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:

\[
\text{NaCl (s)} \xrightarrow{H_2O} \text{NaCl (aq)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)
\]

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\(^{-1}\)

**EXAMPLE 1:** \(\text{Bi}_2\text{S}_3(\text{s}) \rightarrow 2 \text{Bi}^{3+}(\text{aq}) + 3 \text{S}^{2-}(\text{aq})\)

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

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

- **Solid** \(\text{Bi}_2\text{S}_3\) **not included**
EXAMPLE 2:
For a solution of AgCl in water, the equilibrium is:

\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \]

- 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 AgCl(s). \([K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}]\)

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
\]

\[
\text{Ref: solid} \quad \text{Eq: solid} - s \quad s \\
\]

\[
K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10} = (s)(s) = s^2
\]

\[
s = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} \text{ mol L}^{-1}
\]
EXAMPLE 2:
Calcium carbonate, $\text{CaCO}_3$, has a solubility in water of $0.0180 \text{ g L}^{-1}$ at $25 \degree \text{C}$. Calculate the $K_{sp}$ for $\text{CaCO}_3$. [MM of $\text{CaCO}_3 = 100.1 \text{ g mol}^{-1}$]

\[
\text{CaCO}_3 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{CO}_3^{2-} (aq)
\]

By: solid
Eq: solid $- s$ $s$ $s$

\[
K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (s)(s)
\]

\[
K_{sp} = s^2
\]

$s = 0.018 \text{ g L}^{-1}$

To use $K_{sp}$, "$s"$ must be in $\text{mol L}^{-1}$

$\text{g L}^{-1} \Rightarrow \text{mol L}^{-1}$ ($\text{g} \rightarrow \text{mol}$; use MM)

Convert $s$:

\[
\frac{0.018 \text{ g L}^{-1}}{100.1 \text{ g mol}^{-1}} = 1.798 \times 10^{-4} \text{ mol L}^{-1}
\]

Substituting:

\[
K_{sp} = s^2 = (1.798 \times 10^{-4})^2
\]

\[
= 3.2 \times 10^{-8}
\]
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 CaF$_2$ = 78.1 g mol$^{-1}$]

\[
\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^- \\
\text{B_r}: \text{solid} \quad 0 \quad 0 \\
\text{E_q}: \text{solid} - s \quad s \quad 2s
\]

\[
K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]^2 = (s)(2s)^2 = (s)[(2s)(2s)] = 4s^3
\]

\[
s = \frac{0.00170 \text{ g}}{0.100 \text{ L}} = 0.017 \text{ g L}^{-1}
\]

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:

\[
K_{sp} = 4s^3 = 4 \left[(2.18 \times 10^{-4})^3\right] = 4.13 \times 10^{-11}
\]
EXAMPLE 4:
If solid PbCl₂ equilibrates with pure water, what are [Pb²⁺] and [Cl⁻] in the solution at equilibrium? \( K_{sp}(\text{PbCl}_2) = 1.7 \times 10^{-5} \)

\[
\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-
\]

By: solid \( \quad \quad \quad \quad \quad \quad \) 0 \( \quad \quad \quad \quad \quad \quad \) 0
Eq: solid \( \quad \quad \quad \quad \quad \quad \) s \( \quad \quad \quad \quad \quad \quad \) 2s

\[
K_{sp} = [\text{Pb}^{2+}] [\text{Cl}^-]^2
\]
\[
= (s)(2s)^2 = 4s^3
\]
\[
1.7 \times 10^{-5} = 4s^3
\]
\[
1.7 \times 10^{-5} = s^3 = 4.2 \times 10^{-6}
\]
\[
s = \sqrt[3]{4.2 \times 10^{-6}}
\]
\[
= 1.62 \times 10^{-2} \text{ mol L}^{-1}
\]

\[
[\text{Pb}^{2+}] = s = 1.62 \times 10^{-2} \text{ mol L}^{-1}
\]
\[
[\text{Cl}^-] = 2s = 2(1.62 \times 10^{-2})
\]
\[
= 3.24 \times 10^{-2} \text{ mol L}^{-1}
\]
Solubility and the Common Ion Effect

- The "Common Ion Effect" is an illustration of Le Chatelier’s Principle.

- Consider the equilibrium:

\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \]

- 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
  - Shift LEFT, towards AgCl
  - More 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
  - "S" is smaller
  - 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.

\[ \text{Cl}^- \text{ is the common ion } \]

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

\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \quad [\text{Cl}^-]_{\text{NaCl}} = 0.010 \text{M}
\]

\[
\begin{align*}
\text{AgCl} & \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \\
\text{Ref: Solid} & \quad 0 \quad 0.010 \\
\text{EQ: Solid} - s & \quad s \\
\end{align*}
\]

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

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

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 = \(1.3 \times 10^{-5}\) M (p. 143).
In the NaCl solution: only 0.13 % of the solubility in water alone!
EXAMPLE 2:

What is the concentration of \( \text{Ca}^{2+} \) (aq) in \( \text{mol L}^{-1} \), in a solution made by equilibrating \( \text{CaF}_2(s) \) with 0.20 M KF solution? \( \text{F}^- \) is common ion  

\[ \text{K}_\text{sp} \text{ for } \text{CaF}_2 = 4.1 \times 10^{-11} \]  
(Compare this answer with p. 145)

\[
\begin{align*}
\text{KF} & \rightarrow K^+ + F^- \quad \therefore [F^-]_{\text{KF}} = 0.20 \text{ M} \\
\text{CaF}_2 & \rightleftharpoons \text{Ca}^{2+} + 2F^- \\
\text{solid} & \quad \text{s} \quad \text{s} \\
\text{solid} - s & \quad \text{s} \quad 2s + 0.20
\end{align*}
\]

\[
\begin{align*}
\text{K}_\text{sp} &= [\text{Ca}^{2+}] [F^-]^2 \\
4.1 \times 10^{-11} &= (s)(2s + 0.20)^2 \\
s &= \frac{4.1 \times 10^{-11}}{(0.20)^2} = \frac{1.025 \times 10^{-9}}{[\text{Ca}^{2+}]}
\end{align*}
\]
EXAMPLE 3:

Calculate the solubility of PbCl₂, in mol L⁻¹, in a solution of 0.15 M MgCl₂. \[K_{sp} \text{ for PbCl}_2 \text{ is } 1.7 \times 10^{-5}\]

\[
\text{MgCl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^-
\]

\[
[\text{Cl}^-]_{\text{MgCl}_2} = 2 \times 0.15 \text{ mol L}^{-1} = 0.30 \text{ mol L}^{-1}
\]

\[
\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-
\]

\[
\begin{array}{c|c|c}
\text{solid} & 0 & 0.30 \\
\text{solid -s} & s & 2s + 0.30
\end{array}
\]

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

\[
1.7 \times 10^{-5} = (s)(2s + 0.30)^2
\]

\[
s = \frac{1.7 \times 10^{-5}}{(0.30)^2} = 1.9 \times 10^{-4} \text{ mol L}^{-1}
\]
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 as 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.
  \[ A_2B(\text{s}) \rightleftharpoons 2A^+ + B^{2-} \]

- 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.
  \[ 2A^+(aq) + B^{2-}(aq) \rightleftharpoons A_2B(\text{s}); \ A_2B(\text{s}) \rightleftharpoons 2A^+(aq) + B^{2-}(aq) \]

- 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 $\text{Pb(NO}_3\text{)}_2$ must be added to 1.0 L of 0.0010 M $\text{Na}_2\text{SO}_4$ solution for a precipitate of $\text{PbSO}_4$ , $[K_{sp} = 1.6 \times 10^{-8}]$ to form? Assume no change in volume when the solid is added.

\[
\text{Raw: } \text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 (s)
\]

\[
\text{Eq: } \text{PbSO}_4 (s) \rightleftharpoons \text{Pb}^{2+} (aq) + \text{SO}_4^{2-} (aq)
\]

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

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

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

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

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

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

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

\[
\text{Mass} = 1.6 \times 10^{-5} \text{ mol} \times 331.22 \text{ g mol}^{-1}
\]

$= 0.0053\text{ g}$
EXAMPLE 2:

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

Assume 1.0 L of each solution.

(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 \( K_{sp} \)

\[ \text{Eq: } \text{PbCl}_2(s) \rightarrow \text{Pb}^{2+} + 2\text{Cl}^- \]

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

\[ [\text{Pb}^{2+}]_{\text{dil}} = \frac{M_1V_1}{V_2} = \frac{0.03 \text{ M} \times 1.0 \text{ L}}{2.0 \text{ L}} \]

\[ = 0.015 \text{ M} \]

\[ [\text{Cl}^-]_{\text{dil}} = \frac{M_1V}{V_2} = \frac{0.03 \text{ M} \times 1.0 \text{ L}}{2.0 \text{ L}} \]

\[ = 0.015 \text{ M} \]

\[ Q = (0.015)(0.015)^2 \]

\[ = 3.78 \times 10^{-6} \]

\[ Q < K_{sp} \]

\[ \therefore \text{precipitation will not occur} \]
EXAMPLE 3:
An experiment is performed in which 100 mL of 0.300 M Ca(NO₃)₂ are
mixed with 200 mL of 0.20 M NaF. \[ K_{sp} \text{ for } CaF_2 = 3.2 \times 10^{-11} \]

\[ CaF_2 \rightleftharpoons Ca^{2+} + 2F^- \quad K_{sp} = [Ca^{2+}][F^-]^2 \]

i) Will precipitation occur?

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

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

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

\[ Q > K_{sp} \therefore \text{ precipitation will form} \]

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

\[ Ca^{2+} + 2F^- \rightarrow CaF_2 \]

\[ \text{Initial: } \quad 0.03 \quad 0.04 \quad 0 \]

\[ \text{Change: } -0.02 \quad -0.02 \quad 0.02 \text{ mol (solid)} \]

\[ \text{Equilibrium: } \quad 0.01 \text{ mol} \]

\[ \text{Equilibrium: } \quad CaF_2 \rightleftharpoons Ca^{2+} + 2F^- \]

\[ \text{Initial: } \quad \frac{0.01 \text{ mol}}{0.3L} \quad 0 \]

\[ \text{Equilibrium: } \quad 0 \quad 0.0333 \quad 2S \]

\[ K_{sp} = 3.2 \times 10^{-11} = [Ca^{2+}][F^-]^2 \]

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

\[ \therefore [F^-] = 3.10 \times 10^{-5} \text{ M} \]
• 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$_2$?

\[
\text{BaF}_2 (s) \rightleftharpoons \text{Ba}^{2+} + 2\text{F}^-
\]

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

When precipitation occurs: \( Q = K_{sp} \)

Do $M_i V_i = M_2 V_2$ for both $\text{Ba}^{2+}$ and $\text{F}^-$

\[
[\text{Ba}^{2+}] = \frac{0.01 M \times 0.234 L}{(0.123 + 0.234)L} = 0.006555 M
\]

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

\[
Q = [\text{Ba}^{2+}] [\text{F}^-]^2 = (0.006555)(0.01609)^2 = 1.697 \times 10^{-6} = K_{sp}
\]
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 $2.8 \times 10^{-7}$. (So SrSO$_4$ is less soluble.)

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

What is the [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 point of SrSO$_4$ starts to form.

- As further Na$_2$SO$_4$ is added, the [SO$_4^{2-}$] increases and SrSO$_4$ continues to precipitate.

- Precipitation decreases the [Sr$^{2+}$], so a steady increase in [SO$_4^{2-}$] is necessary for the ion product of SrSO$_4$ to be exceeded

<table>
<thead>
<tr>
<th>Sr$^{2+}$</th>
<th>SO$_4^{2-}$</th>
<th>Sr$^{2+}$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>$2.8 \times 10^{-6}$</td>
<td>0.050</td>
<td>$5.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.010</td>
<td>$2.8 \times 10^{-5}$</td>
<td>0.0060</td>
<td>$4.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.0020</td>
<td>$1.4 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Eventually the $[\text{SO}_4^{2-}]$ will be large enough to exceed the ion product for $\text{CaSO}_4$; 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 $\text{SrSO}_4$) the $[\text{Sr}^{2+}]$ will be:

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

Back to $K_{sp}$ for $\text{SrSO}_4$:

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

$$= [\text{Sr}^{2+}] \ (2.4 \times 10^{-4})$$

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

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 $\text{Sr}^{2+}$ 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?

\[
\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-
\]

\[
\begin{array}{c|c|c|c}
\text{By:} & \text{solid} & 0 & 0 \\
\text{Eq: solid} & \text{-5} & 5 & 25
\end{array}
\]

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

\[
= (5) (25)^2
\]

\[
7.9 \times 10^{-6} = \frac{1}{4} \times 3
\]

\[
5^3 = 7.9 \times 10^{-6} = 1.975 \times 10^{-6}
\]

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

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

\[
[\text{OH}^-] = 25 = 2(1.25 \times 10^{-2}) = 2.5 \times 10^{-2} \text{M}
\]

\[
\text{pOH} = 1.60
\]

\[
\text{pH} = 14 - 1.60 = 12.40
\]
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?

\[
\text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^-
\]

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

\[
[\text{OH}^-] = s = \frac{3.42 \times 10^{-7}}{45^3} = 6.84 \times 10^{-7} \text{ mol L}^{-1}
\]

\[
\text{pOH} = 6.16 \quad \therefore \quad \text{pH} = 14 - 6.16 = 7.84
\]

b) What is the maximum \([\text{Cu}^{2+}]\) concentration possible in a neutral solution? (pH = 7)

\[
[H^+] = 1.0 \times 10^{-7} = [\text{OH}^-]
\]

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

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

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

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

\[
[\text{Cu}^{2+}] = 1.60 \times 10^{-5} \text{ mol L}^{-1}
\]
c) What is the maximum pH of a solution in which \([\text{Cu}^{2+}] = 0.50 \, M\)?

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

\([\text{OH}^-] = 5.56 \times 10^{-10}\)

\[
\text{pOH} = 9.25 \quad \Rightarrow \quad \text{pH} = 14 - 9.25 = 4.75
\]

• What conclusion can we draw from this calculation?

\(\text{Cu(OH)}_2\) 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 HNO₃ is added, nothing happens. CH₃COOAg also has a low solubility in water, but dissolves readily if HNO₃ is added. Can we explain this observation qualitatively?

Equilibria:  

\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \]

\[ \text{H}^+ + \text{Cl}^- \rightarrow \text{HCl} \text{ (strong acid)} \]

\[ \text{AgBr(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq) \]

\[ \text{H}^+ + \text{Br}^- \rightarrow \text{HBr} \text{ (strong acid)} \]

\[ \text{AgAc (s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Ac}^-(aq) \]

\[ \text{H}^+(aq) + \text{Ac}^-(aq) \rightarrow \text{HAc} \text{ (weak acid)} \]
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 ($K_{sp} = 1.8 \times 10^{-10}$) dissolves when NH$_3$(aq) or CN$^-$ (aq) is added:

Equilibria:

\[
AgCl \rightleftharpoons Ag^+(aq) + Cl^-(aq)
\]

\[
Ag^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons [Ag(\text{NH}_3)_2]^{+}(aq)
\]

or

\[
Ag^+(aq) + 2 \text{CN}^-(aq) \rightleftharpoons [Ag(\text{CN})_2]^{-}
\]

**EXAMPLE 2:**

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

Equilibria:

\[
\text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+}(aq) + 2 \text{OH}^-(aq)
\]

\[
\text{Cu}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons [\text{Cu(\text{NH}_3})_4]^{2+}
\]