on the bottom, we can be sure there is an equilibrium, and the solution is *saturated*.
  - ✓ At this point, the rate of dissolution and rate of crystallization would be equal.

- Solubility (S)
  - ✓ The maximum amount of solute that dissolves in a fixed quantity of a given amount of solvent at a given temperature.
  - ✓ This will be recorded as either
    - ‣ molar solubility (mole/liter)
    - ‣ gram solubility (grams/liter, sometimes g/100 ml)

Types of Questions

Solubility

Types of Questions

- Given concentration values at equilibrium, calculate K_{sp}

- Given K_{sp}, calculate molar solubility in water

- Given K_{sp}, calculate molar solubility in a solution with some ions in it.

- Pouring two soluble solutions together, does a precipitate form?

  ✓ What is the concentration of one ion when the precipitate starts to form?

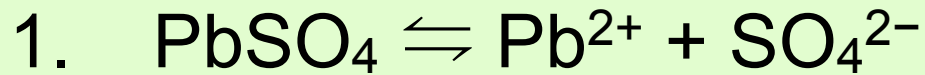Lead(II) sulfate has a solubility at 25ºC of 4.25 x 10^{-3} g/100 ml of solution.

What is the K_{sp}? (MM=303.27 g/mol)

1. write the chemical equation to describe the equilibrium rection as described by K_{sp}.
2. write the equilibrium expression

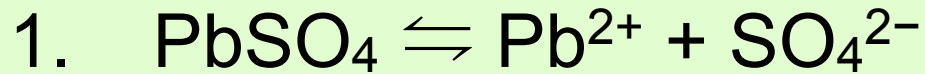Lead(II) sulfate has a solubility at 25ºC of 4.25×10^{-3} g/100 ml of solution.

What is the K_{sp}? (MM=303.27)

1. $PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

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Lead(II) sulfate has a solubility at 25°C of 4.25×10^{-3} g/100 ml of solution. What is the K_{sp}? (MM=303.27)

1. $PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$

$$4.25 \times 10^{-3} g \frac{1 mol}{303.27 g} = 1.4 \times 10^{-5} mol$$

$$\frac{1.14 \times 10^{-5} mol}{0.1L} = 1.4 \times 10^{-4} M \qquad K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

$$K_{sp} = [1.4 \times 10^{-4} M][1.4 \times 10^{-4} M]$$

$$K_{sp} = 1.96 \times 10^{-8}$$

When the maximum amount of lead(II) fluoride is dissolved in pure water at 25ºC, and equilibrium is reached, the solubility is found to be 0.64 g/L.

Calculate the K_{sp}. (MM=245.2 g/mol)

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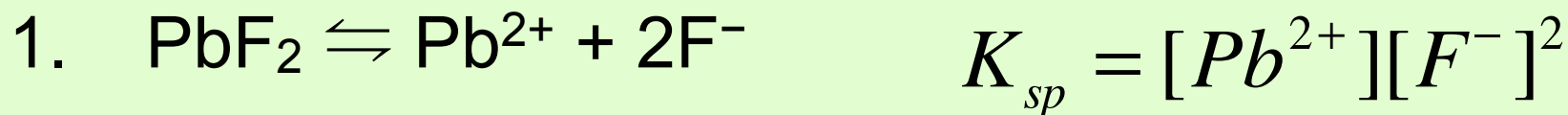
$$K_{sp} = [Pb^{2+}][F^-]^2$$

When the maximum amount of lead(II) fluoride is dissolved in pure water at 25ºC, and equilibrium is reached, the solubility is found to be 0.64 g/L.
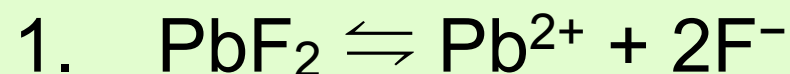
Calculate the K_{sp}. (MM=245.2 g/mol)

1. $PbF_2 \rightleftharpoons Pb^{2+} + 2F^-$

$$[PbF_2] = \left(\frac{0.64\,g}{1L} \right)\left(\frac{1mol}{245.2g} \right) = 2.61 \times 10^{-3}\,M$$

$$[F^-] = 2.61 \times 10^{-3}\,M \left(\frac{2F^-}{1PbF_2} \right) = 5.22 \times 10^{-3}\,M$$

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

$$K_{sp} = [2.61 \times 10^{-3}\,M][5.22 \times 10^{-3}\,M]^2$$

$$K_{sp} = 7.11 \times 10^{-8}$$

The K_{sp} of calcium carbonate is 4.5 × 10⁻⁹. Calculate the molar solubility *and* the gram solubility. (MM=136.15 g/mol)

The K_{sp} of calcium carbonate is 4.5 x 10^{-9}. Calculate the molar solubility *and* the gram solubility. (MM=136.15 g/mol)

R	CaCO$_3$ $\rightleftharpoons$	Ca^{2+}	+ CO$_3{}^{2-}$
I	some	0	0
C			
E			

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

The *K*$_{sp}$ of calcium carbonate is 4.5 x 10^{-9}. Calculate the molar solubility *and* the gram solubility. (MM=136.15 g/mol)

R	CaCO₃ ⇌	Ca²⁺	+ CO₃²⁻
I	some	0	0
C	– s	+ s	+ s
E	less	s	s

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

$$4.5 \times 10^{-9} = [s][s]$$

$$[s] = [Ca^{2+}] = [CO_3^{2-}] = [CaCO_3^{2-}] = 6.7 \times 10^{-5} M$$

$$6.7 \times 10^{-5} M \left(\frac{136.15g}{1mol} \right) = 9.1 \times 10^{-3} g / L$$

The K_{sp} of barium fluoride is 1.7×10^{-6}. Calculate the molar solubility *and* the gram solubility. (MM=175.3 g/mol)

The K_{sp} of barium fluoride is 1.7 x 10^{-6}. Calculate the molar solubility *and* the gram solubility. (MM=175.3 g/mol)

R	BaF$_2$ $\rightleftharpoons$	Ba^{2+}	+ F$^-$
I	some	0	0
C			
E			

$$K_{sp} = [Ba^{2+}][F^-]^2$$

The K_{sp} of barium fluoride is 1.7 x 10^{-6}. Calculate the molar solubility *and* the gram solubility. (MM=175.3 g/mol)

R	BaF$_2$ $\rightleftharpoons$	Ba^{2+}	+ F$^-$
I	some	0	0
C	$- s$	$+ s$	$+ s$
E	less	s	s

$$K_{sp} = [Ba^{2+}][F^-]^2$$

$$1.7 \times 10^{-6} = [s][2s]^2$$

$$1.7 \times 10^{-6} = 4s^3$$

$$[s] = [Ba^{2+}] = \frac{[F^-]}{2} = [BaF_2] = 7.5 \times 10^{-3} M$$

$$7.5 \times 10^{-3} M \left(\frac{175.3g}{1mol} \right) = 1.3g / L$$

And you thought water was just water.

The Water Equilibrium and

pH
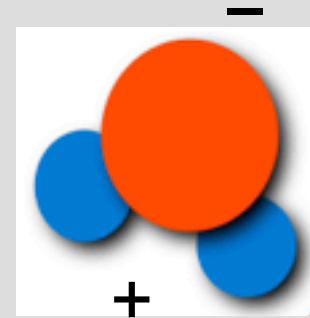
Water is a polar molecule

Although it happens to only a very slight degree, Water molecules "crash" into each other and ionize in *every* aqueous solution.
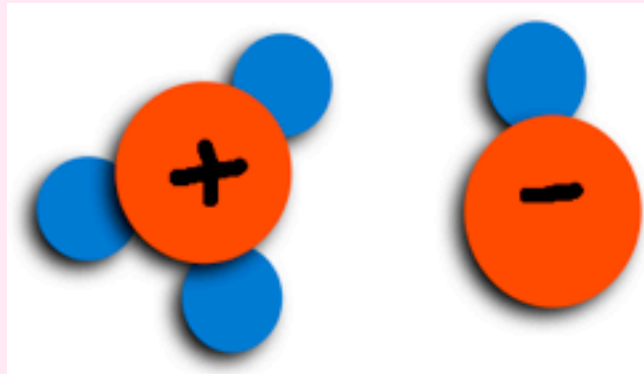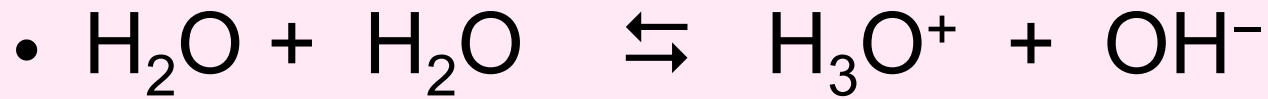
- $H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$

- Or we could pretend water just decomposes:
  - $H_2O \rightleftarrows H^+ + OH^-$ `

The formation of H⁺ and OH⁻ ions in water is always in equilibrium.

- $H_2O \rightleftharpoons H^+ + OH^-$ or $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

- Write a K_{eq} for these reactions above:

- $K_{eq} = [H^+][OH^-]$ or $[H_3O^+][OH^-]$
  - ‣ We call this equilibrium, $K_w = [H^+][OH^-]$

- The amount of *autoionization* is small.
  - ‣ How small....?   `

K_W The Ion Product

- In pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$ M (at 25ºC)

- Thus, $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ (at 25ºC)

- Does this mean that when you drink water you are drinking acid and base?

- Well, yes and no.

  ‣ In pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$ M

  ‣ Since the amounts are equal and small, the water is considered "neutral."

- Here's the punch line"

  ‣ The ion product, K_w is true not just for water, but for *any and all* aqueous solutions.   `

The pH scale

- In most aqueous solutions, $[H^+]$ and $[OH^-]$ are often small quantities, and we would be writing out such small numbers, it is convenient to convert these small numbers to base 10 logs.

- We call this pH = −log $[H^+]$ (or −log $[H_3O^+]$)

- In pure water (at 25ºC) $[H^+] = 1 \times 10^{-7}$
  - ‣ The pH of water = 7

- In an acidic solution, $[H^+]$ might = 1×10^{-4} M,
  - ‣ so pH = −log $[1 \times 10^{-4}$ M$]$ = 4   `

Other "p" scales

- Since its useful to report $[H^+]$ as a log, it can also be useful to report $[OH^-]$ as a log. We call this pOH

  ‣ pOH = −log $[OH^-]$

- So for the pH = 4 solution, $[H^+]$ = 1 x 10^{-4} M

- Since K_w = $[H^+]$ $[OH^-]$ = 1 x 10^{-14}

- For this same solution

  ‣ $[OH^-]$ = 1 x 10^{-10}, so pOH = 10

- Let's compare $[H^+]$ and $[OH^-]$ concentrations, pH and pOH of various common solutions on the next slide. `

Do you notice a relationship between pH and pOH of a solution?

	[H⁺] (M)	pH	pOH	[OH⁻] (M)
	$1\ (1\times10^{-0})$	0.0	14.0	1×10^{-14}
Gastric juice	1×10^{-1}	1.0	13.0	1×10^{-13}
Lemon juice	1×10^{-2}	2.0	12.0	1×10^{-12}
Cola, vinegar	1×10^{-3}	3.0	11.0	1×10^{-11}
Wine Tomatoes	1×10^{-4}	4.0	10.0	1×10^{-10}
Banana Black coffee	1×10^{-5}	5.0	9.0	1×10^{-9}
Rain Saliva	1×10^{-6}	6.0	8.0	1×10^{-8}
Milk Human blood, tears	1×10^{-7}	7.0	7.0	1×10^{-7}
Egg white, seawater Baking soda	1×10^{-8}	8.0	6.0	1×10^{-6}
Borax	1×10^{-9}	9.0	5.0	1×10^{-5}
Milk of magnesia	1×10^{-10}	10.0	4.0	1×10^{-4}
Lime water	1×10^{-11}	11.0	3.0	1×10^{-3}
Household ammonia Household bleach	1×10^{-12}	12.0	2.0	1×10^{-2}
NaOH, 0.1 M	1×10^{-13}	13.0	1.0	1×10^{-1}
	1×10^{-14}	14.0	0.0	$1\ (1\times10^{-0})$

More acidic

More basic

pH related to pOH

- You see that pH + pOH = 14 for a solution.

- Since $[H^+] [OH^-] = K_w = 1 \times 10^{-14}$

- remember your log rules???

  ▸ -log ([H+][OH−]) = -log K_w = -log(1 x 10^{-14})

  ▸ -log[H+] + -log[OH−] = -log K_w = -log(1 x 10^{-14})

- So, pH + pOH = pK_w = 14

- very handy !! `

The pH of a saturated zinc hydroxide solution (produced by placing zinc hydroxide in water) is 8.75

Calculate the K_{sp} of zinc hydroxide.

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$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$ $K_{sp} = [Zn^{2+}][OH^-]^2$

 s   s   2s
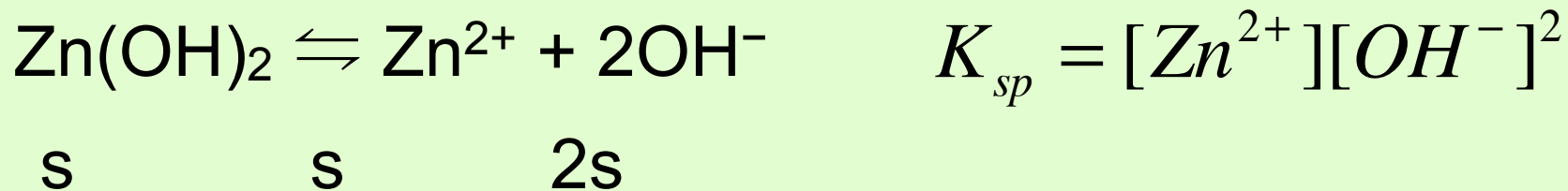
In this problem, pH is just a special way of telling us what the [OH⁻] is

The pH of a saturated zinc hydroxide solution (produced by placing zinc hydroxide in water) is 8.75

Calculate the K_{sp} of zinc hydroxide.

$$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp} = [Zn^{2+}][OH^-]^2$$

$$s \qquad\qquad s \qquad 2s$$
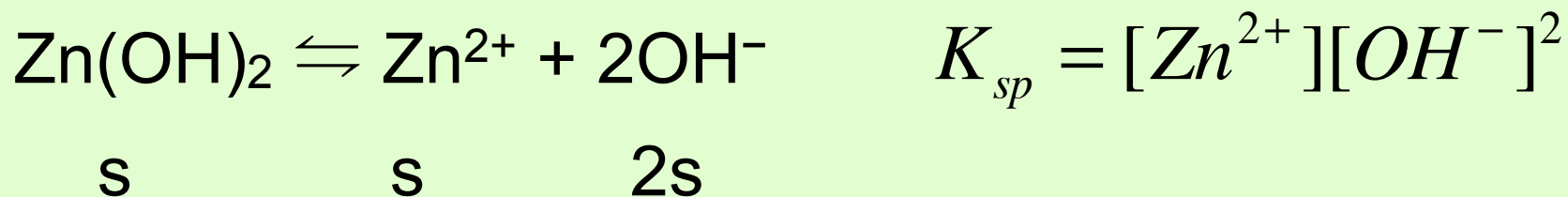
$$pH = 8.75 \qquad pOH = 5.25 \qquad pOH = -\log[OH^-] = 5.25$$

$$[OH^-] = 5.6 \times 10^{-6} \qquad [Zn^{2+}] = 2.8 \times 10^{-6}$$

$$K_{sp} = [2.8 \times 10^{-6}][5.6 \times 10^{-6}]^2 = 8.9 \times 10^{-17}$$

K_{sp} of magnesium hydroxide = 1.6x10⁻¹², calculate the molarity of each ion in 200 ml of a saturated solution, produced by adding solid magnesium hydroxide to water.

K_{sp} of magnesium hydroxide = 1.6×10^{-12}, calculate the molarity of each ion in 200 ml of a saturated solution, produced by adding solid magnesium hydroxide to water.

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

s   s   2s

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

K_{sp} of magnesium hydroxide = 1.6×10^{-12}, calculate the molarity of each ion in 200 ml of a saturated solution, produced by adding solid magnesium hydroxide to water.

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2\,OH^- \qquad K_{sp} = [Mg^{2+}][OH^-]^2$$

$$\ s \qquad\qquad\quad s \qquad\quad 2s$$
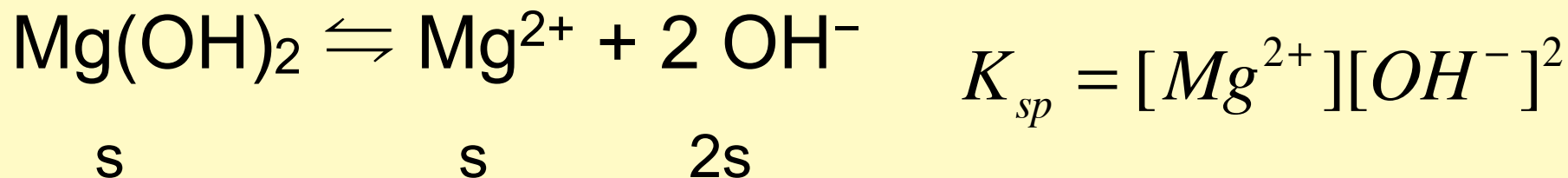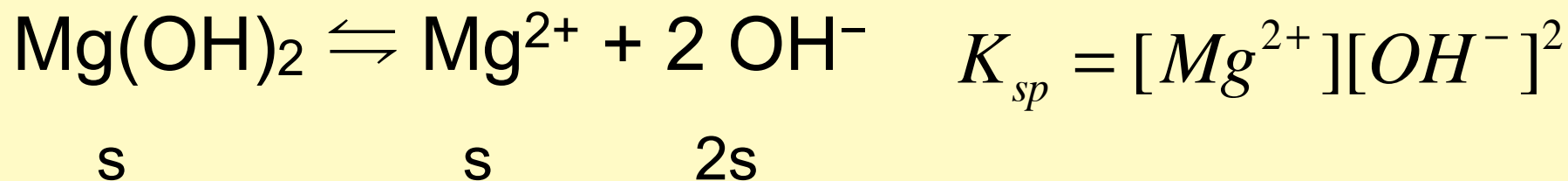
$$1.6 \times 10^{-12} = [s][2s]^2$$
$$1.6 \times 10^{-12} = 4s^3$$

$$[s] = [Mg^{2+}] = 7.4 \times 10^{-5}\,M$$
$$[OH^-] = 2 \times [Mg^{2+}] = 1.5 \times 10^{-4}\,M$$

K_{sp} of magnesium hydroxide = 1.6×10^{-12}, calculate the molarity of each ion in a saturated solution produced by adding solid magnesium hydroxide to water.

What would be the pH of 200 ml of this saturated solution?

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

$$ s \phantom{Mg^{2+}} s 2s$$

$$[OH^-] = 2 \times [Mg^{2+}] = 1.5 \times 10^{-4}\ M$$

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$$s \qquad\qquad s \qquad\qquad 2s$$

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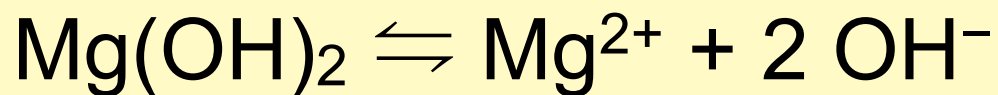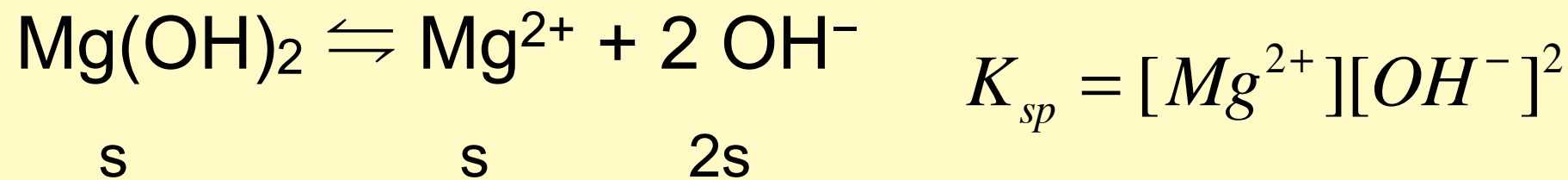
$$[OH^-] = 2 \times [Mg^{2+}] = 1.5 \times 10^{-4}\,M$$

$$[s] = [Mg^{2+}] = 7.4 \times 10^{-5}\,M$$

$$pOH = -\log[OH^-]$$

now, let's calculate the mass of magnesium hydroxide that would be dissolved in a liter of this saturated solution.

$$pOH = -\log[1.5 \times 10^{-4}\,M] = 3.82$$

$$pOH + pH = 14$$

$$pH = 10.18$$

K_{sp} of magnesium hydroxide = 1.6x10^{-12}, calculate the molarity of each ion in a saturated solution produced by adding solid magnesium hydroxide to water.
What would be the pH of 200 ml of this saturated solution?
now, let's calculate the mass of magnesium hydroxide that would be dissolved in a liter of this saturated solution.

- From the previous slide, we know the concentration of the Mg^{2+}, and we know that comes from the quantity of Mg(OH)2 that dissolves.

$$[Mg^{2+}] = Mg(OH)_2 = \frac{7.4 \times 10^{-5}\, mol}{1L} \times \frac{58.33g}{1mol} = \frac{4.32 \times 10^{-3}\, g}{1L}$$

- 0.0043 g/L
- This is the "gram solubility" of magnesium hydroxide

K_{sp} as a Measure of Solubility

Consider the K_{sp} values of the following hypothetical salts and indicate which of these is least soluble in water.

1. MN $\quad$ $K_{sp} = 1 \times 10^{-12}$
2. MN_2 $\quad$ $K_{sp} = 1 \times 10^{-16}$
3. MN_3 $\quad$ $K_{sp} = 1 \times 10^{-20}$
4. MN_4 $\quad$ $K_{sp} = 1 \times 10^{-24}$

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3. MN_3 $K_{sp} = 1 \times 10^{-20}$
4. MN_4 $K_{sp} = 1 \times 10^{-24}$

Counterintuitive to the Ksp values,
The comparative solubility of these 4 salts:
$MN < MN_2 < MN_3 < MN_4$

- Let's take a closer look….   `

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1. MN $K_{sp} = 1\times10^{-12}$
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4. MN_4 $K_{sp} = 1\times10^{-24}$

Counterintuitive to the Ksp values,
Solubility
$MN < MN_2 < MN_3 < MN_4$

- Solve for s which will tell you the molar solubility of the molecule.

- $s^2 = 1\times10^{-12}$ $((s)(s))$ $s = 1 \times 10^{-6}$

- $4s^3 = 1\times10^{-16}$ $((s)(2s)^2)$ $s = 3 \times 10^{-6}$

- $27s^4 = 1\times10^{-20}$ $((s)(3s)^3)$ $s = 4 \times 10^{-6}$

- $256s^5 = 1\times10^{-24}$ $((s)(4s)^4)$ $s = 5 \times 10^{-6}$

- Take note of the effect of the number of ions.

Using K_{sp} to compare Solubilities

- As long as you compare compounds with the same total number of ions in their formulas, K_{sp} values indicate relative solubility.
  - ✓ The higher the K_{sp}, the higher the solubility.

#ions	Formula	cation/anion	K_{sp}	Solubility (M)
2	$PbSO_4$	1/1	6.3×10^{-7}	7.9×10^{-4}
2	$MgCO_3$	1/1	3.5×10^{-8}	1.8×10^{-4}
2	$BaCrO_4$	1/1	2.1×10^{-10}	1.4×10^{-5}

Using K_{sp} to compare Solubilities

- Different number of ions, changes the game, and you can not use Ksp values as a direct measure of gram solubility.

#ions	Formula	cation/anion	K_{sp}	Solubility (M)
3	$Ca(OH)_2$	1/2	6.5×10^{-6}	1.2×10^{-2}
3	BaF_2	1/2	1.7×10^{-6}	7.5×10^{-3}
3	CaF_2	1/2	3.9×10^{-11}	2.1×10^{-4}
3	Ag_2CrO_4	2/1	1.2×10^{-12}	6.7×10^{-5}

- Why does this happen????

Using K_{sp} to compare Solubilities

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2	$MgCO_3$	1/1	3.5×10^{-8}	1.8×10^{-4}
2	$BaCrO_4$	1/1	2.1×10^{-10}	1.4×10^{-5}
3	$Ca(OH)_2$	1/2	6.5×10^{-6}	1.2×10^{-2}
3	BaF_2	1/2	1.7×10^{-6}	7.5×10^{-3}
3	CaF_2	1/2	3.9×10^{-11}	2.1×10^{-4}
3	Ag_2CrO_4	2/1	1.2×10^{-12}	6.7×10^{-5}

- So you see we must be a wee bit careful when wondering about solubility and looking at K_{sp} values.

Which compound would be more soluble in water: silver chloride or magnesium hydroxide?

1. AgCl $K_{sp} = 1.8 \times 10^{-10}$
2. $Mg(OH)_2$ $K_{sp} = 7.1 \times 10^{-12}$

Which compound would be more soluble in water: silver chloride or magnesium hydroxide?

- It turns out that even though the K_{sp} of magnesium hydroxide is smaller, $Mg(OH)_2$ is more soluble.

- AgCl K_{sp} = 1.8 x 10⁻¹⁰, $Mg(OH)_2$ K_{sp} = 7.1 x 10⁻¹²

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

$$1.8 \times 10^{-10} = [s][s]$$

$$K_{sp} = [Mg^+][OH^-]^2$$

$$7.1 \times 10^{-12} = [s][2s]^2$$

$$7.1 \times 10^{-12} = 4s^3$$

$$[s] = [Ag^+] = [Cl^-] = [AgCl] = 1.3 \times 10^{-5} M$$

$$[s] = [Mg^+] = \frac{[OH^-]}{2} = [Mg(OH)_2] = 1.2 \times 10^{-4} M$$

Making Saturated Solutions

Two Paths to Saturated Solutions

- The way that I made the saturated calcium hydroxide solution for our LAD F.2 was to put solid calcium hydroxide into water.

  ‣ This assures the calcium ions and hydroxide ions to be present in solution in the expected 1:2 ratio

  ‣ because of $Ca(OH)_{2(ppt)} \rightleftharpoons Ca^{2+} + 2OH^-$

- A second way that a saturated solution could form is by pouring two aqueous solutions together, with the potential of forming a precipitate.

  ‣ First we should consider if a precipitate forms

  ‣ Second we should realize that if a ppt does form and a solubility equilibrium exists, the ions in solution may not be present in their expected stoichiometric ratio.

If you mix 100 ml of 0.020 M sodium fluoride and 100 ml of 0.005 M barium chloride, will a precipitate form?
K_{sp} of barium fluoride = 1.7×10^{-6}

1. yes
2. no
3. I have no idea how to decide

If you mix 100 ml of 0.020 M sodium fluoride and 100 ml of 0.0050 M barium chloride, will a precipitate form?
K_{sp} of barium fluoride = 1.7×10^{-6}

$$M_c V_c = M_d V_d$$

1. yes

$$(.020 M)(100 ml) = M_d (200 ml) \quad M_d = 0.010 M$$
$$(.0050 M)(100 ml) = M_d (200 ml) \quad M_d = 0.0025 M$$

2. no

- $K_{sp} = [Ba^{2+}][F^-]^2$

- $Q = [0.0025][0.01]^2 = 2.5 \times 10^{-7} < K_{sp} \therefore$ no ppt forms

3. I have no idea how to decide

Common Ion Effect
Common Ion Problems

Consider a saturated solution of barium fluoride with excess precipitate on the bottom. How would adding a small mass of *soluble* solid sodium fluoride affect the mass of the barium fluoride precipitate? K_{sp} of barium fluoride = 1.7×10^{-6} .

$$BaF_2 \rightleftharpoons Ba^{2+} + 2 F^-$$

1. The mass of barium flouride precipitate would remain the same.

2. The mass of barium flouride precipitate would increase.

3. The mass of barium flouride precipitate would decrease.

Consider a saturated solution of barium fluoride with excess precipitate on the bottom. How would adding a small mass of *soluble* solid sodium fluoride affect the mass of the barium fluoride precipitate? K_{sp} of barium fluoride = 1.7×10^{-6} .

$$BaF_2 \rightleftharpoons Ba^{2+} + 2\ F^-$$

1.   The mass of barium flouride precipitate would remain the same.

2.   The mass of barium flouride precipitate would increase.

•   The extra fluoride ions in solution would increase the concentration of F^- which would force the equilibrium to shift left, toward more precipitate, increasing its mass, according to LeChatelier's Principle.

3.   The mass of barium flouride precipitate would decrease.

Consider a saturated solution of barium fluoride. How would adding a small mass of solid sodium fluoride affect the concentration of the barium ions?
K_{sp} of barium fluoride = 1.7x10^{-6} .

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

1. The [Ba^{2+}] would remain the same.

2. The [Ba^{2+}] would increase.

3. The [Ba^{2+}] would decrease.

Consider a saturated solution of barium fluoride. How would adding a small mass of solid sodium fluoride affect the concentration of the barium ions?

K_{sp} of barium fluoride = 1.7×10^{-6} .

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

- The extra fluoride ions in solution would increase the concentration of F^- which would force the equilibrium to shift left, the shift can only occur if F^- ions combine to make ppt.

1. The $[Ba^{2+}]$ would remain the same.

2. The $[Ba^{2+}]$ would increase.

3. The $[Ba^{2+}]$ would decrease.

Consider a saturated solution of barium fluoride. How would adding a small mass of solid sodium fluoride affect the concentration of the barium ions? K_{sp} of barium fluoride = 1.7×10^{-6} .

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

- Calculate the concentration of the barium ions present in 500 ml of a saturated solution

Consider a saturated solution of barium fluoride. How would adding a small mass of solid sodium fluoride affect the concentration of the barium ions?

K_{sp} of barium fluoride = 1.7×10^{-6} .

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

- Calculate the concentration of the barium ions present in 500 ml of a saturated solution

$$1.7 \times 10^{-6} = [s][2s]^2$$
$$1.7 \times 10^{-6} = 4s^3$$

$$[s] = [Ba^{2+}] = [BaF_2] = 7.5 \times 10^{-3} M$$

Consider a saturated solution of barium fluoride. How would adding a small mass of solid sodium fluoride affect the concentration of the barium ions? K_{sp} of barium fluoride = 1.7x10^{-6} .

$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$

- We just calculated the concentration of the fluoride ions present in 500 ml of a saturated solution

$$1.7 \times 10^{-6} = [s][2s]^2 \quad [s] = [Ba^{2+}] = [BaF_2] = 7.5 \times 10^{-3} M$$

- Now lets calculate the concentration of the fluoride ions after 15 g of sodium fluoride is added to 500 ml of a saturated solution (MM = 42 g/mol).

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Consider a saturated solution of barium fluoride. How would adding a small mass of solid barium nitrate affect the concentration of the fluoride ions? K_{sp} of barium fluoride = 1.7x10⁻⁶ .

$$BaF_2 \leftrightharpoons Ba^{2+} + 2F^-$$

- We just calculated the concentration of the fluoride ions present in 500 ml of a saturated solution

$$1.7 \times 10^{-6} = [s][2s]^2 \quad [s] = [Ba^{2+}] = [BaF_2] = 7.5 \times 10^{-3} M$$

- Now lets calculate the concentration of the fluoride ions after 15 g of sodium fluoride is added to 500 ml of a saturated solution (MM = 42 g/mol).

$$15 g \left(\frac{1 mol}{42 g} \right) = 0.36 mol \left(\frac{0.36 mol}{0.5 L} \right) = 0.71 M$$

$$1.7 \times 10^{-6} = [s][0.71]^2$$

$$x = 3.3 \times 10^{-6} M$$

- Yikes! that is quite a bit smaller, the common ion effect!

Consider a saturated solution of barium fluoride. How would adding a small mass of solid barium nitrate affect the concentration of the fluoride ions? K_{sp} of barium fluoride = 1.7×10^{-6} .

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- We just calculated the concentration of the fluoride ions present in 500 ml of a saturated solution

$$1.7 \times 10^{-6} = [s][2s]^2 \quad [s] = [Ba^{2+}] = [BaF_2] = 7.5 \times 10^{-3} M$$

- Now lets calculate the concentration of the fluoride ions after 15 g of sodium fluoride is added to 500 ml of a saturated solution (MM = 42 g/mol).

$$15g \left(\frac{1mol}{42g} \right) = 0.36 mol \quad \left(\frac{0.36 mol}{0.5L} \right) = 0.71 M$$

R	$BaF_2 \rightleftharpoons$	Ba^{2+}	+ F^-
I	some	0.0075	0.015
			0.725
C		-x	-2x
E			

$$1.7 \times 10^{-6} = [s][0.71]^2$$

$$1.7 \times 10^{-6} = [0.0075 - x][0.725 - 2x]^2$$

$$x = 3.3 \times 10^{-6} M$$

- Yikes! that is quite a bit smaller, the common ion effect!

The Common Ion Effect

- Changing the concentration of one of the ions that is participating in the solubility equilibrium, causes a change in the equilbrium concentrations.

- We will come at these problems from "both directions"

  ‣ Adding one of the common ions will decrease the quantity of the other ion to an appreciable degree, while increasing the mass of precipitate

  ‣ How much salt can dissolve (solubility) in an amount of "water" that has one of the common ions already in the "water."

The K_{sp} of calcium fluoride is 3.9×10^{-11}. Calculate its molar solubility (M) in water.

The *K*ₛₚ of calcium fluoride
is 3.9 x 10⁻¹¹. Calculate its molar
solubility (M) in water.

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$$3.9 \times 10^{-11} = [s][2s]^2$$

$$3.9 \times 10^{-11} = 4s^3$$

$$[s] = [Ca^{2+}] = \frac{[F^-]}{2} = [CaF_2] = 2.1 \times 10^{-4}\,M$$

The K_{sp} of calcium fluoride is 3.9×10^{-11}. If you dissolved calcium fluoride in a sodium fluoride solution instead of pure water,

1. the same amount of calcium fluoride would dissolve.

2. more calcium fluoride would dissolve.

3. less calcium fluoride would dissolve.

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1. the same amount of calcium fluoride would dissolve.

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3. less calcium fluoride would dissolve.

The K_{sp} of calcium fluoride is 3.9×10^{-11}. Calculate its molar solubility (M) in 0.025 M sodium fluoride solution

The K_{sp} of calcium fluoride is 3.9×10^{-11}. Calculate its molar solubility (M) in 0.025 M sodium fluoride solution

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$3.9 \times 10^{-11} = [Ca^{2+}][0.025M]^2$$

$$[Ca^{2+}] = 6.24 \times 10^{-8}$$

Thus the amount of CaF_2 that can dissolve is 6.24×10^{-8}, far less than the 2.1×10^{-4} that can dissolve in water.

Calculate the pH of saturated solution of nickel(II) hydroxide.
$K_{sp} = 6.0 \times 10^{-16}$

1. 9.03
2. 4.97
3. 8.72
4. 5.27

Calculate the pH of saturated solution of nickel(II) hydroxide. K_{sp} = 6.0 x 10⁻¹⁶

$$6.0 \times 10^{-16} = [s][2s]^2$$

$$6.0 \times 10^{-16} = 4s^3$$

$$[s] = [Ni^{2+}] = 5.3 \times 10^{-6} M$$

$$2[Ni^{2+}] = [OH^-] = 1.1 \times 10^{-5} M$$

$$pOH = -\log[OH^-] = -\log(1.1 \times 10^{-5})$$
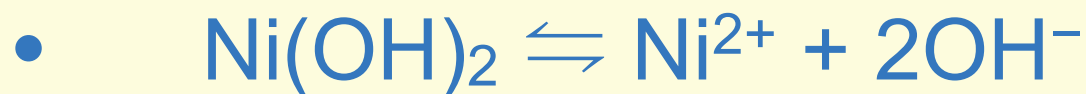
$$pOH = 4.96$$

$$pOH + pH = 14$$

$$pH = 9.04$$

1. 9.03
2. 4.97
3. 8.72
4. 5.27

- $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

In the previous problem, the K_{sp} has 2 sig figs, why does it appear as if the pH is reported with 3 sig figs?
K_{sp} = 6.0 x 10⁻¹⁶

- You see, the 1.1 is what causes the .96

- The number in front of the .96 is a result of the magnitude of the number that is being logged, not a part of its significant figures,

- Thus only the numbers after the decimal are the significant figure part of a pH (or pOH)

$$-\log(1.1\times10^{-1})=0.96$$

$$-\log(1.1\times10^{-3})=2.96$$

$$-\log(1.1\times10^{-5})=4.96$$

$$-\log(1.1\times10^{-6})=5.96$$

$$-\log(1.1\times10^{-10})=9.96$$

Calculate the molar solubility of nickel(II) hydroxide in a 0.20 M nickel(II) nitrate solution.
$K_{sp} = 6.0 \times 10^{-16}$

1. Is nickel(II) hydroxide more soluble in nickel(II) nitrate or in pure water?

2. Use LeChatelier's to explain why.

3. Calculate the molar solubility to support your answer.

Calculate the molar solubility of nickel(II) hydroxide in a 0.20 M nickel(II) nitrate solution. $K_{sp} = 6.0 \times 10^{-16}$

- This is a "common ion" problem. This means you "plug in" the concentration of the "common ion" and solve for the information requested. In this case, the solubility, s
- $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

  s   2s

$$6.0 \times 10^{-16} = [0.2][2s]^2 \qquad [s] = 2.74 \times 10^{-8} M$$

- "s" is the solubility, the amount of nickel(II) hydroxide that can dissolve

Calculate the molar solubility of nickel(II) hydroxide in a 0.20 M nickel(II) nitrate solution. $K_{sp} = 6.0 \times 10^{-16}$

- $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$
  s   2s

$$6.0 \times 10^{-16} = [0.2][2s]^2$$

1. Is nickel(II) hydroxide more soluble in nickel(II) nitrate or in pure water?

- more soluble in water than in a solution that has a "common ion" in it.
  - solubility in water $[s] = 5.3 \times 10^{-6} M$
  - solubility in the solution described above $[s] = 2.74 \times 10^{-8} M$

2. Use LeChatelier's to explain why.

- increasing the concentration of one of the ions puts "stress" on the equilbrium, and caused the reaction to shift left, decreasing the amount that can be dissolved

3. Calculate the molar solubility to support your answer.

- as calculated on previous slide, and result shown above.

Calculate the molar solubility of nickel(II) hydroxide in a solution with a pH 9.70
$K_{sp} = 6.0 \times 10^{-16}$

1. Report your answer

Calculate the molar solubility of nickel(II) hydroxide in a solution with a pH 9.70 $K_{sp} = 6.0 \times 10^{-16}$

1. This is another common ion problem.

2. So change pH to pOH, then "undo" the pOH to determine the [OH⁻], then put the value into the Ksp expression to determine the solubility.

$$pOH + pH = 14$$

$$pOH = 4.30$$

$$pOH = -\log[OH^-]$$

$$[OH^-] = 10^{-4.30} = 5.01 \times 10^{-5}$$

$$6.0 \times 10^{-16} = [s][5.01 \times 10^{-5}]^2$$

$$[s] = 2.39 \times 10^{-7} M$$

3. Do you think this is more or less soluble than in water?

Calculate the molar solubility of nickel(II) hydroxide in a solution with a pH 9.70 $K_{sp} = 6.0 \times 10^{-16}$

1. This is the concentration of Nickel(II) hydroxide that can dissolve in a solution with a pH of 9.70

$$[s] = 2.39 \times 10^{-7} M$$

2. Do you think this is more or less soluble than in water?

$$6.0 \times 10^{-16} = [s][2s]^2$$

$$[s] = 5.3 \times 10^{-6}$$

3. Less soluble, this 5.6×10^{-6} is the solubility in water.

Selective Precipitation Ion Concentration

If you poured 100 ml of 0.20 M gold(III) nitrate into 200 ml of 0.25 M sodium chloride solution, what is the concentration of each ion after equilibrium is established?

K_{sp} $AuCl_3$ = 3.2 x 10^{-25}

If you poured 100 ml of 0.20 M gold(III) nitrate into 200 ml of 0.25 M sodium chloride solution, what is the concentration of each ion after equilibrium is established? K_{sp} $AuCl_3$ = 3.2 x 10^{-25}

- With such a small Ksp, obviously a precipitate will form when these two solutions are poured together.

- $Au^{3+} + 3Cl^- \rightarrow AuCl_3$

- First it will be easiest to calculate the concentration of the spectator ions because all of them are present in the solution.

- sodium [Na$^+$]
  - 0.25M × 200ml = 50 mmoles NaCl,
  - 50 mmoles Na+ $\dfrac{50\,mmoles}{300\,mlTotalVol} = 0.17\,M$
- nitrate [NO$_3^-$]
  - 0.20 M × 100ml = 20 mmoles Au(NO$_3$)$_3$,
  - 20 mmoles NO$_3^-$, since the nitrate is "buy1 − get 3"
  - 60 mmoles NO$_3^-$, $\dfrac{60\,mmoles}{300\,mlTotalVol} = 0.20\,M$

If you poured 100 ml of 0.20 M gold(III) nitrate into 200 ml of 0.25 M sodium chloride solution, what is the concentration of each ion after equilibrium is established? K_{sp} $AuCl_3$ = 3.2 x 10^{-25}

- In Unit B, we considered problems like this.

- $Au^{3+} + 3Cl^- \rightarrow AuCl_3$

- First it will be easiest to calculate the concentration of the spectator ions because all of them are present in the solution.

- sodium [Na^+]
  - 0.25M × 200ml = 50 mmoles NaCl,
  - 50 mmoles Na+ $\dfrac{50\,mmoles}{300\,mlTotalVol} = 0.17\,M$

- nitrate [NO_3^-]
  - 0.20 M × 100ml = 20 mmoles Au(NO_3)$_3$,
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  - 60 mmoles NO_3^-, $\dfrac{60\,mmoles}{300\,mlTotalVol} = 0.20\,M$

If you poured 100 ml of 0.20 M gold(III) nitrate into 200 ml of 0.25 M sodium chloride solution, what is the concentration of each ion after equilibrium is established? K_{sp} $AuCl_3$ = 3.2 x 10^{-25}

- Like in unit B, we must determine the limiting reactant. Use the mmoles calculated on the previous slide

- $Au^{3+} + 3Cl^- \rightarrow AuCl_3$
- from the previous slide: 50 mmoles Cl^- and   20 mmoles Au^+

- Determine that the Cl^- limits the reaction. Determine the amount of excess reactant left in solution.

$$50\,mmol Cl^- \left(\frac{1 Au^{3+}}{3 Cl^-} \right) = 16.7\,mmol Au^{3+} needed \qquad \frac{3.3\,mmol}{300\,ml Total Vol} = 0.011 M Au^{3+}$$

$$20\,mmol Au^{3+} started with - 16.7\,mmol Au^{3+} needed = 3.3\,mmol Au^{3+} in Solution$$

- Back in the day we would have considered the Cl^- ion to be zero, however, we know that it cannot be zero as there must be an equilibrium quantity, no matter how small it may be, so now this has turned into a common ion problem.

$$3.2 \times 10^{-25} = [0.011][Cl^-]^3$$

- The reality is that the gold would be increased by this molarity, but it is too small and insignificant to bother adding it to 0.011 M.

$$[Cl^-] = 3.1 \times 10^{-8}$$

If you had a solution with equal concentrations of copper(I) nitrate and silver nitrate, and you slowly poured in a sodium iodide solution,
K_{sp} CuI = 1.0 x 10^{-12} K_{sp} AgI = 1.8 x 10^{-17}

1.   nothing would happen.

2.   copper iodide would start to precipitate first

3.   silver iodide would start to precipitate first

4.   both silver and copper iodide would start to precipitate at the same time.

If you had a solution with equal concentrations of copper(I) nitrate and silver nitrate, and you slowly poured in a sodium iodide solution,
K_{sp} CuI = 1.0 x 10^{-12} K_{sp} AgI = 1.8 x 10^{-17}

1. nothing would happen
2. copper(I) iodide would start to precipitate
3. silver iodide would start to precipitate

- In this problem, it is easy to say that the salt with the smaller K_{sp} precipitates first, because the salts have the same number of ions.

- Since both copper and silver ions are present at the same concentration, the salt with the lowest K_{sp} will require a smaller I$^-$ concentration inoder to achieve the minimum concentration to cause a precipitate to show.

4. both silver and copper(I) iodide would start to precipitate.

If you had a 500ml solution of 0.20 M copper(I) nitrate and 0.10 M silver nitrate, and you slowly poured in a sodium iodide solution, calculate the concentration of the I⁻ ion when the first precipitate shows up.

K_{sp} CuI = 1.0 x 10⁻¹² K_{sp} AgI = 1.8 x 10⁻¹⁷

If you had a 500ml solution of 0.20 M copper(I) nitrate and 0.10 M silver nitrate, and you slowly poured in a sodium iodide solution, calculate the concentration of the I⁻ ion when the first precipitate shows up.

K_{sp} CuI = 1.0 x 10⁻¹² $\qquad$ K_{sp} AgI = 8.3 x 10⁻¹⁷

- First treat the problem like a common ion problem and calculate the minimum I⁻ concentration required for each precipitate to show up.

$$1.0 \times 10^{-12} = [0.2][I^-]$$
$$[I^-] = 5.0 \times 10^{-12}\, M$$

$$8.3 \times 10^{-17} = [0.1][I^-]$$
$$[I^-] = 8.3 \times 10^{-16}\, M$$

- The calculation clearly supports that the AgI would precipitate first.

If you had a 500ml solution of 0.20 M copper(I) nitrate and 0.10 M silver nitrate, and you slowly poured in a sodium Iodide solution, what is the concentration of Ag^+ ions left in solution when the second precipitate starts to form.
What is the percentage of those Ag^+ ions left in solution?

K_{sp} CuI = 1.0 x 10⁻¹² K_{sp} AgI = 1.8 x 10⁻¹⁷

$$1.0 \times 10^{-12} = [0.2][I^-]$$ $$8.3 \times 10^{-17} = [0.1][I^-]$$

$$[I^-] = 5.0 \times 10^{-12} M$$ $$[I^-] = 8.3 \times 10^{-16} M$$

If you had a 500ml solution of 0.20 M copper(I) nitrate and 0.10 M silver nitrate, and you slowly poured in a sodium Iodide solution, what is the concentration of Ag^+ ions left in solution when the second precipitate starts to form.
What is the percentage of those Ag^+ ions left in solution?

K_{sp} CuI = 1.0 x 10⁻¹² K_{sp} AgI = 1.8 x 10⁻¹⁷

- In this problem, since I^- is continually poured in and precipitates with the Ag^+ as AgI, the Ag^+ concentration will continue to decrease. This allows the I^- concentration to increase as it continues to be poured in.

- On the previous slide we already calculated the concentration that the I^- must get to for the CuI to show up as a precipitate.

$$1.0 \times 10^{-12} = [0.2][I^-] \qquad [I^-] = 5.0 \times 10^{-12} M$$

- Now insert that concentration back into the AgI solubility expression to see how low the concentration must get for the I^- concentration to be 5.0 x 10⁻¹². Then calculate what percentage that very low Ag+ concentration is compared to the 0.10 M at the start.

$$1.8 \times 10^{-17} = [Ag^+][5.0 \times 10^{-12}]$$
$$[Ag^+] = 3.6 \times 10^{-6} M$$

$$\left(\frac{3.6 \times 10^{-6} M}{0.10 M} \right) \times 100 = 0.0036\%$$