Lecture Notes U: Solubility equilibria

1) Orange tornado video
In this demo, a solution of KI is poured into Hg(NO₃)₂. What solid do you think precipitates?

   a) Hg₂I   b) HgI₂   c) HgI₃   d)KNO₃

2) Selective precipitation of ions

Concept
You have a solution in which [Ag⁺]=0.10M and [Mg⁺]=0.1M. You start to add a solution of Sodium carbonate (Na₂CO₃). What happens? (Ksp[Ag₂CO₃] = 6.2x10⁻¹² ; Ksp[MgCO₃] = 4.0x10⁻⁵)

(a) Ag₂CO₃ precipitates first   (b) MgCO₃ precipitates first   (c) both precipitate at the same time
How much Ag⁺ is still in the solution when Mg^{2+} begins to precipitate?

\[ K_{sp} (Ag_2CO_3) = 6.2 \times 10^{-12} = [Ag^+]^2 [CO_3^{2-}] \]

When \[ [CO_3^{2-}] = \frac{4 \times 10^{-4}}{y} \text{ M} \]

\[ \Rightarrow [Ag^+] = \frac{2.5 \times 10^{-3}}{0.1} \text{ M} \]

Extract all but \(2.5 \times 10^{-3} \text{ M}\)

Left \(\frac{2.5 \times 10^{-3}}{0.1} = 2.5\% \) left out

Formation of solid is a common purification scheme.

Re-crytallization
3) **Complex ion formation**

Ligands binding to metals

Research of Jonathan S. Lindsey (http://www2.ncsu.edu/ncsu/chemistry/jsl.html)
Problem

\[
\text{Zn}^{2+} + \text{NH}_3 \Leftrightarrow \text{Zn} (\text{NH}_3)^{2+} \quad K_1 = 1.5 \times 10^2
\]

\[
\text{Zn} (\text{NH}_3)^{2+} + \text{NH}_3 \Leftrightarrow \text{Zn} (\text{NH}_3)_2^{2+} \quad K_2 = 1.8 \times 10^2
\]

\[
\text{Zn} (\text{NH}_3)_2^{2+} + \text{NH}_3 \Leftrightarrow \text{Zn} (\text{NH}_3)_3^{2+} \quad K_3 = 2 \times 10^2
\]

\[
\text{Zn} (\text{NH}_3)_3^{2+} + \text{NH}_3 \Leftrightarrow \text{Zn} (\text{NH}_3)_4^{2+} \quad K_4 = 90
\]

\[
\text{Zn}^{2+} + 4\text{NH}_3 \Leftrightarrow \text{Zn} (\text{NH}_3)_4^{2+} \quad K_f = 4.9 \times 10^8 = K_1 K_2 K_3 K_4
\]

A solution is made that is 0.10M in ZnCl₂ and 1.0M in NH₃. What is the concentration of Zn²⁺, Zn(NH₃)₄²⁺ and Zn(NH₃)₃²⁺ in the solution.

\[
\text{Zn}^{2+} + 4\text{NH}_3 \Leftrightarrow \text{Zn} (\text{NH}_3)_4^{2+} \quad K_f = 4.9 \times 10^8
\]

\[
\begin{array}{c|c|c|c|c|c}
& 0.1 & 1 & -0.1 & -0.4 & 0.1 \\
\hline
\text{Zn}^{2+} & 1-x & x & 0.6 & 0.1-x & 0.6 \\
\text{NH}_3 & 0 & 0.6 & 0.6+y & 0.6+y & 0.6+y \\
\hline
\end{array}
\]

Assume \( x << 0.1 \)

\[
4.9 \times 10^8 = \frac{[\text{Zn} (\text{NH}_3)_4^{2+}]}{([\text{Zn}^{2+}]) ([\text{NH}_3]^4)} = \frac{0.1}{x (0.6)^4}
\]

\[
x = 1.6 \times 10^{-9} = [\text{Zn}^{2+}]
\]

\[
\text{Zn} (\text{NH}_3)_3^{2+} + \text{NH}_3 \rightleftharpoons \text{Zn} (\text{NH}_3)_4^{2+} \quad K_4 = 90
\]

\[
K_4 = 90 = \frac{[\text{Zn} (\text{NH}_3)_4^{2+}]}{[\text{Zn} (\text{NH}_3)_3^{2+}] ([\text{NH}_3])} = \frac{0.1}{x (0.6)^4} \Rightarrow x = 1.8 \times 10^{-3} = [\text{Zn} (\text{NH}_3)_3^{2+}]
\]

\[
K_3 = 200 = \frac{[\text{Zn} (\text{NH}_3)_3^{2+}]}{[\text{Zn} (\text{NH}_3)_2^{2+}] ([\text{NH}_3])} = \frac{x}{0.6} \Rightarrow \int \frac{1.8 \times 10^{-3} = [\text{Zn} (\text{NH}_3)_3^{2+}]}{[\text{Zn} (\text{NH}_3)_2^{2+}] ([\text{NH}_3])} = \frac{1.8 \times 10^{-3} = [\text{Zn} (\text{NH}_3)_3^{2+}]}{1.6 \times 10^{-9} = [\text{Zn}^{2+}]} = 1.4 \times 10^{-7}
\]
Black and white photography

The film is prepared by making an emulsion of silver halides (AgBr) in gelatin. When exposed to light, photochemical reactions convert the silver halide to a photosensitized form:

\[
\text{take picture: } \quad \text{AgBr} + \text{light} \rightarrow \text{photosensitized AgBr}
\]

When exposed to hydroquinone developer, the photosensitized AgBr is reduced to metallic silver.

\[
\text{developer: } \quad \text{photosensitized AgBr} + \text{hydroquinone} \rightarrow \text{Ag}
\]

This development process is stopped with a “stopper” solution KBr, which is first put on the film and then washed off with water.

A fixer solution of sodium thiosulfate (Na\(_2\)S\(_2\)O\(_3\)), also called hypo, is then used to remove the unexposed AgBr. The S\(_2\)O\(_3\)\(^-\) complexes with the silver, and makes the AgBr soluble.

\[
\text{fixer: } \quad \text{Ag}^+ (\text{aq}) + 2 \text{S}_2\text{O}_3^{2-} (\text{aq}) \rightleftharpoons \text{Ag(S}_2\text{O}_3\text{)}_2^{3-} (\text{aq}) \quad K = 1.7 \times 10^{13}
\]

The fixer also contains an acid that hardens the gelatin. The hypo is then washed off, otherwise it turns the films yellow by forming sodium sulfate (Na\(_2\)SO\(_4\)).

So the part of the film that was exposed to light now contains Ag metal. This gives a negative image. You must now repeat the process, to form a positive image on paper.
Compare the solubility of AgBr in water with that in a 0.2M solution of Na₂S₂O₃. (K_{sp} (AgBr) = 7.7 \times 10^{-13}).

\[
\text{AgBr}_{(s)} \rightleftharpoons \text{Ag}^{+} + \text{Br}^{-} \quad \text{K}_{sp} = 7.7 \times 10^{-13}
\]

Excess $S$ $S$

\[
K_{sp} = 7.7 \times 10^{-13} = [\text{Ag}^{+}][\text{Br}^{-}] = S^2 \\
\therefore S = 8.8 \times 10^{-7} \text{ M}
\]

\text{INSOLUBLE}

\[
\text{AgBr}_{(s)} \rightleftharpoons \text{Ag}^{+} + \text{Br}^{-} \quad \text{K}_{sp} = 7.7 \times 10^{-13}
\]

\[
\text{Ag}^{+} + 2S_2O_3^{-2} \rightleftharpoons \text{Ag}(S_2O_3)^{2-3} \\
K = 1.7 \times 10^{13}
\]

\[
\text{AgBr}_{(s)} + 2S_2O_3^{-2} \rightleftharpoons \text{Ag}(S_2O_3)^{2-3} + \text{Br}^{-} \\
K = K_{sp} K_f = 13.1
\]

\[
\text{Excess} \quad 0.2 \quad 0 \quad 0.1
\]

\[
\text{Dissolves until Thiosulfate runs out}
\]

\[
\text{Here} \quad 0.1 \text{ M}
\]
4) Recrystallization as a means of purification

ZONE REFINEMENT OF $\text{Si}$

5) Extraction as a means of purification

TOLUENE $\Leftarrow$ STUFF YOU WANT
WATER $\Leftarrow$ JUNK (ESPECIALLY IONS/SALT)
A solute molecule, $A$, has a partition coefficient of 3 between toluene and water (with 3 times as much in the toluene phase).

\[
A_{\text{(aq)}} \rightleftharpoons A_{\text{TOLUENE}} \quad K = 3 = \frac{[A_{\text{TOLUENE}}]}{[A_{\text{(aq)}}]}
\]

Suppose that 100ml of a 0.01M aqueous solution of $A$ is extracted with toluene. What fraction of $A$ remains in the aqueous phase if an extraction is done with 500ml of toluene.

INITIAL 0.01 M SOLUTION OF $A$ IN H$_2$O

Moles of $A = (0.010 \text{ M}) (0.100)$

$= 0.001 \text{ mole } = 1 \times 10^{-3}$

WATER

$1 \times 10^{-3} - x$

TOLUENE

$x$

VOLUME

0.100L

0.500L

\[
K = 3 = \frac{[A_{\text{TOLUENE}}]}{[A_{\text{(aq)}}]} = \frac{x/0.5}{(1 \times 10^{-3} - x)/0.1} = \frac{x}{5 \times 10^{-3} - x}
\]

$x = 9.77 \times 10^{-4}$ mole of $A$ in TOLUENE

MOLES OF $A$ LEFT IN WATER

$15 \times 1 \times 10^{-3} - 0.977 \times 1\times 10^{-3} = 0.062 \times 10^{-3}$

\[
\frac{0.062}{1.00} = 6.2\% \text{ of } A \text{ REMAINS IN WATER}
\]