

SOLUBILITY AND SOLUBILITY PRODUCT

[MH 5; 16.1 & 16.2]

- In this section we are going to consider the **solubility** of **ionic solids** in water.
- "Solubility" may be considered to be an equilibrium; the equilibrium is between **solid** and **ions** in solution.
- Any **ionic** solid is 100% ionized in aqueous solution; once it actually dissolves.



- The term **solubility** always refers to the amount of **solid** (either in moles or grams) that actually does dissolve in solution, producing ions; this amount can be calculated for a particular solid.
- The term solubility may also be used in a **qualitative** sense; there is no "magic point" above which a salt can be described as "soluble", and below which a salt can be described as "insoluble".

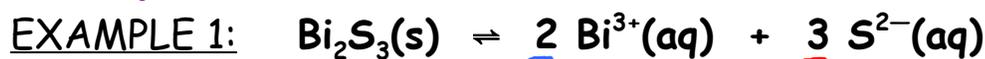
Very roughly.....

"Soluble" - at least 0.1 mol L^{-1} dissolves

"Slightly Soluble" - maybe 0.001 to 0.1 mol L^{-1}

"Insoluble" - less than 0.001 mol L^{-1}

"sparingly soluble"



What is the form of the equilibrium constant for this particular equilibrium?

$$K = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3$$

- solid Bi_2S_3 not included

EXAMPLE 2:

For a solution of AgCl in water, the equilibrium is:

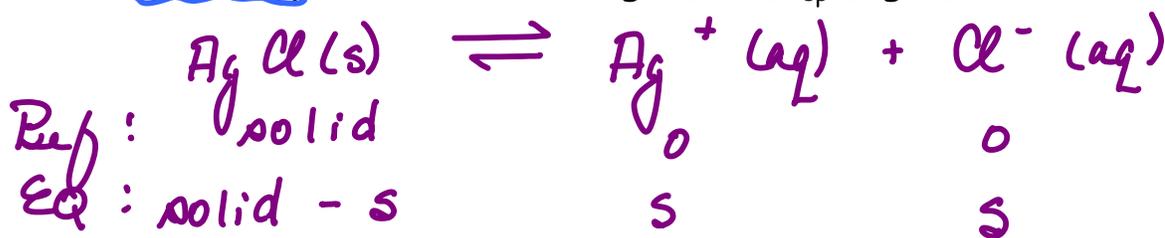


- When the equilibrium is set up all three components **must** be present, to be sure that the system is at equilibrium.
- The equilibrium constant $K = [\text{Ag}^+][\text{Cl}^-]$
- We call this type of K a **Solubility Product Constant**, symbolized by K_{sp} .
- So, $K_{sp}(\text{AgCl})$ is the solubility product constant for AgCl , when it dissolves (or tries to!) according to the above equation.
- Like most K_{eq} 's, its value depends on T ; this is why more solid usually dissolves in a solution at a higher temperature.

Calculations Using K_{sp}

EXAMPLE 1:

Calculate the solubility, in mol L^{-1} , of $\text{AgCl}(s)$. [$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$]



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

$$1.8 \times 10^{-10} = (s)(s) = s^2$$

$$s = \sqrt{1.8 \times 10^{-10}} = \underline{\underline{1.34 \times 10^{-5} \text{ mol L}^{-1}}}$$

EXAMPLE 3:

Calcium fluoride, CaF_2 , dissolves in water to the extent of 0.00170 g per 100 mL. What is the K_{sp} for (CaF_2) ? [MM $\text{CaF}_2 = 78.1 \text{ g mol}^{-1}$]



$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}] [\text{F}^-]^2 \\ &= (s) (2s)^2 = (s) [(2s)(2s)] \\ &= \underline{4s^3} \end{aligned}$$

$$s = \frac{0.0017 \text{ g}}{0.100 \text{ L}} = 0.017 \text{ g L}^{-1}$$

Convert to mol L^{-1} :

$$s = \frac{0.017 \text{ g L}^{-1}}{78.1 \text{ g mol}^{-1}} = 2.18 \times 10^{-4} \text{ mol L}^{-1}$$

Substitute:

$$\begin{aligned} K_{sp} &= 4s^3 \\ &= 4 [(2.18 \times 10^{-4})^3] \\ &= \underline{\underline{4.13 \times 10^{-11}}} \end{aligned}$$

Solubility and the Common Ion Effect

- The "Common Ion Effect" is an illustration of Le Chatelier's Principle.
- Consider the equilibrium:



- What happens to the position of equilibrium if we add some extra chloride ion, Cl^- (or silver ion, Ag^+)? "stress"

- equilibrium shifts so as to offset that stress

\Rightarrow shift LEFT; towards AgCl

\therefore more $\text{AgCl}(s)$ present; less dissolves

- What does this mean, qualitatively, for the solubility of AgCl if there is already Ag^+ or Cl^- in the solution?

- less AgCl dissolves

\therefore "s" is smaller

\Rightarrow solubility decreases in the presence of a "common ion"

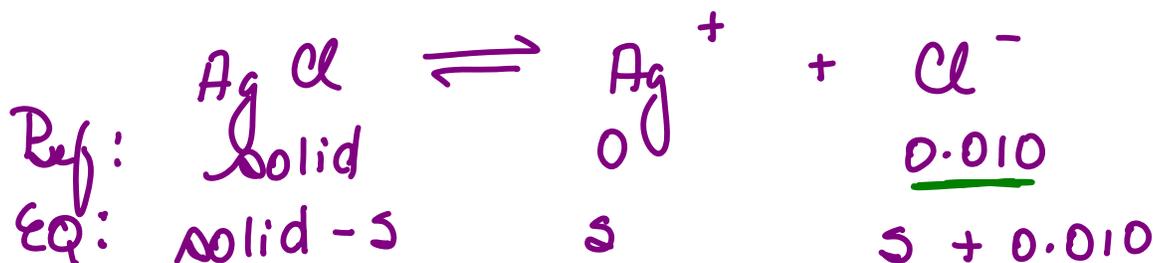
$$K_{sp} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

EXAMPLE 1:

Solid AgCl ($K_{sp} = 1.8 \times 10^{-10}$) is equilibrated with 0.010 M NaCl solution.

$\therefore \text{Cl}^-$ is the common ion

a) How many moles of AgCl will dissolve in 1.0 L of the NaCl solution?



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \qquad s + 0.010 \approx 0.010$$
$$1.8 \times 10^{-10} = (s)(s + 0.010)$$

$$s = \underline{1.8 \times 10^{-8}} \text{ mol L}^{-1}$$

b) What is the solubility of AgCl in the NaCl solution?

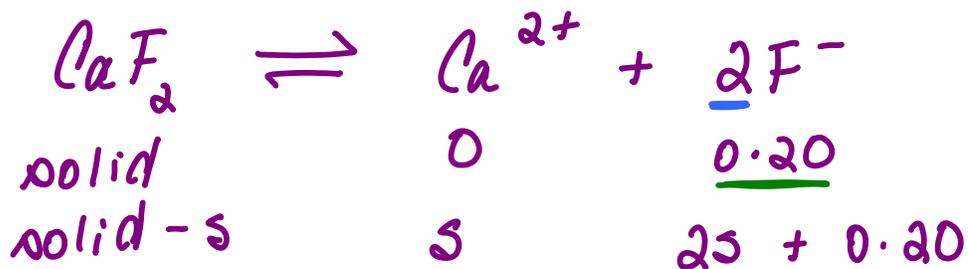
$$s = 1.8 \times 10^{-8} \text{ mol L}^{-1}$$

Solubility of AgCl in pure water = 1.3×10^{-5} M (p. 143).

In the NaCl solution: only 0.13 % of the solubility in water alone!

EXAMPLE 2:

What is the concentration of $\text{Ca}^{2+}(\text{aq})$ in mol L^{-1} , in a solution made by equilibrating $\text{CaF}_2(\text{s})$ with 0.20 M KF solution? F^- is common ion
[K_{sp} for $\text{CaF}_2 = 4.1 \times 10^{-11}$] (Compare this answer with p. 145)



$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^-]^2$$
$$4.1 \times 10^{-11} = (s) (\cancel{2s} + 0.20)^2$$

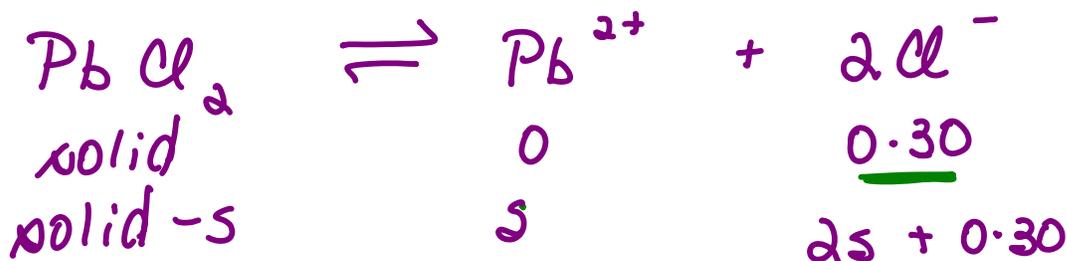
$$s = \frac{4.1 \times 10^{-11}}{(0.20)^2} = \underline{\underline{1.025 \times 10^{-9}}} = [\text{Ca}^{2+}]$$

EXAMPLE 3:

Calculate the solubility of PbCl_2 , in mol L^{-1} , in a solution of 0.15 M MgCl_2 . [K_{sp} for PbCl_2 is 1.7×10^{-5}] Cl^- is common ion



$$\begin{aligned} [\text{Cl}^-]_{\text{MgCl}_2} &= 2 \times 0.15 \text{ mol L}^{-1} \\ &= \underline{0.30 \text{ mol L}^{-1}} \end{aligned}$$



$$K_{sp} = [\text{Pb}^{2+}] [\text{Cl}^-]^2$$
$$1.7 \times 10^{-5} = (s) (\cancel{2s} + 0.30)^2$$

$$s = \frac{1.7 \times 10^{-5}}{(0.30)^2} = \underline{\underline{1.9 \times 10^{-4} \text{ mol L}^{-1}}}$$

Saturated and Unsaturated Solutions

- The term “**saturated**” implies that there is equilibrium between solid and solution.
- If the quantity of a substance in solution is **less** than that required for equilibrium with the solid, the solution is said to be “**unsaturated**”.

This is a common, stable, situation but it is **not** an equilibrium (so K_{sp} doesn't apply).

- If more solid is added to an unsaturated solution, it **dissolves** until the solution is saturated (at which point there is solid in equilibrium with the solvated ions).
- Consider the compound A_2B ; first we dissolve some in water to produce a saturated solution.



- We could write an expression for Q , the Reaction Quotient (p. 139):

$$Q = [A^+]^2 [B^{2-}]$$

- For a **saturated** solution, $Q = K_{sp}$.

- no more solid can dissolve

- Now suppose that we mix two solutions containing the ions $A^+(aq)$ and $B^{2-}(aq)$. The sparingly soluble compound A_2B may be formed.



- Write an expression for Q ; we call this the Ion Product:

$$Q = [A^+]^2 [B^{2-}]$$

- We will assume that precipitation **will** occur at the point where $Q \geq K_{sp}$.
- If $Q < K_{sp}$, the solution is **unsaturated** and no precipitation will occur.
- It is also possible for $Q > K_{sp}$, usually briefly.

This is a non-equilibrium situation for a solution that is **supersaturated**, i.e. has ion concentrations **greater** than equilibrium values.

- We can determine the actual concentrations of one of the ions involved in the formation of a precipitate by setting the Ion Product equal to K_{sp}

EXAMPLE 1:

How much solid $\text{Pb}(\text{NO}_3)_2$ must be added to 1.0 L of 0.0010 M Na_2SO_4 solution for a precipitate of PbSO_4 , [$K_{sp} = 1.6 \times 10^{-8}$] to form?

Assume no change in volume when the solid is added.



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

$$\text{Know: } [\text{SO}_4^{2-}]_{\text{from } \text{Na}_2\text{SO}_4} = 0.001 \text{ M}$$

If a ppt forms; $Q = K_{sp}$

\therefore Solve for $[\text{Pb}^{2+}]$ using K_{sp}

$$1.6 \times 10^{-8} = [\text{Pb}^{2+}] [0.001]$$

$$[\text{Pb}^{2+}] = 1.6 \times 10^{-5} \text{ mol L}^{-1}$$

$$\therefore \text{In } 1.0 \text{ L, mol Pb}^{2+} = 1.6 \times 10^{-5} = \text{mol Pb}(\text{NO}_3)_2$$

$$\text{mass} = 1.6 \times 10^{-5} \text{ mol} \times 331.22 \text{ g mol}^{-1}$$

$$= \underline{\underline{0.0053 \text{ g}}}$$

EXAMPLE 2:

PbCl_2 has $K_{sp} = 1.7 \times 10^{-5}$. If equal volumes of 0.030 M $\text{Pb}(\text{NO}_3)_2$ and 0.030 M KCl are mixed, will precipitation occur?

- assume 1.0 L of each solutions

(Remember that dilution will occur: If "equal volumes" are mixed, the concentration of each solute is halved.) $V_{\text{total}} = 2.0 \text{ L}$

Compare Q to K_{sp}



$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$\begin{aligned} \frac{[\text{Pb}^{2+}]_{\text{dil}}}{M_2} &= \frac{M_1 V_1}{V_2} = \frac{0.03 \text{ M} \times 1.0 \text{ L}}{2.0 \text{ L}} \\ &= 0.015 \text{ M} \end{aligned}$$

$$\begin{aligned} \frac{[\text{Cl}^-]_{\text{dil}}}{M_2} &= \frac{M_1 V}{V_2} = \frac{0.03 \text{ M} \times 1.0 \text{ L}}{2.0 \text{ L}} \\ &= 0.015 \text{ M} \end{aligned}$$

$$\begin{aligned} Q &= (0.015)(0.015)^2 \\ &= 3.78 \times 10^{-6} \end{aligned}$$

$$Q < K_{sp}$$

\therefore precipitation will not occur

EXAMPLE 3:

An experiment is performed in which 100 mL of 0.300 M $\text{Ca}(\text{NO}_3)_2$ are mixed with 200 mL of 0.20 M NaF. $[K_{sp} \text{ for } \text{CaF}_2 = 3.2 \times 10^{-11}]$



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

i) Will precipitation occur?

$$M_2 \text{ for } \text{Ca}^{2+} : [\text{Ca}^{2+}] = \frac{0.300 \text{ M} \times 0.100 \text{ L}}{0.3 \text{ L}} = 0.10 \text{ M}$$

$$M_2 \text{ for } \text{F}^- : [\text{F}^-] = \frac{0.20 \text{ M} \times 0.2 \text{ L}}{0.3 \text{ L}} = 0.133 \text{ M}$$

$$Q = [\text{Ca}^{2+}][\text{F}^-]^2 = (0.10)(0.133)^2 = 1.78 \times 10^{-3}$$

$Q > K_{sp} \therefore$ precipitate will form

ii) What is the concentration of F^- in the solution when the reaction is complete?



* moles	Before:	0.03	0.04	0
	After:	0.03 - 0.02	0	0.02 mol (solid)
		= 0.01 mol		

* mol L ⁻¹	Eq:	CaF_2	\rightleftharpoons	Ca^{2+}	+	2F^-
	Before:	solid		$\left(\frac{0.01 \text{ mol}}{0.3 \text{ L}}\right)$		0
	Eq:	solid - s		s + 0.0333		2s

$$K_{sp} = 3.2 \times 10^{-11} = (x + 0.0333)(2s)^2$$

$$3.2 \times 10^{-11} = (0.0333)[\text{F}^-]^2$$

$$\therefore [\text{F}^-] = 3.10 \times 10^{-5} \text{ M}$$

- We can also determine the K_{sp} of a compound experimentally, by carefully measuring the amounts of solutions needed to precipitate the compound in question.
- Take a sample of a solution that contains one of the ions in the compound. That sample must be of known volume and molarity.
- To this solution, carefully add a second solution which contains the other ion present in the compound. The molarity of this second solution must also be known.
- As soon as precipitation of the compound begins to occur, the volume of the second solution is measured.
- The molarities of both ions in the compound are now determined and an Ion Product is calculated. This Ion Product must be equal to K_{sp} .

EXAMPLE:

When 123.0 mL of a 0.0467 M KF solution is added to 234.0 mL of a 0.0100 M solution of $Ba(NO_3)_2$, the first trace of a precipitate of BaF_2 is seen. What is the K_{sp} for BaF_2 ?



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

When precipitation occurs; $Q = K_{sp}$

Do $M_1V_1 = M_2V_2$ for both Ba^{2+} and F^{-}

$$[Ba^{2+}] = \frac{0.0100 M \times 0.234 L}{(0.123 + 0.234) L} = 0.006555 M$$

$$[F^{-}] = \frac{0.0467 M \times 0.123 L}{(0.123 + 0.234) L} = 0.01609$$

$$Q = [Ba^{2+}][F^{-}]^2 = (0.006555)(0.01609)^2 = 1.697 \times 10^{-6} = K_{sp}$$

Selective Precipitation Problems [MH5; page 430]

- Where there is a possibility for two salts to precipitate, the less soluble will precipitate first.

EXAMPLE:

CaSO_4 has $K_{sp} = 2.4 \times 10^{-5}$ and SrSO_4 has a K_{sp} of 2.8×10^{-7} . (So SrSO_4 is less soluble.)

A solution has a concentration of 0.10 M of both Ca^{2+} and Sr^{2+} ; then $\text{Na}_2\text{SO}_4(\text{s})$ is slowly added.

What is the $[\text{SO}_4^{2-}]$ at the point where precipitation starts?

- SrSO_4 has the lower K_{sp} and will precipitate first, when: $Q = K_{sp}$

$$K_{sp}(\text{SrSO}_4) = 2.8 \times 10^{-7} = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$$

$$2.8 \times 10^{-7} = (0.10)[\text{SO}_4^{2-}]$$

$$\therefore [\text{SO}_4^{2-}] = 2.8 \times 10^{-6} \text{ M}$$

When ppt of SrSO_4 starts to form.

- As further Na_2SO_4 is added, the $[\text{SO}_4^{2-}]$ increases and SrSO_4 continues to precipitate.
- Precipitation **decreases** the $[\text{Sr}^{2+}]$, so a steady **increase** in $[\text{SO}_4^{2-}]$ is necessary for the ion product of SrSO_4 to be exceeded

$[\text{Sr}^{2+}]$	$[\text{SO}_4^{2-}]$	$[\text{Sr}^{2+}]$	$[\text{SO}_4^{2-}]$
0.10	2.8×10^{-6}	0.050	5.6×10^{-5}
0.010	2.8×10^{-5}	0.0060	4.7×10^{-5}
0.0020	1.4×10^{-4}		

- Eventually the $[\text{SO}_4^{2-}]$ will be large enough to exceed the ion product for CaSO_4 ; it starts to precipitate when the $[\text{SO}_4^{2-}]$ is:

$$K_{sp} (\text{CaSO}_4) = [\text{Ca}^{2+}] [\text{SO}_4^{2-}]$$

$$2.4 \times 10^{-5} = (0.10) [\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = 2.4 \times 10^{-4} \text{ M}$$

- At this point (still saturated in SrSO_4) the $[\text{Sr}^{2+}]$ will be:

$$\hookrightarrow [\text{SO}_4^{2-}] = 2.4 \times 10^{-4} \text{ M}$$

Back to K_{sp} for SrSO_4 :

$$\begin{aligned} K_{sp} = 2.8 \times 10^{-7} &= [\text{Sr}^{2+}] [\text{SO}_4^{2-}] \\ &= [\text{Sr}^{2+}] (2.4 \times 10^{-4}) \end{aligned}$$

$$\therefore [\text{Sr}^{2+}] = 1.2 \times 10^{-3} \text{ mol L}^{-1}$$

- As a fraction of the amount originally present,

$$\text{Sr}^{2+} \text{ remaining} = \frac{0.0012 \text{ M}}{0.100 \text{ M}} = 0.012$$

- Nearly 99% of the Sr^{2+} has precipitated!
- This effect can be used in Semi-micro Qualitative Analysis schemes.....[MH5; page 436]

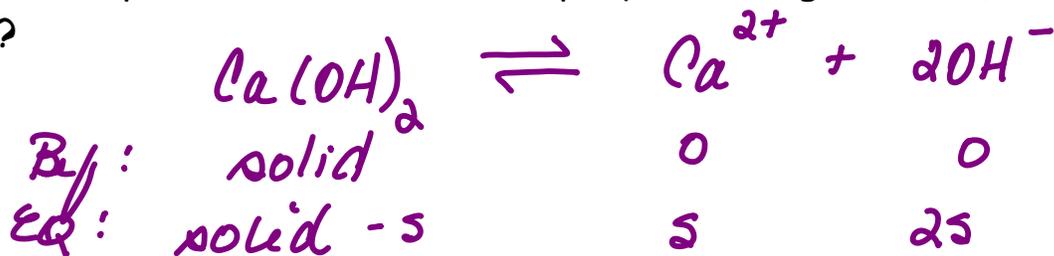
Solubility and pH (and Complexation) Problems [MH5; 16.2]

- The solubility of many substances influences, and is influenced by, the pH of the solution.
- Metal Hydroxides often have low solubility.

EXAMPLE 1:

Ca(OH)_2 has $K_{sp} = 7.9 \times 10^{-6}$.

What is the pH of a solution made by equilibrating solid Ca(OH)_2 with water?



$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{OH}^-]^2 \\ &= (s)(2s)^2 \\ 7.9 \times 10^{-6} &= 4s^3 \end{aligned}$$

$$s^3 = \frac{7.9 \times 10^{-6}}{4} = 1.975 \times 10^{-6}$$

$$s = \sqrt[3]{1.975 \times 10^{-6}}$$

$$= 1.25 \times 10^{-2} = [\text{Ca}^{2+}]$$

$$[\text{OH}^-] = 2s = 2(1.25 \times 10^{-2}) = 2.5 \times 10^{-2} \text{ M}$$

$$\text{pOH} = 1.60$$

$$\begin{aligned} \text{pH} &= 14 - 1.60 \\ &= \underline{\underline{12.40}} \end{aligned}$$

- Many metal hydroxides have solubilities so low that their saturated solutions are **not** appreciably basic.

EXAMPLE 2:



Cu(OH)_2 has $K_{sp} = 1.6 \times 10^{-19}$

a) What is the pH of a saturated solution of Cu(OH)_2 ?

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

$$= 4s^3$$

$$\therefore s = \frac{3.42 \times 10^{-7}}{4} = [\text{Cu}^{2+}]$$

$$[\text{OH}^-] = 2s = 6.84 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{pOH} = 6.16 \quad \therefore \text{pH} = 14 - 6.16 = \underline{\underline{7.84}}$$

b) What is the maximum $[\text{Cu}^{2+}]$ concentration possible in a neutral solution? (pH = 7) $[\text{H}^+] = 1.0 \times 10^{-7} = [\text{OH}^-]$

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

$$Q = [\text{Cu}^{2+}](1.0 \times 10^{-7})^2$$

$$= K_{sp} = 1.6 \times 10^{-19}$$

$$\Rightarrow 1.6 \times 10^{-19} = [\text{Cu}^{2+}](1.0 \times 10^{-7})^2$$

$$[\text{Cu}^{2+}] = \underline{\underline{1.60 \times 10^{-5} \text{ mol L}^{-1}}}$$

c) What is the maximum pH of a solution in which $[Cu^{2+}] = 0.50 \text{ M}$?

$$Q = (0.50) [OH^-]^2 = K_{sp} = 1.6 \times 10^{-19}$$

$$[OH^-] = 5.56 \times 10^{-10}$$

$$pOH = 9.25 \quad \Rightarrow \quad pH = 14 - 9.25 \\ = \underline{\underline{4.75}}$$

• What conclusion can we draw from this calculation?

$Cu(OH)_2$ is only appreciably soluble in acidic solution.

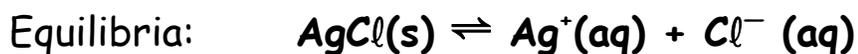
• The solubilities of salts of weak acids are very much affected by the pH of the solution; to be discussed qualitatively only.

EXAMPLE:

AgCl and AgBr are **not** appreciably soluble. When HNO_3 is added, nothing happens.

CH_3COOAg also has a low solubility in water, but dissolves readily if HNO_3 is added.

Can we explain this observation qualitatively?

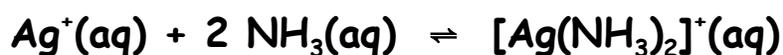


Complexation can increase solubility

- The solubility of many salts can be increased by the addition of a species that can form a complex ion with one of the ions (usually the cation) formed when a poorly soluble salt dissolves.

EXAMPLE 1:

AgCl ($K_{\text{sp}} = 1.8 \times 10^{-10}$) dissolves when $\text{NH}_3(\text{aq})$ or $\text{CN}^-(\text{aq})$ is added:



EXAMPLE 2:

$\text{Cu}(\text{OH})_2$ (1.6×10^{-19}) similarly dissolves when $\text{NH}_3(\text{aq})$ is added:

