Lecture Notes T: Solubility equilibria

1) Acid Mine Drainage

Water leaving a mine in Pennsylvania. The red color is from solid Fe(OH)₃ precipitating as the mine water mixes with river water.

Overall reaction

\[
4 \text{FeS}_2 + 15 \text{O}_2 + 14 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3 \downarrow + 8 \text{H}_2\text{SO}_4
\]

Pyrite + Oxygen + Water → "Yellowboy" + Sulfuric Acid

Four subreactions

\[
2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{SO}_4^{2-} + 4 \text{H}^+
\]

Pyrite + Oxygen + Water → Ferrous Iron + Sulfate + Acidity

\[
4 \text{Fe}^{2+} + \text{O}_2 + 4 \text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O}
\]

Ferrous Iron + Oxygen + Acidity → Ferric Iron + Water

\[
4 \text{Fe}^{3+} + 12 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3 \downarrow + 12 \text{H}^+
\]

Ferric Iron + Water → Ferric Hydroxide (yellowboy) + Acidity

\[
\text{FeS}_2 + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+
\]

Pyrite + Ferric Iron + Water → Ferrous Iron + Sulfate + Acidity
A surprising solubility behavior in acid mine drainage

Say I have a solution with 100ml of water and some salt at the bottom (a saturated solution). If I add water, what will happen to the amount of salt:

a) amount of salt increases  
b) amount of salt decreases  
c) amount of salt stays the same

Let’s try it with some acid mine effluent

2) Solubility of ionic solids (salts)

- All nitrates (NO$_3^-$) are soluble
- All chlorates (ClO$_3^-$) are soluble
- Most perchlorates (ClO$_4^-$) are soluble except K(ClO$_4$)
- Almost all Group I (Li, Na, K, Rb, Cs) salts are soluble, K(ClO$_4$) is an exception
- Most halides are soluble (except AgCl, AgBr, AgI, Hg$_2$Cl$_2$, Hg$_2$Br$_2$, HgI$_2$, MgF$_2$, CaF$_2$, PbI$_2$)

- Most sulfates (SO$_4^{2-}$) are soluble except CaSO$_4$, Ag$_2$SO$_4$, Hg$_2$SO$_4$, SrSO$_4$, BaSO$_4$, PbSO$_4$
- Most sulfides (S$^{2-}$) (except Group I and II) are insoluble
- Most carbonates (CO$_3^{2-}$) (except Group I and NH$_4^+$ salt) are insoluble
- Most sulfites (SO$_3^{2-}$) (except Group I and NH$_4^+$ salt) are insoluble
- Most phosphates (PO$_4^{3-}$) (except Group I and NH$_4^+$ salt) are insoluble
- Most hydroxides (OH$^-$) (except Group I and Ba$^{2+}$ salt) are insoluble
3) **Saturated Solution, and the solubility product**

Consider a beaker containing 100ml of water, with solid AgCl on the bottom.

What is the concentration of \([\text{Ag}^+]\) and \([\text{Cl}^-]\) in the solution?

How many grams of AgCl are dissolved in the water?

What is the solubility of AgCl in grams/liter?

How much AgCl dissolves in 100ml vs. 200ml of water?
Concept

If NaCl is added to the above solution, the amount of AgCl solid at the bottom of the beaker

a) increases  

b) decreases  

c) stays the same

4) The common ion effect

What is the solubility of AgCl in 0.1M NaCl?

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

\[ \text{ASSUM} \quad x << 0.1 \]

\[ k_{sp} = [\text{Ag}^+] [\text{Cl}^-] = x (0.1) = 1.6 \times 10^{-9} \]

\[ x = 1.6 \times 10^{-9} \]

\[ [\text{Ag}^+] = 1.6 \times 10^{-9} \text{ m} \]

Solubility = \[ \frac{1.6 \times 10^{-9} \text{ m} \times (143.32 \text{ g AgCl/mole})}{1 \text{ m} \text{ H}_2 \text{O}} = 2.3 \times 10^{-7} \text{ g AgCl/mole} \]

In water, sol = 1.8 \times 10^{-3} \text{ M} \text{AgCl} \leftarrow 10^4 \text{ DIFF}
ACID MINE EFFLUENT

PH IS ACIDIC

$\text{H}_2\text{O}$

DILUTE THE ACID

PH BECOMES MORE NEUTRAL

$\text{Na}_2\text{(OH)}_3$
5) **pH effects on solubility**

**Concept**

Which of the following will AgOH \((K_{sp}=1.5\times10^{-8})\) be most soluble in?

(a) pure water  
(b) a buffer solution at pH=11  
(c) a buffer solution at pH=4

\[
\text{AgOH} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{OH}^- (aq)
\]

**Pure Water**

\[
\text{AgOH} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{OH}^- (aq)
\]

Excess S S

\[K_{sp} = 1.5 \times 10^{-8}
\]

\[\text{[OH}^-\text{]} = 1.2 \times 10^{-4} \quad \rho_{\text{M}} = 10.1\]

**Buffer with pH=11**

\[\text{[H}^+\text{]} = 10^{-1} \quad \text{[OH}^-\text{]} = 10^{-3}
\]

\[\text{AgOH} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{OH}^- (aq)
\]

Excess S S

\[K_{sp} = 1.5 \times 10^{-8} \Rightarrow S = 1.5 \times 10^{-5} \text{ M}
\]

**Buffer with pH=4**

\[\rho_{\text{M}} = 10^{-10}
\]

\[\text{AgOH} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{OH}^- (aq)
\]

Excess S S

\[K_{sp} = 1.5 \times 10^{-8} = S (10^{-10})
\]

\[S = 150 \text{ M}
\]

Breaking soluble the buffer
Tooth Decay

The enamel covering of your teeth contains the mineral hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, which dissolves in water to give:

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 (s) \rightleftharpoons 10 \text{ Ca}^{2+} + 6 \text{ PO}_4^{3-} + 2 \text{ OH}^-$$

**Concept**

Is hydroxyapatite more soluble in:

a) acidic solution                 b) neutral water                  c) basic solution

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 (s) \rightleftharpoons 10 \text{ Ca}^{2+} + 6 \text{ PO}_4^{3-} + 2 \text{ OH}^-$$

**TREATMENT**

$\text{F}^-$ is a weak base

$$\text{F}^- + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}^-$$

Strong base $\rightarrow$ Weak base

**DIAGRAM**

- Teeth dissolve $\rho \text{H} < 5.5$
- Bacteria $\rho \text{H} = 5$
- Vomit $\rho \text{H} = 1.5$
- $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 (s) \rightleftharpoons 10 \text{ Ca}^{2+} + 6 \text{ PO}_4^{3-} + 2 \text{ OH}^-$

**FLOURIDOR**

$\text{F}^- \text{TREATMENT}$