

## Chapter 20: Equilibria in Aqueous Solutions - III

### Solubility Product

We are now going to consider compounds that are only slightly soluble or "insoluble" in aqueous solutions. Quotation marks are used since nearly all compounds are soluble in water to some extent.

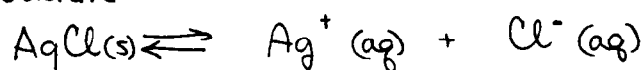
Rule of thumb used by some (but don't worry about it) : If a compound dissolves in water to give 0.020 moles /L in solution, it is considered to be soluble. But there is a large gray area where substances are considered slightly soluble.

To work with slightly soluble compounds, a special equilibrium constant is used : the SOLUBILITY PRODUCT.

Consider  $\text{AgCl}$  :

This compound appears on the chart on back of exam envelope called SOLUBILITY PRODUCTS. So we know it is "insoluble" or rather slightly soluble.

In aqueous solution



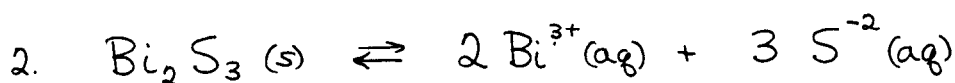
$$K_c = K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \quad \text{at } 25^\circ\text{C}$$

$\uparrow$   
 solubility  
 product

Examples of solubility product expressions :



$$K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3 = 1.9 \times 10^{-33}$$



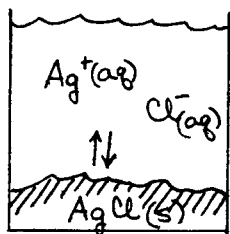
$$K_{sp} = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3 = 1.6 \times 10^{-72}$$

In general,  $M_n X_y(s) \rightleftharpoons n M^{y+}(aq) + y X^{n-}(aq)$

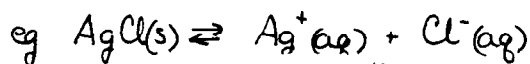
$$K_{sp} = [M^{y+}]^n [X^{n-}]^y$$

Note: as the  $K_{sp}$  value gets smaller, the solid becomes less soluble  
as the  $K_{sp}$  value gets larger, the solid becomes more soluble.

What does the solubility expression mean? It allows us to calculate the concentrations of the ions at equilibrium with the parent solid in aqueous solution at 25°C, provided we know the  $K_{sp}$  value.



when the system is at equilibrium  
solid  $\rightleftharpoons$  ions



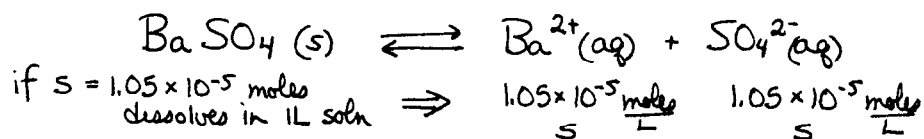
and  $K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$

the solution is called SATURATED!!

How is  $K_{sp}$  determined for solids? The solid is put in water at 25°C and stirred until solid dissolves as much as it can forming a saturated solution. The molar solubility of the solid is measured +  $K_{sp}$  is calculated. So, what is molar solubility?

molar solubility: the number of moles of a compound that dissolve to give one liter of saturated solution.

Example: The molar solubility,  $s$ , of barium sulfate ( $BaSO_4$ ) is  $1.05 \times 10^{-5}$  M.  
What is  $K_{sp}$  of  $BaSO_4$ ?



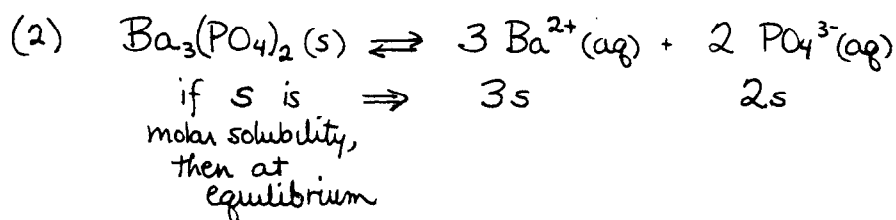
$$\therefore K_{sp} = [Ba^{2+}][SO_4^{2-}] = s^2 = (1.05 \times 10^{-5})^2 = 1.1 \times 10^{-10}$$

where  $s$  = molar solubility

Example: One liter of a saturated solution of barium phosphate ( $\text{Ba}_3(\text{PO}_4)_2$ ,  $\text{MW} = 601.8 \text{ g/mol}$ ) contains  $3.94 \times 10^{-4} \text{ g}$  of  $\text{Ba}_3(\text{PO}_4)_2$ . Calculate the  $K_{sp}$  for  $\text{Ba}_3(\text{PO}_4)_2$ .

Plan: (1) calculate  $s$ , molar solubility  
 (2) write the  $K_{sp}$  expression in terms of  $s$   
 (3) solve for  $K_{sp}$ .

$$(1) \text{ molar solubility} = \frac{\text{moles } \text{Ba}_3(\text{PO}_4)_2}{\text{liter soln}} = \frac{(3.94 \times 10^{-4} \text{ g} / 601.8 \text{ g/mol})}{1 \text{ liter}} = 6.55 \times 10^{-7} \text{ M}$$

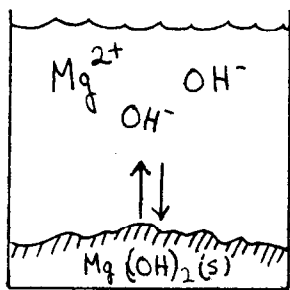


$$\therefore K_{sp} = [\text{Ba}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3s)^3 (2s)^2 = 27s^3 \times 4s^2 = 108s^5$$

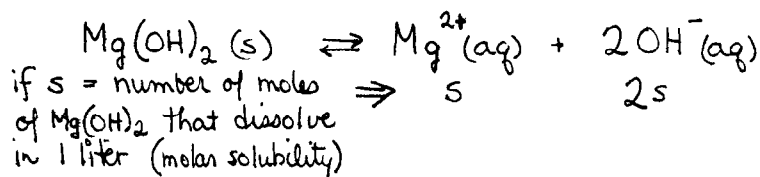
$$(3) K_{sp} = 108 (6.55 \times 10^{-7})^5 = (108)(1.21 \times 10^{-31}) = 1.30 \times 10^{-29}$$

Example: Given a saturated solution of  $\text{Mg}(\text{OH})_2$  ( $K_{sp} = 1.5 \times 10^{-11}$ )

- (a) What is the molar solubility of  $\text{Mg}(\text{OH})_2$ ? What is solubility ( $\text{g}/100 \text{ mL}$ )?  
 (b) What are the concentrations of  $\text{Mg}^{2+}$  and  $\text{OH}^-$  and the pH in saturated solution?



for every 1 mole of  $\text{Mg}(\text{OH})_2(s)$  that dissolves, we get 1 mole of  $\text{Mg}^{2+}$  ions and 2 moles of  $\text{OH}^-$  ions.



$$(a) K_{sp} = 1.5 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (s)(2s)^2 = 4s^3$$

$$\therefore s^3 = \frac{1.5 \times 10^{-11}}{4} = 3.75 \times 10^{-12}$$

molar solubility,  $s = \sqrt[3]{3.75 \times 10^{-12}} = (3.75 \times 10^{-12})^{\frac{1}{3}} = 1.55 \times 10^{-4} \text{ M}$

Note: to take the third root on calculator (or any root)

I enter  $3.75 \times 10^{-12}$   
 push  $\sqrt[x]{y}$  or  $\text{inv } y^x$   
 enter 3  
 push =

II enter  $3.75 \times 10^{-12}$   
 push  $y^x$   
 enter  $\frac{1}{3} = 0.333$   
 push =

III enter  $3.75 \times 10^{-12}$   
 push log  
 push  $\div, 3, =$   
 push inv log

$$\therefore \text{solubility} \left( \frac{\text{g}}{100 \text{ mL}} \right) = \frac{1.55 \times 10^{-4} \text{ moles}}{1 \text{ liter}} \times \frac{58 \text{ g}}{1 \text{ mole}} \times \frac{0.10 \cancel{\text{L}}}{100 \text{ mL}} = 8.9 \times 10^{-4} \frac{\text{g}}{100 \text{ mL}}$$

do not divide by 100

OR we can reason:

we know,  $1.55 \times 10^{-4}$  moles of  $\text{Mg}(\text{OH})_2$  are dissolved in 1 liter solution

$\therefore 1.55 \times 10^{-5}$  moles of  $\text{Mg}(\text{OH})_2$  are dissolved in 100 mL (=0.1L) soln

and  $? \text{ g} = 1.55 \times 10^{-5} \text{ moles} \times 58 \text{ g/mol} = 8.9 \times 10^{-4} \text{ g}$

$$\therefore \text{solubility} \left( \frac{\text{g}}{100 \text{ mL}} \right) = \frac{8.9 \times 10^{-4}}{1.21 \times 10^{-3}} \text{ g} / 100 \text{ mL}$$

(b) molar solubility =  $S = [\text{Mg}^{2+}] = 1.55 \times 10^{-4} \text{ M}$

$2S = [\text{OH}^-] = 3.1 \times 10^{-4} \text{ M}$

$\text{pOH} = 3.51$

$\text{pH} = 14 - 3.51 = 10.49$

### Common Ion Effect

In the calculations we have done so far, a solid has dissolved in water until an equilibrium is reached between the solid and its dissolved ions. What happens to the equilibrium if we add more of one of the ions?

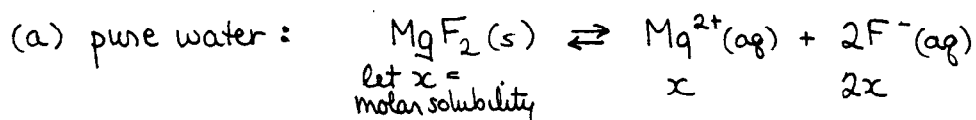
Consider a saturated solution of magnesium fluoride:  $\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$   
 $K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^{-}]^2$

What happens if more  $\text{Mg}^{2+}$  ions or more  $\text{F}^{-}$  ions are added?

The equilibrium shifts to the reactant side. The concentrations of ions, due to the dissolution of  $\text{MgF}_2$ , decreases;  $\text{MgF}_2$  becomes less soluble and precipitates out until equilibrium is reached.

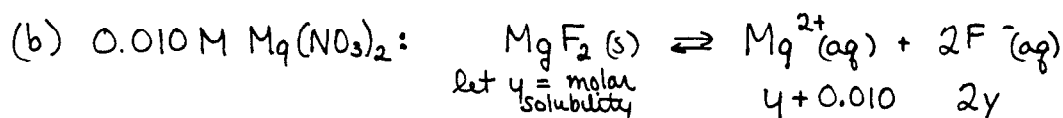
Example: Calculate the moles of  $\text{MgF}_2$  that will dissolve in 1.00 L of  
 (a) pure water (b) 0.010 M  $\text{Mg}(\text{NO}_3)_2$  and (c) 0.010 M NaF.

Note: we are calculating molar solubility.  $K_{sp} \text{ MgF}_2 = 6.4 \times 10^{-9}$



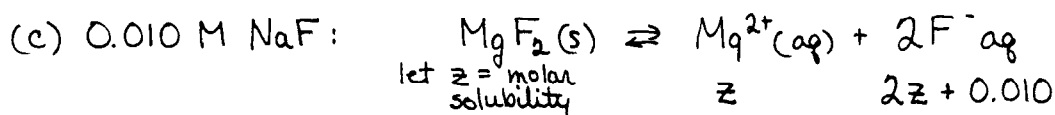
$$K_{sp} = 6.4 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3$$

$\therefore x = 1.2 \times 10^{-3} \text{ M} = \text{moles of MgF}_2 \text{ required to make 1 L saturated soln}$



$$K_{sp} = 6.4 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 \stackrel{\text{Rule of Thumb}}{=} (y + 0.010)(2y)^2 = (0.010)4y^2$$

$\therefore y = 4.0 \times 10^{-4} \text{ M} = \text{moles/L required to make saturated solution}$



$$K_{sp} = 6.4 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 \stackrel{\text{Rule of Thumb}}{=} (z)(2z + 0.010)^2 = (z)(0.010)^2$$

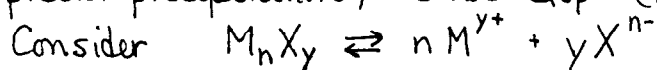
$z = 6.4 \times 10^{-5} \text{ M} = \text{mol/L required to prepare saturated solution}$

Therefore in a solution with a common ion, the solubility of the compound decreases dramatically.

More Uses of the Solubility Product - Systems with NO solid present initially.

I When given a solution containing ions, it is useful to know if a precipitate will form.

To predict precipitation, we use  $Q_{sp}$  (Reaction Quotient - Ch 17)



$$Q_{sp} = [\text{M}^{y+}]^n [\text{X}^{n-}]^y$$

where conc<sup>n</sup> are NOT necessarily the equil. conc<sup>n</sup>.

$$\text{If } Q_{sp} = K_{sp}$$

the system is at equilibrium  
the ions are forming a precipitate just as fast as the solid is dissolving  
the solution is saturated.

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

the solution is supersaturated - the solubility is exceeded  
a precipitate will form and will continue to form until the concentration of ions in the solution decrease to such a point that  $Q_{sp} = K_{sp}$ .  
when the system is at equilibrium.

$$Q_{sp} < K_{sp}$$

the solution is undersaturated  
no precipitation will occur.

Example: If equal amounts of 0.010 M  $K_2SO_4$  and 0.10 M  $Pb(NO_3)_2$  solutions are mixed, will a precipitate form?

Step 1: What could the precipitate be?

The ions present are  $K^+$ ,  $SO_4^{2-}$ ,  $Pb^{2+}$  and  $NO_3^-$

Possible choices (switching partners):  $KNO_3$ ? nope - is soluble

$PbSO_4$ ? yes

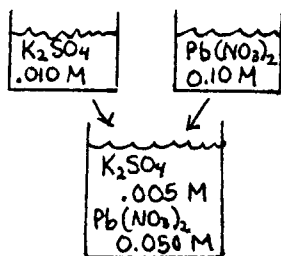
$$K_{sp} = 1.8 \times 10^{-8}$$

$\therefore PbSO_4$  may precipitate if  $Q_{sp} > K_{sp}$

Step 2: Write the solubility product expression:

$$K_{sp} = 1.8 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}] \text{ at equilibrium}$$

Step 3: Calculate  $Q_{sp}$  for the final solution.



$$\begin{aligned} Q_{sp} &= [Pb^{2+}][SO_4^{2-}] \\ &= (0.050 M)(0.005 M) \\ &= 2.5 \times 10^{-4} \end{aligned}$$

Since equal volumes of the solutions are added together the concentration of each compound is halved in the final solution.

Step 4 : Compare  $Q_{sp}$  with  $K_{sp}$  :

in this case  $Q_{sp} > K_{sp}$   $\therefore$  the solution is supersaturated and a precipitate will form until the concentrations of the ions satisfy the solubility product expression.

Aside - for your interest : What are the concentrations of  $Pb^{2+}$  and  $SO_4^{2-}$  remaining in solution after the system reached equilibrium

$$\begin{array}{lcl}
 & K_{sp} = 1.8 \times 10^{-8} & = [Pb^{2+}][SO_4^{2-}] \\
 & & = (0.05 - x)(0.005 - x) \\
 \text{since } Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 & & \\
 \begin{array}{l} t=0 \quad 0.05 \quad 0.005 \\ t=t_{eq} \quad 0.05-x \quad 0.005-x \end{array} & 1.8 \times 10^{-8} = & x^2 - 0.055x + 2.5 \times 10^{-4} \\
 & 0 = & x^2 - 0.055x + 2.5 \times 10^{-4} \quad \text{solve by quadratic} \\
 & x = & \underline{0.05}; 0.005
 \end{array}$$

What does this mean? That at equilibrium, nearly all of the  $SO_4^{2-}$  ions have been removed from solution.  $\therefore x = 0.004999\dots$

Let's solve for  $x$

$$\begin{aligned}
 1.8 \times 10^{-8} &= (0.05 - \overset{x}{0.005})(0.005 - x) \quad \text{where } x \text{ is very close to } 0.005. \\
 &= (0.045)(0.005 - x) \\
 0.005 - x &= 4 \times 10^{-7} \\
 x &= 0.0049996
 \end{aligned}$$

$\therefore$  concentrations still in solution:  $[Pb^{2+}] = 0.045 \text{ M}$   
 $[SO_4^{2-}] = 4.0 \times 10^{-7} \text{ M}$

Example:

- (a) If equal amounts of 0.004 M  $\text{Pb}(\text{NO}_3)_2$  and 0.004 M  $\text{Na}_2\text{SO}_4$  are mixed will a precipitate form?
- (b) if equal amounts of 0.004 M  $\text{Pb}(\text{NO}_3)_2$  and 0.004 M  $\text{KF}$  are mixed will a precipitate form?

Step 1. What could the precipitate be?

- (a) ions present:  $\text{Pb}^{2+}$   $\text{NO}_3^-$   $\text{Na}^+$   $\text{SO}_4^{2-}$   
 possible choices (switch partners):  $\text{NaNO}_3$  - nope - is soluble  
 $\text{PbSO}_4$  - yes  
 $K_{sp} = 1.8 \times 10^{-8}$

$\therefore$  if  $Q_{sp} > K_{sp}$ , a precipitate of  $\text{PbSO}_4$  will form

- (b) ions present:  $\text{Pb}^{2+}$   $\text{NO}_3^-$   $\text{K}^+$   $\text{F}^-$   
 possible choices (switch partners):  $\text{KNO}_3$  - nope - is soluble too  
 $\text{PbF}_2$  - yes  
 $K_{sp} = 3.7 \times 10^{-8}$

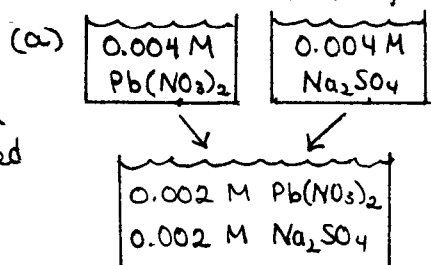
$\therefore$  if  $Q_{sp} > K_{sp}$ , a precipitate of  $\text{PbF}_2$  will form.

Step 2. Write the solubility product expression.

- (a) for  $\text{PbSO}_4$   $K_{sp} = 1.8 \times 10^{-8} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$   
 (b) for  $\text{PbF}_2$   $K_{sp} = 3.7 \times 10^{-8} = [\text{Pb}^{2+}][\text{F}^-]^2$

Step 3. Calculate  $Q_{sp}$  for final solution

Note: since equal volumes are added together, the concentration of each is halved

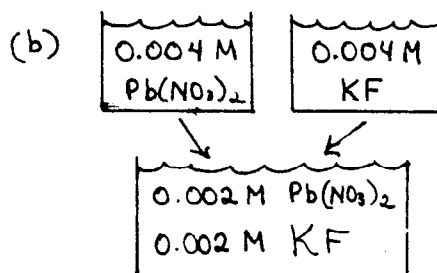


$$Q_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$= (0.002)^2$$

$$= 4 \times 10^{-6}$$

$Q_{sp} > K_{sp} \therefore$  precipitation



$$Q_{sp} = [\text{Pb}^{2+}][\text{F}^-]^2$$

$$= (0.002)(0.002)^2$$

$$= 8 \times 10^{-9}$$

$Q_{sp} < K_{sp} \therefore$  no precipitation



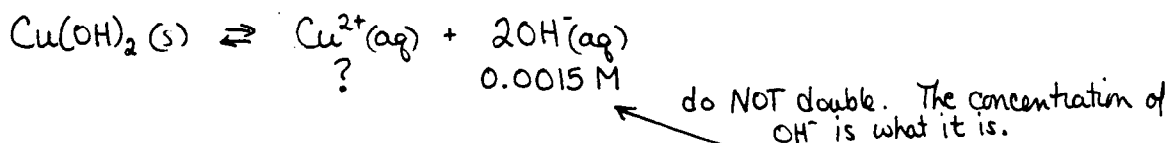
In-Class Quiz

- Write the solubility product expressions for  
 (a) calcium hydroxide,  $\text{Ca(OH)}_2$       (b)  $\text{Sr}_3(\text{PO}_4)_2$ , strontium phosphate
- Write the above  $K_{sp}$  expressions in terms of  $s$ , the molar solubility
- Calculate the molar solubility for  $\text{Sr}_3(\text{PO}_4)_2$ .  $K_{sp} = 1.0 \times 10^{-31}$
- If equal volumes of the following solutions are mixed, will a precipitate form?  
 (a)  $3.0 \times 10^{-6} \text{ M NiCl}_2$  and  $6.0 \times 10^{-4} \text{ M Na}_2\text{CO}_3$  ( $K_{sp} \text{ NiCO}_3 = 6.6 \times 10^{-9}$ )  
 (b)  $2.0 \times 10^{-2} \text{ M NaF}$  and  $2.0 \times 10^{-3} \text{ M MgCl}_2$  ( $K_{sp} \text{ MgF}_2 = 6.4 \times 10^{-9}$ )

Answers:

- (a)  $K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$       (b)  $K_{sp} = [\text{Sr}^{2+}]^3[\text{PO}_4^{3-}]^2$
- (a)  $\underset{s = \text{molar solubility}}{\text{Ca(OH)}_2(s)} \rightleftharpoons \underset{s}{\text{Ca}^{2+}(aq)} + \underset{2s}{2\text{OH}^-(aq)}$        $K_{sp} = (s)(2s)^2 = 4s^3$   
 (b)  $\underset{s = \text{molar solubility}}{\text{Sr}_3(\text{PO}_4)_2(s)} \rightleftharpoons \underset{3s}{3\text{Sr}^{2+}(aq)} + \underset{2s}{2\text{PO}_4^{3-}(aq)}$        $K_{sp} = (3s)^3(2s)^2 = (27s^3)(4s^2) = 108s^5$
- $K_{sp} = 1.0 \times 10^{-31} = 108s^5$  (see 2 b)  
 $s^5 = 9.26 \times 10^{-34}$   
 $s = 2.5 \times 10^{-7} \text{ M}$
- (a)  $Q_{sp} = [\text{Ni}^{2+}][\text{CO}_3^{2-}] = (1.5 \times 10^{-6} \text{ M})(3.0 \times 10^{-4} \text{ M}) = 4.5 \times 10^{-10}$   
 $Q_{sp} < K_{sp} \therefore \text{NiCO}_3$  does NOT precipitate  
 (b)  $Q_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2 = (1.0 \times 10^{-3} \text{ M})(1.0 \times 10^{-2} \text{ M})^2 = 1.0 \times 10^{-7}$   
 $Q_{sp} > K_{sp} \therefore \text{MgF}_2$  will precipitate.

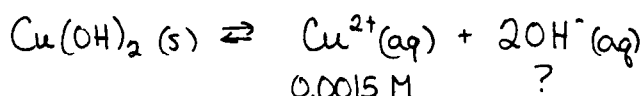
II. Example (a) What concentration of  $\text{Cu}^{2+}$  is necessary to initiate precipitation from a solution containing 0.0015 M KOH?  $K_{sp} \text{ Cu(OH)}_2 = 1.6 \times 10^{-19}$   
(Hint: precipitation is initiated at equilibrium!!) (This is #25 in Ch 20)



$$K_{sp} = 1.6 \times 10^{-19} = [\text{Cu}^{2+}][\text{OH}^{-}]^2 = [\text{Cu}^{2+}](0.0015 \text{ M})^2$$

$$\therefore [\text{Cu}^{2+}] = 7.1 \times 10^{-14} \text{ M}$$

(b) Suppose more solid  $\text{Cu(NO}_3)_2$  was added until  $[\text{Cu}^{2+}] = 0.0015 \text{ M}$ . What would be  $[\text{OH}^{-}]$  in the solution? What is pH? (ignore effect of  $\text{Cu}^{2+}$  a weak acid)

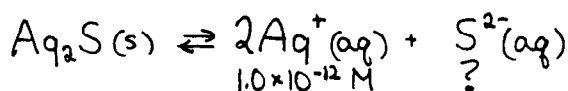


$$K_{sp} = 1.6 \times 10^{-19} = [\text{Cu}^{2+}][\text{OH}^{-}]^2 = (0.0015 \text{ M})[\text{OH}^{-}]^2$$

$$[\text{OH}^{-}]^2 = 1.07 \times 10^{-16}$$

$$[\text{OH}^{-}] = 1.0 \times 10^{-8} \text{ M}; \text{ pOH} = 8.00; \text{ pH} = 6.00$$

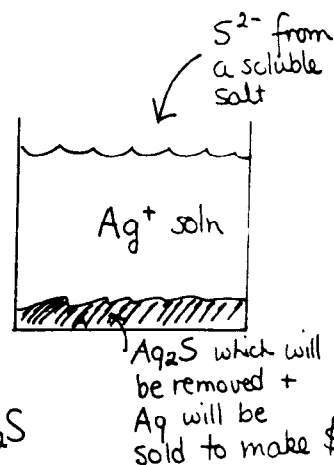
Example: If silver ions are to be removed from solution by precipitation, of  $\text{Ag}_2\text{S}$ , what final concentration of sulfide ions are required to reduce the  $\text{Ag}^{+}$  concentration to  $1.0 \times 10^{-12} \text{ M}$ ?  $K_{sp} \text{ Ag}_2\text{S} = 1.0 \times 10^{-49}$



$$K_{sp} = 1.0 \times 10^{-49} = [\text{Ag}^{+}]^2[\text{S}^{2-}]$$

$$= (1.0 \times 10^{-12})^2 [\text{S}^{2-}]$$

$$\therefore [\text{S}^{2-}] = 1.0 \times 10^{-25} \text{ M}$$

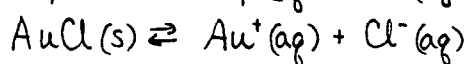
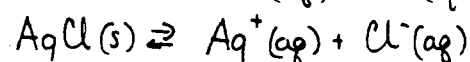
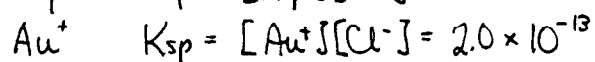
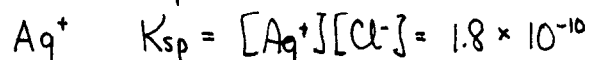
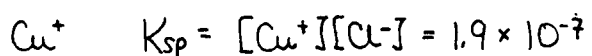


As more & more  $\text{S}^{2-}$  (from  $\text{Na}_2\text{S}$ ) added, more & more  $\text{Ag}_2\text{S}$  precipitates out, but there is a tiny amount of  $\text{S}^{2-}$  and  $\text{Ag}^{+}$  ions that are in solution at all times.

## Fractional Precipitation (For Interest Only)

Fractional precipitation is the process whereby some ions are removed from solution while leaving other ions with similar properties still in solution.

Example: If solid NaCl is added slowly to a solution that is 0.010 M each in  $\text{Cu}^+$ ,  $\text{Ag}^+$  and  $\text{Au}^+$ , which salt precipitates first?



We are adding  $\text{Cl}^-$  ions. In which system does  $Q_{sp} > K_{sp}$  first?

ANSWER: The system with the smallest  $K_{sp}$  (with most insoluble salt)

$\therefore \text{Au}^+$  precipitates out first as  $\text{AuCl}$ , then  $\text{Ag}^+$ , then  $\text{Cu}^+$   
 $\text{AgCl}$ 
 $\text{CuCl}$

Further calculations can be made : see Examples 20-8, 20-9 in text book.