

Week 2 Discussion Worksheet Answers

1) The K_{sp} for $Pb(OH)_2$ is 1.4×10^{-20} .

a) Will this salt dissolve more easily in an acidic, neutral, or basic solution? Or would it be the same in each?

Should dissolve more easily in acidic solutions since hydronium ions present will neutralize the hydroxide salt as it dissolves.

b) Calculate the solubility of lead hydroxide in pure water.

$$K_{sp} = 1.4 \times 10^{-20} = [Pb^{2+}][OH^-]^2$$

$$[OH^-] = 2[Pb^{2+}]$$

$$K_{sp} = 4[Pb^{2+}]^3 \Rightarrow \left(\frac{1.4 \times 10^{-20}}{4}\right)^{1/3} = [Pb^{2+}]$$

$$= 1.5 \times 10^{-7} M$$

$$\boxed{\text{Solubility is } 1.5 \times 10^{-7} M}$$

Note, we ignored water dissociation here, which is not exactly a good approximation, though we are not more off than 33% so its okay.

c) Calculate the solubility of lead hydroxide at $pH=12$.

$$K_{sp} = 1.4 \times 10^{-20} = [Pb^{2+}](10^{-(14-12)})^2$$

$$[Pb^{2+}] = 1.4 \times 10^{-16}$$

$$\text{Solubility of } Pb(OH)_2 \text{ at } pH \ 12 \text{ is } \boxed{1.4 \times 10^{-16} M}$$

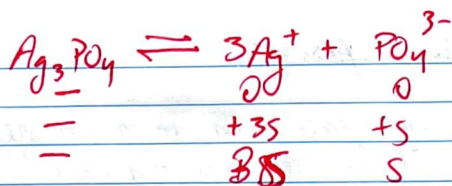
d) Was your prediction correct?

Yes. Lead hydroxide is more soluble in acidic conditions, and less soluble in basic.

2) So how 'insoluble' are ionic solids in water? Let's investigate.

a) What minimum volume of water would be needed to dissolve exactly 1.00 g of Ag_3PO_4 ? Assume negligible volume change.

$$K_{sp} \text{ of } Ag_3PO_4 \text{ is } 8.90 \times 10^{-17}.$$



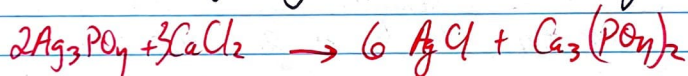
$$1.00 \text{ g Ag}_3\text{PO}_4 \times \frac{1 \text{ mol}}{418.67 \text{ g}} = 2.39 \times 10^{-3} \text{ mol Ag}_3\text{PO}_4$$

$$K_{sp} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] = (3s)^3 s = 27s^4$$

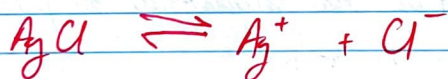
$$8.90 \times 10^{-17} = 27s^4 \quad s = 4.26 \times 10^{-5} \text{ M Ag}_3\text{PO}_4$$

$$V = \frac{n}{M} = \frac{2.39 \times 10^{-3} \text{ mol}}{4.26 \times 10^{-5} \text{ M}} = \boxed{56.1 \text{ L pure water}}$$

b) If 1.00 g CaCl_2 were added to the solution prepared in part (a) above, which solid(s) would you expect to precipitate, if any? Show all work to justify your answer.



AgCl & $\text{Ca}_3(\text{PO}_4)_2$ are both viable precipitates.



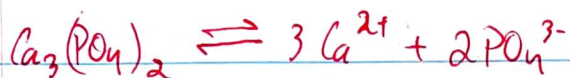
$$\text{From (a), } [\text{Ag}^+] = 3s = 1.28 \times 10^{-4} \text{ M}$$

$$1.00 \text{ g CaCl}_2 \times \frac{1 \text{ mol}}{110.98 \text{ g CaCl}_2} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol}} = 0.018 \text{ mol Cl}^-$$

$$\Rightarrow \frac{0.018 \text{ mol Cl}^-}{56.1 \text{ L}} = 3.21 \times 10^{-4} \text{ M Cl}^-$$

$$Q_{sp} = [\text{Ag}^+][\text{Cl}^-] = [1.28 \times 10^{-4}][3.21 \times 10^{-4} \text{ M}]$$

$K_{sp} < Q_{sp} \Rightarrow \text{AgCl (s)} \text{ will precipitate.}$



$$(A) \text{ above} \Rightarrow [\text{PO}_4^{3-}] = s = 4.26 \times 10^{-5} \text{ M}$$

$$[\text{Ca}^{2+}] = \frac{3}{2} [\text{PO}_4^{3-}] = 1.61 \times 10^{-4} \text{ M Ca}^{2+}$$

$K_{sp} < Q_{sp} \Rightarrow \text{Ca}_3(\text{PO}_4)_2$ will also precipitate.

3) Lets examine the conditions for precipitation to occur.

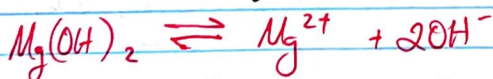
a) If a solution is prepared by mixing a soluble salt (such as $\text{Mg}(\text{NO}_3)_2$) with another soluble salt (such as NaOH), under what conditions will precipitation of the resultant slightly soluble salt (such as $\text{Mg}(\text{OH})_2$) occur? Explain.

When $Q_{sp} > K_{sp}$, the salt will precipitate. This is because K_{sp} refers to



Meaning $K_{sp} = [\text{cation}][\text{anion}]$. Hence, $Q_{sp} > K_{sp} \Rightarrow$ initial concentrations too high and they will decrease concentration via forming solids.

b) Will a precipitate form when 100.0 mL of $4.0 \times 10^{-4} \text{ M}$ $\text{Mg}(\text{NO}_3)_2$ is added to 100.0 mL of $2.0 \times 10^{-4} \text{ M}$ NaOH ? Explain. K_{sp} for $\text{Mg}(\text{OH})_2$ is 8.9×10^{-12} .



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 8.9 \times 10^{-12}$$

$$V_{\text{TOT}} = 200.0 \text{ mL} = 0.2000 \text{ L}$$

$$[\text{Mg}^{2+}]_0 = \frac{100.0 \text{ mL}}{1} \cdot \frac{1 \text{ L}}{1000 \text{ mL}} \cdot \frac{4.0 \times 10^{-4} \text{ mol}}{\text{L}} \times \frac{1}{0.2000 \text{ L}} = \boxed{2.0 \times 10^{-4} \text{ M Mg}^{2+}}$$

$$[\text{OH}^-]: M_1 V_1 = M_2 V_2 \Rightarrow (2 \times 10^{-4} \text{ M})(100.0 \text{ mL}) = [\text{OH}^-]_0 (200 \text{ mL})$$

$$\Rightarrow [\text{OH}^-]_0 = 1.0 \times 10^{-4} \text{ M OH}^-$$

$$Q_0 = [\text{Mg}^{2+}]_0 [\text{OH}^-]_0^2 = (2.0 \times 10^{-4}) (1.0 \times 10^{-4})^2 = 2 \times 10^{-12} < K_{sp}$$

No precipitation will occur.

- c) Determine an inequality describing concentrations for which magnesium hydroxide will precipitate when 100.0 mL of x M $\text{Mg}(\text{NO}_3)_2$ is mixed with 100.0 mL of y M NaOH .

$$[\text{Mg}^{2+}]_0 = \left(\frac{100.0 \text{ mL}}{200.0 \text{ mL}} \right) x = \frac{1}{2} x$$

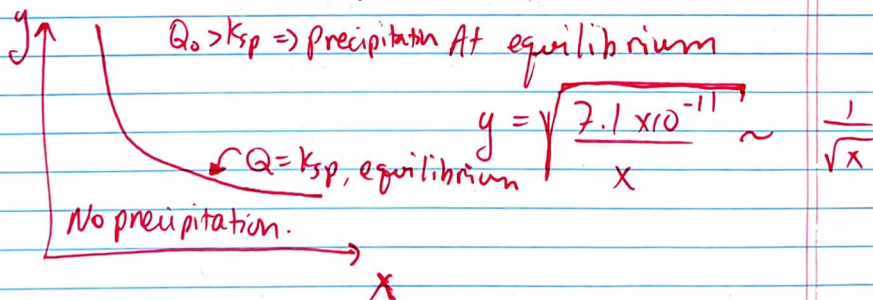
$$[\text{OH}^-]_0 = \frac{1}{2} y \quad Q_0 = [\text{Mg}^{2+}]_0 [\text{OH}^-]_0^2 = \left(\frac{1}{2} x \right) \left(\frac{1}{2} y \right)^2 = \frac{1}{8} x y^2$$

$$Q_0 > K_{sp} \Rightarrow \text{precipitation.}$$

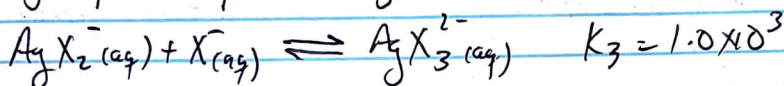
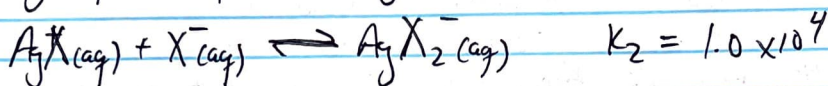
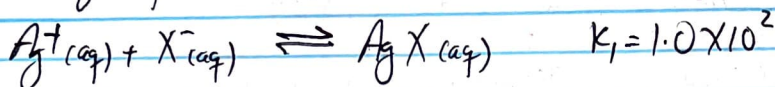
$$\frac{1}{8} x y^2 > K_{sp} \Rightarrow \frac{x y^2}{K_{sp}} > 8$$

$$\text{or } \boxed{x y^2 > 7.1 \times 10^{-11}}$$

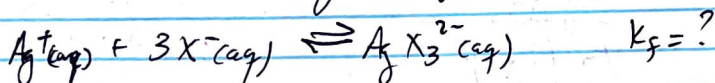
- d) Draw a diagram of y versus x , labeling regions for which ~~precipitation~~ ~~hydroxide~~ precipitation will occur, not occur, and equilibrium.



- 4) A solution is formed by mixing 25.0 mL of 20.0 M NaX with 25.0 mL of 4.0×10^{-3} M AgNO_3 and 50.0 mL of water, where Ag^+ forms complex ions with X^- :



with the overall reaction given by



- a) Write equations for K_1 , K_2 , K_3 , and K_f in terms of $[\text{Ag}^+]$, $[\text{AgX}]$, $[\text{AgX}_2^-]$, $[\text{AgX}_3^{2-}]$, and $[\text{X}^-]$.

$$K_1 = \frac{[\text{AgX}]}{[\text{Ag}^+][\text{X}^-]} \quad K_2 = \frac{[\text{AgX}_2^-]}{[\text{AgX}][\text{X}^-]} \quad K_3 = \frac{[\text{AgX}_3^{2-}]}{[\text{AgX}_2^-][\text{X}^-]}$$

$$K_f = \frac{[\text{AgX}_3^{2-}]}{[\text{Ag}^+][\text{X}^-]^3}$$

- b) How is K_f related to K_1 , K_2 , and K_3 ? What is the value of K_f ?

$$K_f = K_1 K_2 K_3 = 1.0 \times 10^9$$

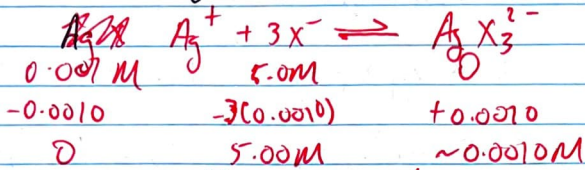
- c) What are the initial concentrations of X^- and Ag^+ ?

$$V_{\text{TOT}} = 100 \text{ mL} = 0.1000 \text{ L}$$

$$[\text{Ag}^+]_0 = 25.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{4.0 \times 10^{-3} \text{ mol}}{\text{L}} \times \frac{1}{0.1000 \text{ L}} = 1.0 \times 10^{-4} \text{ M Ag}^+$$

$$[\text{X}^-]_0 = 25.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{20.0 \text{ mol NaX}}{1 \text{ L}} \times \frac{1}{0.1000 \text{ L}} = 5.00 \text{ M X}^-$$

d) Calculate the following concentrations at equilibrium.
 AgX_3^{2-} , Ag^+ , AgX_2^-



(Assuming reaction goes to completion since K_f large.)

$$[\text{AgX}_3^{2-}] = 0.0010 \text{ M}$$

$$K_f = \frac{[\text{AgX}_3^{2-}]}{[\text{Ag}^+][\text{X}^-]^3} \Rightarrow 1.0 \times 10^7 = \frac{(0.0010)}{(5.00)^3 [\text{Ag}^+]} \Rightarrow [\text{Ag}^+] = 8.0 \times 10^{-15} \text{ M}$$

$$K_3 = \frac{[\text{AgX}_3^{2-}]}{[\text{AgX}_2^-][\text{X}^-]} \Rightarrow 1.0 \times 10^3 = \frac{(0.0010)}{[\text{AgX}_2^-] 5.00}$$

$$\Rightarrow [\text{AgX}_2^-] = 2.0 \times 10^{-7} \text{ M}$$