

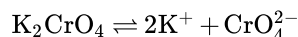
## 16.E: Solubility and Precipitation (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed [here](#).

### Q5

State the balanced equation representing the dissolution of potassium chromate and write its solubility product expression.

**Answer**

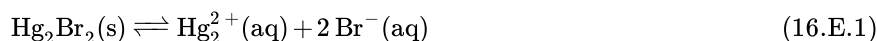


$$K_{sp} = [\text{K}^+]^2[\text{CrO}_4^{2-}]$$

### Q11

Consider Mercury(I) bromide. Estimate the concentration of  $\text{Hg}_2^{2+}$  and  $\text{Br}^-$  given the  $K_{sp}$  as  $5.6 \times 10^{-23}$ .

**Answer**



$$K_{sp} = 5.6 \cdot 10^{-23} = [\text{Hg}_2^{2+}][\text{Br}^-]^2 = x(2x)^2 \quad (16.\text{E}.2)$$

$$x = 2.41 \times 10^{-8} = [\text{Hg}_2^{2+}]$$

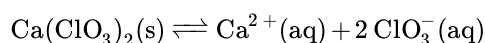
$$[\text{Br}^-] = 4.82 \times 10^{-8}$$

### Q13

The solubility product constant of Calcium chlorate ( $\text{Ca}(\text{ClO}_3)_2$ ) of water is  $7.1 \times 10^{-7}$  at  $25^\circ\text{C}$ . How many grams of  $\text{Ca}(\text{ClO}_3)_2$  were dissolved in 750 mL?

**Answer**

First, write out the solubility product constant expression for  $\text{Ca}(\text{ClO}_3)_2$



$$K_{sp} = [\text{Ca}^{2+}][\text{ClO}_3^-]^2$$

ICE Table	$\text{Ca}(\text{ClO}_3)_2$	$\text{Ca}^{2+}$	$\text{ClO}_3^-$
Initial	-	0	0
Change	-	+x	+2x
Equilibrium	-	x	2x

$\text{Ca}(\text{ClO}_3)_2$  does not matter because it is a solid

$$K_{sp} = [x] \cdot [2x]^2$$

$$7.1 \times 10^{-7} = 4x^3$$

$$x = 0.0056 \text{ M}$$

The number of moles of  $\text{Ca}^{2+}$  is the same as the number of moles of  $\text{Ca}(\text{ClO}_3)_2$  because matter cannot be created or destroyed.

$$\frac{0.0056 \text{ moles}}{\text{L}} \times 0.750 \text{ L} = 0.0042 \text{ moles } \text{Ca}(\text{ClO}_3)_2$$

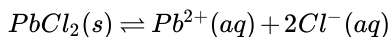
Finally, the mass can be calculated by multiplying the number of moles with the molar mass:

$$0.0042 \text{ moles Ca}(\text{ClO}_3)_2 \times \left( \frac{206.98 \text{ g}}{1 \text{ mole}} \right) = 0.872 \text{ g}$$

### Q15

At 25°C, water dissolves 0.8108 g of  $\text{PbCl}_2$  per liter, calculate the  $K_{sp}$  of  $\text{PbCl}_2$  at 25°C.

**Answer**



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

$$n(\text{PbCl}_2) = \frac{0.8108 \text{ g}}{278.1 \text{ g/mol}} = 2.9155 \times 10^{-3} \text{ mol} = n(\text{Pb}^{2+}) = 0.5n(\text{Cl}^-)$$

$$K_{sp} = \frac{2.9155 \times 10^{-3} \text{ mol}}{1 \text{ L}} \cdot \left( \frac{5.831 \times 10^{-3} \text{ mol}}{1 \text{ L}} \right)^2 = 9.91 \times 10^{-8}$$

### Q17

0.986635 g of  $\text{BaCO}_3$  is dissolved in 1.00 dm<sup>3</sup> water at 80°C. the solution was then cooled down to 25°C. Given that the  $K_{sp}$  of  $\text{BaCO}_3$  in water is  $2.58 \times 10^{-9}$  at 25°C, determine with an explanation whether or not a precipitate will form at 25°C.

**Answer**

x moles of  $\text{BaCO}_3$  dissolves into x moles of  $\text{Ba}^{2+}$  and x moles  $\text{CO}_3^{2-}$  due to equal stoichiometric coefficients (since solution is 1.00L, the moles also equal to molarities). Calculate the moles of  $\text{BaCO}_3$ , then square the result to find  $Q_{sp}$ , then compare  $Q_{sp}$  to  $K_{sp}$  at 25°C.

$$\text{moles of BaCO}_3 = 0.986635 \text{ g} \times \left( \frac{137.327 \text{ g}}{\text{mol}} + 12 \frac{\text{g}}{\text{mol}} + 3 \times 16 \frac{\text{g}}{\text{mol}} \right) = 5.0 \times 10^{-3} \text{ mol}$$

$$Q_{sp} = (5.0 \times 10^{-3} \text{ M})^2 = 2.5 \times 10^{-5}$$

$$2.5 \times 10^{-5} > 2.58 \times 10^{-9}$$

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

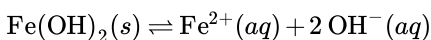
Therefore, precipitate forms.

### Q19

Suppose that you take a solution of 500.0-mL of 0.001234 M  $\text{FeF}_2$  and mix it well with a 500.0-mL solution of 0.003142 M  $\text{KOH}$  at 25°C. Given that  $K_{sp} = 4.87 \times 10^{-17}$  is for  $\text{Fe}(\text{OH})_2$ , determine whether or not a precipitate will be formed from the mixture.

**Answer**

Before starting any calculations it is important to write down the equation for precipitation of the  $\text{Fe}(\text{OH})_2$ .



State the solubility product expression and set it equal to the solubility product constant:

$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 4.87 \times 10^{-17}$$

Now that the essential basic steps are out of the way, find the new concentrations of both  $\text{Fe}^{2+}$  and  $\text{OH}^-$  by first finding the number of moles in the original unmixed solutions and then dividing that number by the total new volume in liters.

$$\text{moles Fe}^{2+} = 500 \cancel{\text{ mL}} \left( \frac{1 \cancel{\text{ L}}}{1000 \cancel{\text{ mL}}} \right) \left( \frac{0.001234 \text{ mol}}{1 \cancel{\text{ L}}} \right) = 6.17 \times 10^{-4} \text{ mol Fe}^{2+}$$

$$[Fe^{2+}] = \left( \frac{6.17 \times 10^{-4} \text{ mol } Fe^{2+}}{1000 \cancel{mL}} \right) \left( \frac{1000 \cancel{mL}}{1 \text{ L}} \right) = 6.17 \times 10^{-4} \text{ M } Fe^{2+}$$

$$\text{moles OH}^- = 500 \cancel{mL} \left( \frac{1 \cancel{L}}{1000 \cancel{mL}} \right) \left( \frac{0.003142 \text{ mol}}{1 \cancel{L}} \right) = 1.57 \times 10^{-3} \text{ mol OH}^-$$

$$[OH^-] = \left( \frac{1.57 \times 10^{-3} \text{ mol OH}^-}{1000 \cancel{mL}} \right) \left( \frac{1000 \cancel{mL}}{1 \text{ L}} \right) = 1.57 \times 10^{-3} \text{ M OH}^-$$

Now that the new concentrations have been found they can be substituted in the  $Q_{sp}$  equation and solved for.

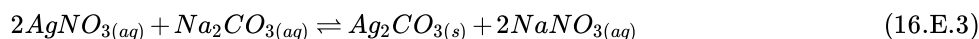
$$Q_{sp} = [6.17 \times 10^{-4}][1.57 \times 10^{-3}]^2 = 1.52 \times 10^{-9}$$

As shown above the  $Q_{sp} > K_{sp}$ , therefore a precipitate does in fact form.

### Q23

The solubility product constant of  $Ag_2CO_3$  is  $8.1 \times 10^{-12}$  at  $25^\circ\text{C}$ . Calculate  $[Ag^+]$  and  $[CO_3^{2-}]$  in the solution at equilibrium when 6 mL of 0.1M  $Na_2CO_3$  are mixed with 3 mL of 0.5M  $AgNO_3$ .

**Answer**



$$mole_{AgNO_3} = mole_{Ag^+} = (0.003 \text{ L})(0.5 \text{ M}) = 1.5 \times 10^{-3} \text{ mol} \quad (16.E.4)$$

$$mole_{Na_2CO_3} = mole_{CO_3^{2-}} = (0.006 \text{ L})(0.1 \text{ M}) = 6 \times 10^{-4} \text{ mol} \quad (16.E.5)$$

$$\text{Total Volume} = 3 \text{ mL} + 6 \text{ mL} = 9 \text{ mL} = 0.009 \text{ L} \quad (16.E.6)$$

$$M_{CO_3^{2-}} = \frac{6 \times 10^{-4} \text{ mol}}{0.009 \text{ L}} = 0.0667 \text{ M} \quad (16.E.7)$$

$$M_{Ag^+} = \frac{1.5 \times 10^{-3} \text{ mol}}{0.009 \text{ L}} = 0.1667 \text{ M} \quad (16.E.8)$$



	$2 Ag^+$	$CO_3^{2-}$	$Ag_2CO_3$
Initial	0.1667M	0.0667M	X
Change	-2x	-x	X
Equilibrium	0.1667-2x	0.0667-x	X

$$K_{sp} = 8.1 \times 10^{-12} = [CO_3^{2-}][Ag^+]^2 \quad (16.E.10)$$

$$8.1 \times 10^{-12} = [0.0667 - x][0.1667 - 2x]^2 \quad (16.E.11)$$

$$x = 0.06669999 \text{ M} \quad (16.E.12)$$

$$[Ag^+] = 0.1667 - 2x = 0.03336 \text{ M} \quad (16.E.13)$$

$$[CO_3^{2-}] = 0.0667 - x = 7.30 \times 10^{-9} \quad (16.E.14)$$

### Q25

Your nemesis has prepared a perfectly saturated solution of  $CaF_2$ . To sabotage their work, you add 10 M NaF to their solution. How many grams of  $CaF_2$  fall out of solution if they had prepared 500 mL.

$$CaF_2 : K_{sp} = 4.0 \times 10^{-11}$$

## Answer

First, calculate the molar solubility of  $\text{CaF}_2$  from its  $K_{sp}$  with the expression:

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

$$4.0 \times 10^{-11} = 4s^3$$

$$s = 2.15 \times 10^{-4}$$

Then, create an ICE table for the addition of  $\text{F}^-$  as  $\text{NaF}$ :

Products	$\text{F}^-$	$\text{Ca}^{2+}$
Initial	$s+10$	$s$
Change	$-2x$	$-x$
Equilibrium	$(s+10) - 2x$	$s-x$

Now, it's reasonable to assume that  $10 \gg x$  and  $s$ , so our expression simplifies to:

$$K_{sp} = 10^2(s-x)$$

Solving for  $x$  yields the moles/L which fall out, so multiplying  $x$  by 0.5 L (500 mL) yields the correct answer.

$$K_{sp} = 4.0 \times 10^{-11} = 10^2(s-x)$$

$$x = 0.000215 \text{ M}$$

$$0.5 \text{ L}(0.000215 \text{ M})(78.07 \frac{\text{g}}{\text{mol}}) = 0.00839 \text{ g}$$

## Q27

Given copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$ . The concentration of  $\text{Cu}^{2+}$  and  $\text{OH}^-$  at equilibrium in 25°C water is  $1.765 \times 10^{-7} \text{ M}$  and  $3.530 \times 10^{-7} \text{ M}$  respectively.

- Find the  $K_{sp}$ .
- Find the molar solubility of  $\text{Cu}(\text{OH})_2$  in 0.100M  $\text{NaOH}$ .

## Answer



1)

Since the solubilities given are already at equilibrium,  $K_{sp}$  is found as such:

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (1.765 \times 10^{-7} \text{ M})(3.530 \times 10^{-7} \text{ M})^2 = 2.2 \times 10^{-20} \quad (16.E.16)$$

2)

ICE Table	$\text{Cu}(\text{OH})_{2(s)}$	$\text{Cu}_{(aq)}^{2+}$	$\text{OH}_{(aq)}^-$
Initial	-	0	0.100
Change	-	+Z	+2Z
Equilibrium	-	Z	0.100+2Z

Apply the ice table result to the  $K_{sp}$  found in 1), we get

$$K_{sp} = 2.2 \times 10^{-20} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (z)(0.100 + 2z)^2 \quad (16.E.17)$$

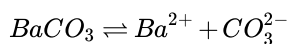
Z can be found either by plugging in quadratic formula or finding intersection in a graphing calculator.

$$K_{sp} = 2.2 \times 10^{-20} = (z)(0.100 + 2z)^2 \quad (16.E.18)$$

$$z = 2.2 \times 10^{-18} \text{ M}$$

## Q28

Barium Carbonate ( $\text{BaCO}_3$ ) has a solubility product of  $K_{sp} = 8.1 \times 10^{-9}$  at  $25^\circ\text{C}$  for the equilibrium



- Calculate the molar solubility of Barium Carbonate in the water at  $25^\circ\text{C}$ .
- Calculate the molar solubility of Barium Carbonate in  $0.1\text{M PbCO}_3$ .

## Answer

- The expression for solubility product is

$$[\text{Ba}^{2+}][\text{CO}_3^{2-}] = K_{sp} \quad (16.E.19)$$

Let

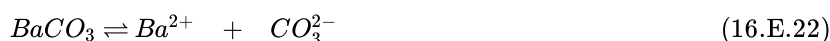
$$[\text{Ba}^{2+}] = S \quad (16.E.20)$$

$$S^2 = K_p = 8.1 \times 10^{-9} \quad (16.E.21)$$

Hence,  $S = 9 \times 10^{-5}$

Molar Solubility of Barium Carbonate =  $9 \times 10^{-5} \text{ M}$

- due to the common ion effect,  $\text{PbCO}_3$  reduces the molar solubility of Barium Carbonate.



	$\text{Ba}^{2+}$	$\text{CO}_3^{2-}$
Initial	0	0.1
Change	+S	+S
Final	+S	0.1+S

$$[\text{Ba}^{2+}][\text{CO}_3^{2-}] = K_{sp} \quad (16.E.23)$$

$$S(0.1 + S) = K_{sp} \quad (16.E.24)$$

$$S + 0.1 \approx 0.1 \quad (16.E.25)$$

$\Rightarrow$

$$S(0.1) = K_{sp} \quad (16.E.26)$$

$\Rightarrow$

$$S = \frac{8.1 \times 10^{-9}}{0.1} = 8.1 \times 10^{-8} \quad (16.E.27)$$

$\Rightarrow$

$$S = 8.1 \times 10^{-8} \ll 0.1 \quad (16.E.28)$$

Hence, Molar Solubility =  $8.1 \times 10^{-8} \text{ M}$

## Q33

Determine how will the solubility of the following compounds change (increase, decrease, or unchanged) if the neutral solution is made to be more acidic. Explain your answer in one sentence.

- a.  $\text{NO}_3^-$
- b.  $\text{NH}_3$
- c.  $\text{CO}_3^{2-}$

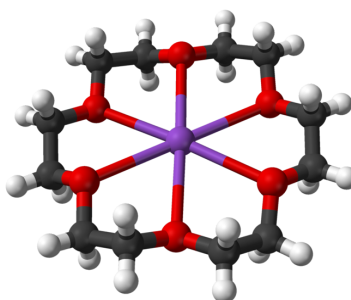
### Answer

As the acidity of a solution increases, the solubility of salts consist of conjugate bases of weak acids will increases.

- a.  $\text{NO}_3^-$  is the conjugate base of a strong acid so the solubility will not change
- b.  $\text{NH}_3$  is the conjugate base of a weak acid so the solubility will increase
- c.  $\text{CO}_3^{2-}$  is also a conjugate base of a weak acid so the solubility will increase

### Q37

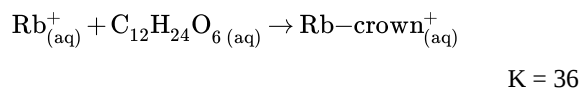
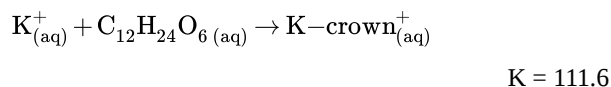
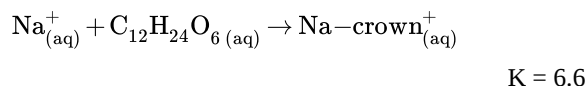
18-crown-6, or  $\text{C}_{12}\text{H}_{24}\text{O}_6$ , is an organic compound that can bind to group 1 metal ions by wrapping around them when in aqueous solutions. Due to its particular size, it can fit the  $\text{K}^+$  ion better than any other.



Ball-and-stick model of the 18-crown-6 potassium complex in crystalline (18-crown-6)potassium chlorochromate,  $[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)] [\text{CrClO}_3]$ . X-ray diffraction data from S. A. Kotlyar, R. I. Zubatyuk, O. V. Shishkin, G. N. Chuprin, A. V. Kiriya and G. L. Kamalov (February 2005). "(18-Crown-6)potassium chlorochromate". *Acta. Cryst.* **E61** (2): m293-m295.

DOI:10.1107/S1600536805000085. (Public domain; Ben Mills).

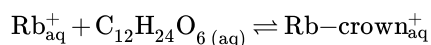
This physical property can be seen in the equilibrium constants for 18-crown-6 and various alkali metals:



If an aqueous solution is made that is 0.006 M in both 18-crown-6 and  $\text{Rb}^+$ , what is the concentration of unbound  $\text{Rb}^+$  at equilibrium? If the same solution is made, but with  $\text{K}^+$  instead of  $\text{Rb}^+$  ions, what is the concentration of unbound  $\text{K}^+$  ions at equilibrium?

### Answer

First, construct an ICE table.



	$\text{Rb}^+$	$\text{C}_{12}\text{H}_{24}\text{O}_6$	$\text{Rb-crown}^+$
I	0.006	0.006	0
C	-x	-x	+x

	Rb <sup>+</sup>	C <sub>12</sub> H <sub>24</sub> O <sub>6</sub>	Rb-crown <sup>+</sup>
E	0.006-x	0.006-x	x

Then, use the K value of the reaction to solve for x. Use x to solve for the concentration of the desired ion.

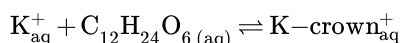
$$K = \frac{[Rb - crown^+]}{[Rb^+][C_{12}H_{24}O_6]}$$

$$36 = \frac{[x]}{[0.006 - x][0.006 - x]}$$

$$x = 9.2954 \times 10^{-4}$$

$$[Rb^+] = 0.0507 M$$

Repeat this process for the other reaction.



	K <sup>+</sup>	C <sub>12</sub> H <sub>24</sub> O <sub>6</sub>	K-crown <sup>+</sup>
I	0.006	0.006	0
C	-x	-x	+x
E	0.006-x	0.006-x	x

$$K = \frac{[K - crown^+]}{[K^+][C_{12}H_{24}O_6]}$$

$$111.6 = \frac{[x]}{[0.006 - x][0.006 - x]}$$

$$x = 0.0019$$

$$[K^+] = 0.0041 M$$

### Q39

Is it easier to dissolve CuBr into 1M of NaBr solution than to dissolve it into pure water? Does the answer change if when the concentration of NaBr is 0.5M?

#### Answer

- When CuBr is added into NaBr solution, the common ion effect occurs. Common ion effect explains that the solvent is responsible for the decrease in the solubility of the precipitate when the soluble compound contains one of the ions of the precipitate that is added to the solution in equilibrium. According to Le Chatelier's principle, some of the ions in excess should be removed from the solution. So it is harder to dissolve CuBr into NaBr solution than dissolve it into pure water.
- If the concentration is changed to 0.5M, it is still harder to dissolve CuBr in NaBr solution, but less difficult.

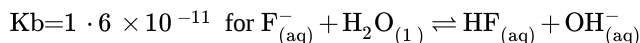
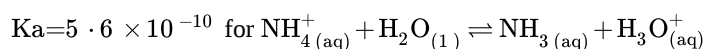
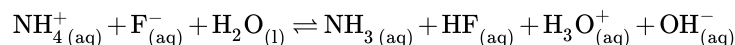
### Q41

Identify the salt NH<sub>4</sub>F as either acidic, basic, or neutral. Then explain the mechanism behind why the salt is acidic, basic, or neutral using chemical equations and their K<sub>a</sub> or K<sub>b</sub> values provided [here](#) and [here](#).

#### Answer

- For a salt to have an acidic character, it must be able to accept OH<sup>-</sup> ions when it dissociates in an aqueous solution and leave an excess of H<sup>+</sup> in the solution to have an acidic effect.
- For a salt to have a basic character, it must be able to either accept an H<sup>+</sup> when it dissociates in an aqueous solution and leave an excess of OH<sup>-</sup> in the solution to have a basic effect.

$\text{NH}_4\text{F}$  can be classified as either acidic or basic depending upon which species is present in a greater concentration ( $\text{H}^+$  or  $\text{OH}^-$ ) in the solution when  $\text{NH}_4\text{F}$  is added.



Since  $K_a > K_b$ ,  $\text{NH}_4^+$  has a greater effect on the solution and therefore the salt is acidic.

\*\* See [key for problem 15.23](#) on how to calculate  $K_b$  or  $K_a$  given  $K_a$  or  $K_b$

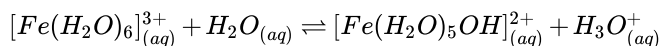
### Q43

For the complex ion,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , the acid ionization constant for 298K is  $7.7 \times 10^{-3}$ . What is the pH of a 50 mL solution that contains 0.02 mols of  $\text{Fe}(\text{NO}_3)_2$ ?

#### Answer

Complex ion problems are solved identically to other equilibrium problems.

First, write the balanced equation:



Then, create and solve an ICE table.

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$\text{H}_2\text{O}$	$\text{H}_3\text{O}^{3+}$	$[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$
0.40	-	0	0
-x	-	+x	+x
0.40-x	-	x	x

From the ICE table:

$$K_a = \frac{[\text{H}_3\text{O}^{3+}][\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}$$

$$7.7 \times 10^{-3} = K_a = \frac{[x][x]}{[0.4 - x]}$$

By rearranging the equation:

$$x^2 + 0.0077x - 0.00308 = 0$$

and using the quadratic,

$$\frac{-0.0077 \pm \sqrt{0.0077^2 - 4(1)(-0.00308)}}{2}$$

$$x = 0.05178$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 1.286$$

### Q45

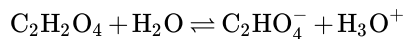
Calculate the concentration of  $\text{H}_3\text{O}^+$  in a 0.3 M solution of oxalic acid ( $\text{pK}_{a1} = 1.25$ ;  $\text{pK}_{a2} = 3.81$ ).

#### Answer



$$K_a = 10^{-1.25} = 0.0562$$

Balanced equation:



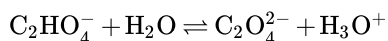
	$\text{C}_2\text{H}_2\text{O}_4$	$\text{C}_2\text{HO}_4^-$	$\text{H}_3\text{O}^+$
I	0.3	0	0
C	-x	+x	+x
E	0.3-x	x	x

At equilibrium:

$$\frac{(x)^2}{(0.3 - x)} = K_{a1}$$

$$x = 0.1048$$

Balanced equation:



	$\text{C}_2\text{HO}_4^-$	$\text{C}_2\text{O}_4^{2-}$	$\text{H}_3\text{O}^+$
I	0.1048	0	0.1048
C	-x	+x	+x
E	0.1048-x	x	x+0.1048

At equilibrium:

$$K_{a2} = 10^{-3.81}$$

$$\frac{x(x + 0.1048)}{(0.1048 - x)} = K_{a2}$$

$$x = 0.000154$$

$$[\text{H}_3\text{O}^+] = 0.1048 + 0.000154 \text{ M} = 0.105 \text{ M}$$

#### Q49

An aqueous solution at 25 °C is 0.10 M in both  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  ions. One wants to separate the two ions by taking advantage of the different solubility of  $\text{BaCO}_3$  and  $\text{CaCO}_3$ .

$$\text{BaCO}_3 \quad K_{sp} = 2.58 \times 10^{-9} \text{ M}$$

$$\text{CaCO}_3 \quad K_{sp} = 3.36 \times 10^{-9} \text{ M}$$

What is the highest possible  $\text{CO}_3^{2-}$  concentration that allows only one salt to present at equilibrium? Which ion is present in the solid,  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$ ?

**Answer**

$$\text{BaCO}_{3(s)} \rightleftharpoons \text{Ba}_{(aq)}^{2+} + \text{CO}_{3(aq)}^{2-}$$

$$[\text{CO}_3^{2-}] < \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{2.58 \times 10^{-9}}{0.1 \text{ M}} = 2.58 \times 10^{-8} \text{ M (Using the formula for } K_{sp})$$

$$\text{CaCO}_{3(s)} \rightleftharpoons \text{Ca}_{(aq)}^{2+} + \text{CO}_{3(aq)}^{2-}$$

$$[\text{CO}_3^{2-}] < \frac{K_{\text{sp}}}{[\text{Ca}^{2+}]} = \frac{3.36 \times 10^{-9}}{0.1 \text{ M}} = 3.36 \times 10^{-8} \text{ M}$$

Therefore, the highest possible  $\text{CO}_3^{2-}$  concentration that allows only one salt to present at equilibrium is  $2.58 \times 10^{-8} \text{ M}$ .  $\text{Ba}^{2+}$  is present in the solid.

### Q51

A solution was created by dissolving 1.31 kg of  $\text{Ba}(\text{NO}_3)_2$  into 1 L of 0.50 M  $\text{Ca}(\text{NO}_3)_2$ . Determine which molecule is more soluble. Then determine the concentration of  $\text{SO}_4$  ion is needed to precipitate all of one molecule but leave the other molecule completely unreacted, use [Table E3](#).

#### Answer

First we must determine the mass action equation for dissolving the salts:

$$K_{\text{sp}} = [\text{Ba}^+][\text{SO}_4^-] = 1.08 \times 10^{-10}$$

$$K_{\text{sp}} = [\text{Ca}^+][\text{SO}_4^-] = 4.93 \times 10^{-5}$$

We will use  $\text{CaSO}_4$  as the salt because it is the most soluble.

For  $\text{Ca}^+$  to remain in solution, its reaction quotient must remain smaller than then its  $K_{\text{sp}}$ :

$$Q = [\text{Ca}^+][\text{SO}_4^-] < 4.93 \times 10^{-5}$$

Now we just need to impute the concentration of  $\text{Ca}^+$  and solve for the concentration of  $\text{SO}_4$  ion:

$$[0.5 \text{ M}][\text{SO}_4^-] < 4.93 \times 10^{-5}$$

$$[\text{SO}_4^-] < 9.86 \times 10^{-5} \text{ M}$$

So as long as the concentration of  $\text{SO}_4$  ion is smaller than  $9.86 \times 10^{-5} \text{ M}$ , no  $\text{CaSO}_4$  will precipitate

### Q55

Let's say you have a solution that is saturated with  $\text{HF}$  at a concentration of  $[\text{HF}] = 0.20 \text{ M}$ .

- If you want some element  $X$  whose concentration is equal to 0.20 M to exist entirely in this solution, what will be the highest pH possible for this mixture? ( $K_a$  of  $\text{HF}$  is  $6.6 \times 10^{-4}$  and  $K$  of  $\text{XF}(s) = 2.5 \times 10^{-16}$ ). Hint: the reaction is given as  $\text{XF}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{X}(aq) + \text{F}^-(aq) + \text{OH}^-(aq)$
- What would be the concentration of some element  $G$  in equilibrium with solid  $\text{GF}$  in this solution at the pH value found in part a) given that  $K$  of  $\text{GF}(s) = 4.9 \times 10^{-22}$ .

#### Answer

Part a)

Since you have the equation  $\text{XF}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{X}(aq) + \text{F}^-(aq) + \text{OH}^-(aq)$ , the equilibrium constant  $K$  will be equal to

$$K = [\text{X}][\text{F}^-][\text{OH}^-] = 2.5 \times 10^{-16}$$

We now replace these variables above with known derived equations

$$K = [\text{X}] \left( \frac{[\text{K}_a][\text{HF}]}{[\text{H}_3\text{O}^+]} \right) \left( \frac{[\text{K}_w]}{[\text{H}_3\text{O}^+]} \right) = 2.5 \times 10^{-16}$$

Plug in known values and solve for  $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{(0.20)(6.6 \times 10^{-4})(0.20)(1.0 \times 10^{-14})}{2.5 \times 10^{-16}}}$$

$$[\text{H}_3\text{O}^+] = 0.0325 \text{ M}$$

Now we solve for pH and see that

$$pH = -\log(0.0325) = 1.50$$

Part b)

For part b), we solve the question in a very similar manner as used in part a) with the only differences being a few different variables we plug in. Now, we are solving for our concentration of some element  $G$  using the value of  $H_3O^+$  we found above.

Given the reaction  $GF(s) + H_2O(l) \rightleftharpoons G(aq) + F^-(aq) + OH^-(aq)$ , the equilibrium constant  $K$  will be equal to

$$K = [G] [F^-] [OH^-] = 4.90 \times 10^{-22}$$

We now replace these variables above with known derived equations and this time, solve for  $[G]$  using the  $[H_3O^+]$  value found above

$$K = [G] \left( \frac{[K_a][HF]}{[H_3O^+]} \right) \left( \frac{[K_w]}{[H_3O^+]} \right) = 4.9 \times 10^{-22}$$

$$[G] = 3.92 \times 10^{-7} M$$

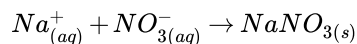
### Q63

200 mL of 0.5M NaCl and 800 mL of 0.10M AgNO<sub>3</sub> are mixed together. Calculate the mass of NaNO<sub>3</sub> precipitated. Assume:

- that the volumes are additive,
- that AgCl is completely insoluble, and
- any other substances that may form are completely soluble.

#### Answer

Because NaCl and AgNO<sub>3</sub> are strong electrolytes, they dissolve in water by dissociation. NaNO<sub>3</sub> precipitates according to the net ionic equation



First calculate the moles of each ion present.

$$n_{Na^+} = 0.2L \times 0.5M = 0.1molNa^+$$

$$n_{NO_3^-} = 0.8L \times 0.1M = 0.08molNO_3^-$$

Assuming that NaNO<sub>3</sub> is completely insoluble, the reaction continues until the entire 0.08 mol of NO<sub>3</sub><sup>-</sup> is consumed, which is the limiting reactant, creating 0.08 mol NaNO<sub>3</sub>.

$$0.08 mol NaNO_3 \left( 84.99 \frac{g}{mol} \right) = 6.80 g NaNO_3$$

### Q69

Siobhan has a 1L solution with containing 0.050M of  $CO_3^{2-}_{(aq)}$  and 0.100M of  $F^-_{(aq)}$ . She titrates the solution with a 0.100 M titrant of Iron Iodide,  $FeI_2$ . The  $K_{sp}$  expressions are:

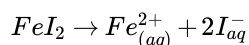
$$FeCO_3(s) \rightleftharpoons CO_3^{2-}_{(aq)} + Fe^{2+}_{(aq)} \quad K_{sp} = 3.13 \times 10^{-11}$$

$$FeF_2(s) \rightleftharpoons 2F^-_{(aq)} + Fe^{2+}_{(aq)} \quad K_{sp} = 2.36 \times 10^{-6}$$

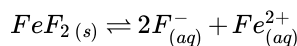
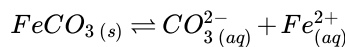
At what volume of iron iodide will the precipitate  $FeCO_3(s)$  appear? How about  $FeF_2(s)$ ?

#### Answer

This problem primarily focuses on expanding on how the solubility constant  $K_{sp}$  can predict which solution will titrate first. When Iron Iodide is dripped into the solution, it disassociates into Iron(II) and Iodide Ions.



This facilitates a "common ion effect", where the ions from the dissolution of the titrand Iron Iodide contribute to shifting the concentration of the other two reactions:



As seen here, the introduction of  $Fe^{2+}$  ions will mean there is a larger iron ion concentration, which shifts both of the above reactions to the left. This concept that explains this phenomena is colloquially known as Le Chatelier's principle. However, in order to precisely determine at what point precipitate will form, the  $K_{sp}$  values need to be taken into consideration. Recall that the K constant is defined in terms of either concentrations or partial pressures. As the species in this problem are only aqueous solutes and not gaseous compounds, the resulting  $K_{sp}$  will be defined by concentrations as depicted below:

$$FeCO_3(s) \rightleftharpoons CO_3^{2-}(aq) + Fe^{2+}(aq) \quad K_{sp} = \frac{[CO_3^{2-}][Fe^{2+}]}{1} = 3.13 \times 10^{-11}$$

$$FeF_2(s) \rightleftharpoons 2F^-(aq) + Fe^{2+}(aq) \quad K_{sp} = \frac{[F^-]^2[Fe^{2+}]}{1} = 2.36 \times 10^{-6}$$

Notice that each  $K_{sp}$  is divided by 1. This is to represent the solid reactants. Also, based on the information above, recognize that, at equilibrium, the product of the concentrations of the two ions should equal to their  $K_{sp}$ , and since the problem provided both  $[CO_3^{2+}]$  and  $[F^-]$ . By substituting these concentrations into the respective  $K_{sp}$  formulas, the equations can be algebraically manipulated to provide the  $[Fe^{2+}]$  at equilibrium. This process is seen below for  $FeF_2$ . The process is basically the same to finding  $[Fe^{2+}]$  for  $[CO_3^{2+}]$ , but there is no need to square root the value since there is no stoichiometric coefficients for that particular equation. In contrast,  $F^-$  has a stoichiometric coefficient of 2). Since only initial concentrations were given, we can determine at which point  $Q_{sp} > K_{sp}$

$$Q_{sp} = \frac{[F^-]^2[Fe^{2+}]}{1} = 2.36 \times 10^{-6}$$

$$Q_{sp} = (0.05M)^2[Fe^{2+}] = 2.36 \times 10^{-6}$$

$$[Fe^{2+}] = \frac{2.36 \times 10^{-6}}{(0.100M^2)} = 2.36 \times 10^{-4}M$$

$$\text{Therefore, } [Fe^{2+}] \text{ for } FeF_2 = 2.36 \times 10^{-4}M$$

$$\text{And } [Fe^{2+}] \text{ for } FeCO_3 = 6.26 \times 10^{-10}M, \text{ using the same method.}$$

What this information tells us is the calculated  $[Fe^{2+}]$  is the concentration of  $Fe^{2+}$  that one would expect to be in equilibrium at the given concentration of the other ion. Therefore, if  $[Fe^{2+}]$  is higher than this value, then the resulting reaction quotient will be larger than  $K_{sp}$ , causing the reaction to shift towards the product and consequently causing the precipitate to form. From the values, it is clear that  $FeCO_3(s)$  will end up precipitating first, and then  $FeF_2$ .

Finding the exact volume that the precipitate for each reaction will form is relatively straightforward. Based on the information overviewed before, after the  $[Fe^{2+}]$  reaches the calculated point, precipitate will form. Therefore, to find the volume of titrant needed, just set up the following equation:

$$\text{molarity}_{\text{titrant}} \times V_{\text{titrant}} = \text{mol}_{\text{titrant}} = \text{mol}_{Fe^{2+} \text{ to precipitate}}$$

$$0.100M \times V_{\text{titrant}} = (6.26 \times 10^{-10}M)(1L)$$

$$0.100M \times V_{\text{titrant}} = 6.26 \times 10^{-10}mol$$

$$V_{\text{titrant}} = \frac{6.26 \times 10^{-10}mol}{0.100M}$$

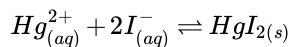
$$V_{\text{titrant}} = 6.26 \times 10^{-9}L \text{ for } FeCO_3(s) \text{ precipitate to form.}$$

Via the same process,  $V_{\text{titrant}} = 0.00236L$  for  $FeF_2(s)$  to form.

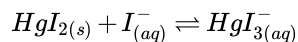
**Abstract:** Use  $K_{sp}$  to determine  $Q_{sp}$  concentration  $[Fe^{2+}]$ . Divide by molarity of titrant to get desired volume for precipitate to form.

## Q73

Complex ion plays an important role in the level of solubility. For example:



This reaction results in the formation of solid  $\text{HgI}_2$ . However, when solid  $\text{HgI}_2$  reacts in the same process:



The solubility increases greatly and the reaction results in an aqueous product. Explain this phenomenon.

**Answer**

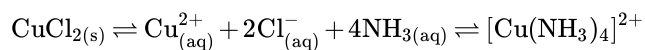
The first reaction produces a solid precipitate and the second reaction is soluble because complex ions are created in the reaction.  $\text{HgI}_3^{-}$  is a complex ion, which means it has Hg ion in the center that is surrounded by iodine molecules that are able to act as Lewis bases and attract the protons of the Lewis acid in the reaction. These properties are brought out as a result of the reaction and result in an aqueous product.

## Q73

Why does the inclusion of  $\text{NH}_3$  increase the solubility of  $\text{CuCl}_2$  in an aqueous solution?

**Answer**

The solubility of  $\text{Cu}^{2+}$  increases when  $\text{NH}_3$  present because  $\text{NH}_3$  forms a complex ion with  $\text{Cu}^{2+}$ . The corresponding the chemical reaction for is as follows,



The formation of the complex ion pulls equilibrium towards the right which allows more  $\text{CuCl}_2$  to dissolve.

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