"A" students work (without solutions manual) ~ 10 problems/night.

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Module #19:
Precipitation Reactions

Introduction/
Context

Solution Equilibria: Solubility

In homes older than 1980 most of the plumbing is lead pipe (Pb = plumbose). Even in newer homes with copper pipe, solder joints are a lead/tin alloy. Even without solder joints, many of the faucet heads are machined with a 10-20% lead content brass.

The limit on lead is set to be
<5 g Pb/10⁹ g water
< 5 x10⁻⁹ g Pb/g water
< 5 ppb

What do you think the average homeowner prefers?

Roman pipes at Pompei

Solutions:
1. Take out all plumbing
2. Place water filtration devices at all outlets (sinks, showers, hoses).
3. Have the water department take care of it somehow.

What makes insoluble salts?
hint: same concepts as govern what ions are or are not spectators.

Coat the pipes from the inside out with a dense impermeable quasi-permanent layer

= insoluble salt
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Module #19: Precipitation Reactions

Review Charge

Density

Energy_{electrostatic} = k \left( \frac{q_1 q_2}{d^2} \right)

Charge on object 1 or 2, in coulombs
Distance between the objects

\[ E_{el} = k \left( \frac{q_1 q_2}{r_1 + r_2^2} \right) \]
Coulomb's Law

Review: Module 5

Are there differences in predicted electrostatic effect?

<table>
<thead>
<tr>
<th>Ion</th>
<th>Symbol</th>
<th>Charge</th>
<th>Radius (pm)</th>
<th>Charge/radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>D+</td>
<td>1</td>
<td>4</td>
<td>0.25</td>
</tr>
<tr>
<td>lithium</td>
<td>Li+</td>
<td>1</td>
<td>89.66666667</td>
<td>0.01152416</td>
</tr>
<tr>
<td>sodium</td>
<td>Na+</td>
<td>1</td>
<td>127.4285714</td>
<td>0.007647534</td>
</tr>
<tr>
<td>potassium</td>
<td>K+</td>
<td>1</td>
<td>164</td>
<td>0.0069761</td>
</tr>
<tr>
<td>cesium</td>
<td>Ca+</td>
<td>1</td>
<td>192.8333333</td>
<td>0.005185825</td>
</tr>
<tr>
<td>beryllium</td>
<td>Be2+</td>
<td>2</td>
<td>59</td>
<td>0.033898305</td>
</tr>
<tr>
<td>magnesium</td>
<td>Mg2+</td>
<td>2</td>
<td>85</td>
<td>0.023529412</td>
</tr>
<tr>
<td>calcium</td>
<td>Ca2+</td>
<td>2</td>
<td>129.5</td>
<td>0.015444015</td>
</tr>
<tr>
<td>strontium</td>
<td>Sr2+</td>
<td>2</td>
<td>143.3333333</td>
<td>0.013953488</td>
</tr>
<tr>
<td>barium</td>
<td>Ba2+</td>
<td>2</td>
<td>149</td>
<td>0.01342819</td>
</tr>
<tr>
<td>oxide</td>
<td>O2-</td>
<td>-2</td>
<td>124.2</td>
<td>-0.01610306</td>
</tr>
<tr>
<td>sulfide</td>
<td>S2-</td>
<td>-2</td>
<td>176</td>
<td>-0.01764708</td>
</tr>
<tr>
<td>selenide</td>
<td>Se2-</td>
<td>-2</td>
<td>184</td>
<td>-0.01086565</td>
</tr>
<tr>
<td>telluride</td>
<td>Te2-</td>
<td>-2</td>
<td>207</td>
<td>-0.00968136</td>
</tr>
<tr>
<td>fluoride</td>
<td>F-</td>
<td>-1</td>
<td>116.625</td>
<td>-0.008574491</td>
</tr>
<tr>
<td>chloride</td>
<td>Cl-</td>
<td>-1</td>
<td>167</td>
<td>-0.005988024</td>
</tr>
<tr>
<td>bromide</td>
<td>Br-</td>
<td>-1</td>
<td>182</td>
<td>-0.005494505</td>
</tr>
<tr>
<td>iodine</td>
<td>I-</td>
<td>-1</td>
<td>206</td>
<td>-0.004854369</td>
</tr>
</tbody>
</table>

Review: Module 5

\[ k = 8.99 \times 10^9 \frac{J m}{C^2} \]

It’s all about charge.

Some of the points don’t fall within a “cluster”

Review: Module 5
Charge is Distributed Throughout The volume

Low charge Density NOT an Alpha dog

Who precipitates and who stays soluble?

<table>
<thead>
<tr>
<th>Low Charge Density</th>
<th>Intermediate Charge Density</th>
<th>High Charge Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>Clean Socks</td>
<td>Oh Card me Pleeesa!!</td>
</tr>
<tr>
<td>NO₃⁻ Cl⁻ SO₄²⁻</td>
<td>OH⁻ CO₃²⁻ PO₄³⁻ S²⁻</td>
<td></td>
</tr>
</tbody>
</table>

Group 1 cations (1+)
NH₄⁺ Weak Electrostatic Interaction = Soluble

Group 2 lg cations (2+)
Transition metal cations (usually sm size 2+)
AgCl Strong Electrostatic Interaction results in precipitation

Extremes
1. Low-Low charge density ion interactions - weak electrostatic energy Stay soluble
2. High-High charge density ion interactions - strong electrostatic energy Precipitate
3. High-Intermediate charge density ion interactions – generally strong electrostatic energy – precipitate

In Between
1. Low – High charge density ion interactions – generally weak electrostatic energy: Soluble with exceptions
2. Low – Intermediate charge density ion interactions – generally weak electrostatic energy: Soluble with exceptions

Who gives up and who holds onto a hydroxide?

<table>
<thead>
<tr>
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<th>Intermediate Charge Density</th>
<th>High Charge Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>Clean Socks</td>
<td>Oh Card me Pleeesa!!</td>
</tr>
<tr>
<td>H⁺</td>
<td>STRONG acids</td>
<td>WEAK acids</td>
</tr>
<tr>
<td>Group 1 cations (1+)</td>
<td>Strong Bases</td>
<td></td>
</tr>
<tr>
<td>Group 2 cations (2+)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Weak bases are produced by an alternative manner

Review Acid Base Definitions. Module 6
Mathematically Express These Concepts:
(Memorization Table is a short hand)

\[ MX_s + H_2O(l) \rightarrow M^{+}_{aq} + X^{-}_{aq} \]

\[ K_{eq} = \left[ \frac{M^{+}_{aq}}{MX_s} \right] \frac{[X^{-}_{aq}]}{[H_2O(l)]} \]

Didn’t we learn
A trick about this?

\[ K_{solubility \ product} = K_{eq}[H_2O(l)] = 55K_{eq} = \left[ \frac{M^{+}_{aq}}{MX_s} \right] \frac{[X^{-}_{aq}]}{[H_2O(l)]} \]

\[ K_{sp} = \left[ \frac{M^{+}_{aq}}{X^{-}_{aq}} \right] \]

The smaller K, the less aquated ions, the less soluble the material

**Example 1:** Calculate the \( K_{sp} \) of Bismuth sulfide if there is \( 1.0 \times 10^{-15} \) mol/L of the compound in solution at 25 °C.

Bismuth is a post transition metal with the electronic configuration of?:

Bi \( s^2d^{10}p^3 \)

What do you think it will do to become a cation?

Lose three e

Bi \( s^2d^{10}p^3 \)

Bi\(^{3+}\) \( s^2d^{10}p^0 \)

The electron configuration on S is:

S \( s^2p^4 \)

What will it do to get to the noble gas?
Gain two e:
\[
\begin{align*}
S & : s^2p^4 \\
S^{2-} & : s^2p^6
\end{align*}
\]
Formula?: Bi\(^{3+}\) with S\(^{2-}\)
\[
\text{Bi}_2S_3
\]

Calculate the Ksp of Bismuth sulfide if there is \(1.0 \times 10^{-15}\) mol/L of the compound in solution at 25°C.

**Reaction:**
\[
\text{Bi}_2S_3(solid) \rightarrow 2\text{Bi}^{3+}\text{aq} + 3\text{S}^{2-}\text{aq}
\]

\[
K_{sp} = [A]^{2}[B]^6
\]
\[
K_{sp} = [Bi^{3+}_{aq}]^2[S^{2-}_{aq}]^3
\]

Now What?

What do we know/don’t know/want?

**solubility of solid** \(= s = 1.0 \times 10^{-15} \text{ mole/L}

<table>
<thead>
<tr>
<th>stoic</th>
<th>\text{Bi}_2S_3(solid)</th>
<th>2\text{Bi}^{3+}\text{aq}</th>
<th>3\text{S}^{2-}\text{aq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init</td>
<td>solid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+2x</td>
<td>+3x</td>
</tr>
<tr>
<td>Equil.</td>
<td>(1.0 \times 10^{-15})</td>
<td>(2.0 \times 10^{-15})</td>
<td>(3.0 \times 10^{-15})</td>
</tr>
</tbody>
</table>

\[
K_{sp} = [\text{Bi}^{3+}_{aq}]^2[\text{S}^{2-}_{aq}]^3
\]

\[
K_{sp} = [2x]^2[3x]^3
\]

\[
K_{sp} = 4x^2 \times 27x^3 = 108x^5
\]

Or you can do it:

\[
K_{sp} = (1.0 \times 10^{-15})^2 \times (3.0 \times 10^{-15})^3
\]

\[
K_{sp} = 1.08 \times 10^{-73}
\]

For an enormous list of Ksp:

[http://www.northland.cc.mn.us/chemistry/solubility_products.htm](http://www.northland.cc.mn.us/chemistry/solubility_products.htm)
Example Calculation 2 Calculate Solubility, $s$, and ion concentrations from $K_{sp}$

Candidates for water treatment for lead?

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbF$_2$</td>
<td>4x10$^{-8}$</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>1.6x10$^{-5}$</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>1.4x10$^{-8}$</td>
</tr>
<tr>
<td>PbSO$_4$</td>
<td>1.3x10$^{-8}$</td>
</tr>
<tr>
<td>PbCrO$_4$</td>
<td>2x10$^{-16}$</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>1.5x10$^{-15}$</td>
</tr>
<tr>
<td>Pb(OH)$_2$</td>
<td>1.2x10$^{-15}$</td>
</tr>
<tr>
<td>PbS</td>
<td>7x10$^{-29}$</td>
</tr>
<tr>
<td>Pb$_3$(PO$_4$)$_2$</td>
<td>1x10$^{-54}$</td>
</tr>
</tbody>
</table>

Do our “rules” clue us to $K_{sp}$ values?

Criteria you will use?

Solubility = $s$ = amount of compound that is soluble in water

Is this below the federal standards (5 ppb)?

Yes: $[Pb^{2+}_{aq}] = 1.8 \times 10^{-11}$

\[
\left(1.8 \times 10^{-11} \frac{\text{mole Pb}}{L}\right) \left(\frac{1 \text{ L}}{10^3 \text{ g water}}\right) \left(\frac{207 \text{ g Pb}}{\text{mole}}\right) = 3.85 \times 10^{-12} \frac{\text{g Pb}}{\text{g water}}
\]

\[
\left(3.85 \times 10^{-12} \frac{\text{g Pb}}{\text{g water}}\right) \left(\frac{10^9}{10^9}\right) = 3.85 \times 10^{-3} \frac{\text{g Pb}}{10^9 \text{ g water}} = 3.85 \times 10^{-3} \text{ ppb}
\]
Will the actual amount of lead be more or less than this value?

LeC principle: **Common ion effect**

\[ \text{add continuously } PO_4^{3-} \]

\[ \text{Pb}_3(PO_4)_2 \rightarrow 3 \text{Pb}^{2+} + 2 \text{PO}_4^{3-} \]

Constant flow of phosphate will suppress lead dissociation, value should be even lower.

- **Zinc orthophosphate**
  - Formula: \( \text{Zn}_3(\text{PO}_4)_2 \)
  - MM: 386.05
  - \( K_{\text{sp}} \): \( 4.0 \times 10^{-33} \)

- **Zinc pyrophosphate**
  - Formula: \( \text{Zn}_2\text{P}_2\text{O}_7 \)
  - MM: 304.685

**Water quality plants use either polyphosphate or pyrophosphate (NOT orthophosphate)**

- **Polyphosphate**
  - \( \text{P}_3\text{O}_{10}^5- \rightarrow 2\text{PO}_4^{3-} + 2\text{H}^+ + \text{PO}_4^{3-} \)

- **Pyrophosphate**
  - \( \text{P}_2\text{O}_7^4- \rightarrow 2\text{P}_2\text{O}_4^{3-} + 2\text{H}^+ \)
  - \( \text{P}_3\text{O}_{10}^5- \rightarrow 3\text{PO}_4^{3-} + 4\text{H}^+ \)
Example Calculation 3

Common Ion
What will be the solubility of lead if a constant stream of 0.001 M phosphate is fed through the water system?

Notice the set up here
1. Looks like accounting for H+ from water
2. Called a “common ion” (ion from another rx)

<table>
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<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
<th>Change</th>
<th>Equil?</th>
<th>Assume</th>
</tr>
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<tbody>
<tr>
<td>Zn₂P₂O₇</td>
<td>2Zn²⁺ 2PO₄³⁻</td>
<td>0.001</td>
<td>-x</td>
<td>3x</td>
</tr>
<tr>
<td>Pb₃(PO₄)₂</td>
<td>3Pb²⁺ 2PO₄³⁻</td>
<td></td>
<td>3x</td>
<td>3x</td>
</tr>
</tbody>
</table>

 stoic 1 3 2
Init solid 0 0.001
Change -x 3x 2x
Equil? - 3x 0.001+2x
Assume 3x 0.001

What will be the solubility of lead if a constant stream of 0.001 M phosphate is fed through the water system?

\[
\begin{align*}
\text{Zn}_2\text{P}_2\text{O}_7 & \quad 2\text{Zn}^{2+} \quad 2\text{PO}_4^{3-} \\
\text{Pb}_3(\text{PO}_4)_2 & \quad 3\text{Pb}^{2+} + 2\text{PO}_4^{3-} \\
\text{stoic} & \quad 1 \quad 3 \quad 2 \\
\text{Init} & \quad \text{solid} \quad 0 \quad 0.001 \\
\text{Change} & \quad -x \quad 3x \quad 2x \\
\text{Equil?} & \quad - \quad 3x \quad 0.001+2x \\
\text{Assume} & \quad 3x \quad 0.001
\end{align*}
\]

\[
K_w = 1\times10^{-74} \left[ \text{Pb}^{2+} \right] \left[ \text{PO}_4^{3-} \right] = \frac{1\times10^{-74}}{27\times10^{-5}} = x \quad \left[ \text{Pb}^{2+} \right] = 3x
\]

\[
K_w = 1\times10^{-74} = 3\times(3.47\times10^{-17})
\]

\[
K_w = 1\times10^{-74} = 27x^2(10^{-6}) \quad x = 3.47\times10^{-17} \quad \left[ \text{Pb}^{2+} \right] = 1.04\times10^{-18}
\]

\[
2x = 2(3.47\times10^{-17}) < 0.001?
\]

Example Calculation 3

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What will be the solubility of lead if a constant stream of 0.001 M phosphate is fed through the water system?

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<td>2Zn²⁺ 2PO₄³⁻</td>
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 stoic 1 3 2
Init solid 0 0.001
Change -x 3x 2x
Equil? - 3x 0.001+2x
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What will be the solubility of lead if a constant stream of 0.001 M phosphate is fed through the water system?

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\text{stoic} & \quad 1 \quad 3 \quad 2 \\
\text{Init} & \quad \text{solid} \quad 0 \quad 0.001 \\
\text{Change} & \quad -x \quad 3x \quad 2x \\
\text{Equil?} & \quad - \quad 3x \quad 0.001+2x \\
\text{Assume} & \quad 3x \quad 0.001
\end{align*}
\]

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<td>Pb₃(PO₄)₂</td>
<td>3Pb²⁺ 2PO₄³⁻</td>
<td></td>
<td>3x</td>
<td>3x</td>
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Equil? - 3x 0.001+2x
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\text{Pb}_3(\text{PO}_4)_2 & \quad 3\text{Pb}^{2+} + 2\text{PO}_4^{3-} \\
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\text{Init} & \quad \text{solid} \quad 0 \quad 0.001 \\
\text{Change} & \quad -x \quad 3x \quad 2x \\
\text{Equil?} & \quad - \quad 3x \quad 0.001+2x \\
\text{Assume} & \quad 3x \quad 0.001
\end{align*}
\]

What will be the solubility of lead if a constant stream of 0.001 M phosphate is fed through the water system?

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K_w = 1\times10^{-74} \left[ \text{Pb}^{2+} \right] \left[ \text{PO}_4^{3-} \right] = \frac{1\times10^{-74}}{27\times10^{-5}} = x \quad \left[ \text{Pb}^{2+} \right] = 3x
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\]

\[
2x = 2(3.47\times10^{-17}) < 0.001?
\]
LeC principle: Common ion effect
Can help ppt
Can prevent ppt
Addition of phosphate should suppress solubility

\[
\text{add continuously } \rightarrow \ \text{Zn}_2P_2O_7^{\text{aq}} \rightarrow 2\text{Zn}^{2+} + 2\text{PO}_4^{3-} + 2\text{H}^+
\]

\[
Pb_3(PO_4)_2^{2-} + 3\text{Pb}^{2+} + 2\text{PO}_4^{3-}
\]

Removal of lead
Under basic conditions
Should also enhance solubility

Removal of phosphate
Under acidic conditions
Should enhance solubility

\[
\text{PO}_4^{3-} + \text{H}_2\text{O}^+ \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}
\]

Hydroxide (pH) vs Carbonate

American Waterworks Association

At intermediate pH
Pb(OH)_2 drops out soln
At high carbonate
PbCO_3 should drop,
BUT not very insoluble

Solubility, s,
Depends on pH
is high at High pH, (Pb(OH)_3^-)
and high at low pH, Pb^{2+}
If little dissolved carbonate
Suppress effects
With phosphate

NOTE Scale change!

First Draw
Plot of amount of lead
In morning water

D.C. to Examine 60 Service Pipes
Leads Tests Expand
Montgomery, Prince George's

Second Draw
Other

Pb pipes
Cu pipe
Brass fixture
Unknown pipes

260 ppb Lead.
“A” students work (without solutions manual) ~ 10 problems/night.

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Module #19: Precipitation Reactions

Qualitative Analysis: Intro

Qualitative Analysis

First known text on chemical (as opposed of alchemical) analysis

Qualitative Analysis

Muriatic acid “of or pertaining to brine Or salt” HCl

Qualitative Analysis

<table>
<thead>
<tr>
<th>Hydroxide</th>
<th>Carbonate</th>
<th>Phosphate</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>CO₃²⁻</td>
<td>PO₄³⁻</td>
<td>S²⁻</td>
</tr>
</tbody>
</table>

\[ M^{2+} + X^{-} \leftrightarrow \text{precipitate} \]
\[ M(OH)_{2,x} \]
\[ + \]
\[ MS \]
\[ nL^{2-} \]
\[ MCO_3 \]
\[ \downarrow \]
\[ M_{x,y}(PO_4)_2 \]
\[ ML_{x,y} \]

Move back and forth between precipitate And soluble species
Preceding example was:
  How to get rid of Pb\(^{2+}\) by precipitation as a phosphate

Next example:
  How to bring it back into solution
  a. With acid
  b. With a ligand

Dissolving Precipitates

1. **Strong acid**

   ![LeChatlier's Principle](image)

   Acid dissolves: **chromates**; carbonates, sulfides,

Dissolving Precipitates

1. **Strong acid**

   ![LeChatlier's Principle](image)

   Acid dissolves: chromates, carbonates; **sulfides**

Dissolving Precipitates

1. **Strong acid**

2. **Complex forming reagents (:\text{NH}_3, :\text{OH}^-)**

   ![LeChatlier's Principle](image)

   Complexes
Dissolving Precipitates
1. Strong acid
2. Complex forming reagents (:OH)

Neutral can result in a solid

Ligands like :NH₃ and :OH can bring various precipitates into solution

<table>
<thead>
<tr>
<th>Complex</th>
<th>Kᵣ</th>
<th>Complex Kᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(NH₃)₂⁺</td>
<td>1.8 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>Cu(NH₃)⁴⁺</td>
<td>2 x 10¹²</td>
<td></td>
</tr>
<tr>
<td>Zn(OH)²⁺</td>
<td>3.6 x 10⁸</td>
<td></td>
</tr>
<tr>
<td>Cd(OH)²⁺</td>
<td>2.8 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>Ni(OH)⁴⁻</td>
<td>9 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>Al(OH)³⁻</td>
<td>1 x 10¹³</td>
<td></td>
</tr>
</tbody>
</table>

Example 4: Calculate moles AgCl dissolved in 1 L of 6.0 M NH₃ at a temperature of 298 K

LeChatelier’s Principle

Bring Silver Into solution

<table>
<thead>
<tr>
<th>Know</th>
<th>Don’t Know</th>
<th>Red Herring</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0 M NH₃</td>
<td>s</td>
<td>298K</td>
</tr>
<tr>
<td>reaction</td>
<td>Kᵣ = 1.8 x 10⁻¹⁰</td>
<td>Kᵢ = 1.7 x 10⁶</td>
</tr>
<tr>
<td>AgCl(s)_aq + Ag⁺_aq + Cl⁻_aq</td>
<td>Ag⁺_aq + 2NH₃_aq + Ag(NH₃)₂⁺_aq</td>
<td></td>
</tr>
<tr>
<td>Kᵣ = (1.8 x 10⁻¹⁰)(1.7 x 10⁶) = 3.1 x 10⁻⁴</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AgCl_3</th>
<th>[NH₃]</th>
<th>[Ag(NH₃)₂⁺]</th>
<th>[Cl⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>stoic</td>
<td>n.a.</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Init</td>
<td>6.0 M</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Equil</td>
<td>6.0-2x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
Example: Calculate moles AgCl dissolved in 1 L of 6.0 M NH₃ at a temperature of 298 K

\[
\begin{array}{|c|c|c|c|}
\hline
& \text{AgCl}_s & [\text{NH}_3] & [\text{Ag(NH}_3)_2^{+}] & [\text{Cl}^-] \\
\hline
\text{stoic} & \text{n.a.} & 2 & 1 & 1 \\
\text{init} & 6.0 \text{ M} & 0 & 0 & \text{x} \\
\text{change} & -2x & x & x & \text{x} \\
\text{equil} & 6.0-2x & x & x & \text{x} \\
\hline
\end{array}
\]

\[ K_{\text{reaction}} = 3.1 \times 10^{-3} = \frac{[\text{Ag(NH}_3)_2^{+}] [\text{Cl}^-]}{[\text{NH}_3]^2} \]

\[ X = \text{moles complex} = \text{moles AgCl dissolved} \]

\[ 0.0556(6.0 - 2x) = x \]

\[ 0.334 - 0.1112x = x \]

\[ 0.334 = 1.1112x \]

\[ x = 0.300216 \]

We can calculate the solubility of AgCl as a function of the ammonia concentration

\[ K_a = \frac{x}{[\text{NH}_3]^2} \]

\[ \sqrt{K_a} = \frac{x}{[\text{NH}_3]^2 - 2x} \]

\[ \frac{[\text{Ag(NH}_3)_2^{+}]}{[\text{NH}_3]} = x(1 + 2\sqrt{K_a}) \]

AgCl becomes soluble

Around 1 M ammonia

“I WANT YOU TO PRACTICE EVERY DAY!”

“A” students work (without solutions manual)

~ 10 problems/night.

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Module #19:
Precipitation Reactions

Qualitative Analysis:
Cl to separate Pb, Hg₂²⁺, Ag

Using pH and complexation to Separate Ions
For Qualitative Analysis
Separation in lab is not always the same
As in the text.

Text starts with 6 M Cl⁻ = pCl = -.778

The separation below
Corresponds to
What goes on in lab

<table>
<thead>
<tr>
<th>pCl</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>-2</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
<td>1</td>
</tr>
</tbody>
</table>

Questions:
1. How does Cl⁻ do the first step?
2. Why can we get Pb²⁺ from Hg and Ag with hot water?
\[ \text{Pb}^{2+} + \text{Cl}^- \rightleftharpoons \text{PbCl}^2_\text{aq} \quad K_{f1} \]
\[ \text{PbCl}^2_\text{aq} + \text{Cl}^- \rightleftharpoons \text{PbCl}_2 \quad K_{f2} \rightleftharpoons \text{PbCl}_2^2 \]
\[ \text{PbCl}_2^2 + \text{Cl}^- \rightleftharpoons \text{PbCl}_2 \quad K_{f3} \]
\[ \text{PbCl}_2 + \text{Cl}^- \rightleftharpoons \text{PbCl}_2^2 \quad K_{f4} \]

\[ \text{Ag}^{+} + \text{Cl}^- \rightleftharpoons \text{AgCl}^+_\text{aq} \quad K_{f1} \]
\[ \text{AgCl}^+_\text{aq} + \text{Cl}^- \rightleftharpoons \text{AgCl}_2 \quad K_{f2} \rightleftharpoons \text{AgCl}_2^2 \]
\[ \text{AgCl}_2 + \text{Cl}^- \rightleftharpoons \text{AgCl}_2^2 \quad K_{f3} \]

For lead it was $\text{pCl}_2 = 0$, $\text{Cl}^- = 0.01$, $[\text{Cl}^-] = 1$

For mercury it was $\text{pCl}_2 = 3.5$, $\text{Cl}^- = 0.00035$
Lower chloride concentration by placing ppt in hot water. PbCl₂ dissolves; AgCl and Hg₂Cl₂ remain insoluble.

Questions:
1. How does Cl⁻ do the first step?
2. Why can we get Pb²⁺ from Hg and Ag with hot water?
3. How do we ppt. Pb²⁺?

Candidates for precipitating Pb²⁺ from supernatant?

<table>
<thead>
<tr>
<th>Compound</th>
<th>K_{sp} Pb</th>
<th>K_{sp} Cd</th>
<th>K_{sp} Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbF₂</td>
<td>4x10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>1.6x10⁻⁵</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PbI₂</td>
<td>1.4x10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PbSO₄</td>
<td>1.3x10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PbCrO₄</td>
<td>2x10⁻¹⁶</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PbCO₃</td>
<td>1.5x10⁻¹⁵</td>
<td>5.5x10⁻¹³</td>
<td>5.0x10⁻¹³</td>
</tr>
<tr>
<td>Pb(OH)₂</td>
<td>1.7x10⁻¹⁵</td>
<td>6.45x10⁻⁶</td>
<td>6.3x10⁻¹⁷</td>
</tr>
<tr>
<td>PbS</td>
<td>7x10⁻²⁰</td>
<td>-</td>
<td>1.99x10⁻²⁵</td>
</tr>
<tr>
<td>Pb₃(PO₄)₂</td>
<td>1x10⁻⁵⁴</td>
<td>-</td>
<td>3.8x10⁻³⁶</td>
</tr>
</tbody>
</table>

OH⁻, CO₃²⁻ bring Cd²⁺;
S²⁻, PO₄³⁻ bring Zn²⁺

Makes a very nice, older, chrome pigment!!

Example Calculation 5. Before lead in paint was discontinued, lead chromate was a common pigment in yellow paint. A 1.0 L solution is prepared by mixing 0.50 mg of lead nitrate with 0.020 mg of potassium chromate. Will a precipitate form?

P is like Q

\[
P = \frac{[\text{Pb}^{2+}][\text{CrO}_4^{2-}]}{K_{sp}(\text{PbCrO}_4)} > K_{sp}(\text{PbCrO}_4) \times 10^{-16}?
\]

\[
P = \frac{0.50 \text{mg} \text{Pb}^{2+} \times 10^{-3}}{331 \text{g} \text{Pb(NO}_3)_2} \times \frac{1 \text{g} \text{NO}_3^-}{10^5 \text{mg}} = 1.51 \times 10^{-6} \text{MPb}^{2+}
\]

\[
P = \frac{0.020 \text{mg} \text{K}_2\text{CrO}_4 \times 10^3 \text{mg} \text{K}_2\text{CrO}_4}{194.2 \text{g} \text{K}_2\text{CrO}_4} \times \frac{1 \text{g} \text{CrO}_4^-}{10^7 \text{mg}} = 1.029 \times 10^{-7} \text{MCrO}_4^{2-}
\]

\[
P = (1.51 \times 10^{-6}) (1.029 \times 10^{-7}) = 1.554 \times 10^{-13} > K_{sp}(\text{PbCrO}_4) \times 10^{-16}
\]
Questions:
1. How does Cl\(^-\) do the first step?
2. Why can we get Pb\(^{2+}\) from Hg and Ag with hot water?
3. What is the purpose of NH\(_3\) to get Ag\(^{3+}\)?

We did an example in which we calculated the Solubility of AgCl in the presence of ammonia:

\[
\text{AgCl}_{(s)} + \text{Ag}^{+} + \text{Cl}^- + \text{NH}_3 \rightarrow \text{Ag(NH}_3\text{)}^+ + \text{Cl}^- + \text{H}_2\text{O}
\]

\[
K_p = 18 \times 10^{-10}
\]

\[
K_f = 1.7 \times 10^7
\]

\[
K_{reaction} = 3.1 \times 10^{-3}
\]

Which number is larger?
Which has the higher solubility?
water or ammonia

\[\frac{\sqrt{K_p [\text{NH}_3]}}{1 + 2K_f} = x\]

“\(x\)” students work
(without solutions manual)
~ 10 problems/night.

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Module #19:
Precipitation Reactions

Qualitative Analysis:
S to separate Cu\(^{2+}\), Hg\(^{2+}\), Bi\(^{3+}\), Cd\(^{2+}\)
Questions: 1. How does H₂S do the second step?

Strong precipitators with S²⁻:
- Cu²⁺: logKsp = -48.5
- Bi³⁺: logKsp = -52.7
- Hg²⁺: logKsp = -52.7
- Cd²⁺: logKsp = -27.0
- Al³⁺: logKsp = -2.7
- Fe³⁺: logKsp = -10.5
- Cr³⁺: logKsp = -24.7
- Mn²⁺: logKsp = -9.5
- Zn²⁺: logKsp = -24.7
- Ba²⁺: logKsp = -10.5
- Ca²⁺: logKsp = -24.7

Weak precipitators with [S²⁻]:
- Will ppt only at higher [S²⁻]

How can we control [S²⁻] Easily?

Control [S²⁻] through pH

"A" students work (without solutions manual)
~ 10 problems/night.

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Module #19: Precipitation Reactions

Qualitative Analysis:
S to separate Zn²⁺, Co²⁺, Mn²⁺, Ni²⁺.
Questions:
1. How does \((\text{NH}_4)_2\text{S}\) do the first step?
2. Why is the solution basic (pH 8) in next step?

\[
\text{Buffer pH to basic solution of 9.599 to ppt hydroxides}
\]

\[
\begin{align*}
\text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+} & \text{ come along as a hydroxides} \\
\text{Ppt out sulfides}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_4^+ + \text{NH}_3 + H^+ & \\
K_c &= 5.6 \times 10^{-11} \\
pH &= pK_a + \log \left[ \frac{[A]}{[HA]} \right] \\
pH &= -\log(5.6 \times 10^{-11}) + \log \frac{5M}{2M} \\
pH &= 9.25 + 0.397 = 9.65
\end{align*}
\]

\[
\begin{align*}
\log K_{sp} S^{2-} & \\
\text{Cu}^{2+} &= 48.5 \\
\text{Bi}^{3+} &= -52.7 \\
\text{Hg}^{2+} &= -27.0 \\
\text{Al}^{3+} & \\
\text{Fe}^{3+} & \\
\text{Cr}^{3+} & \\
\text{Mn}^{2+} & \\
\text{Zn}^{2+} & \\
\text{Ba}^{2+} & \\
\text{Ca}^{2+} & \\
\end{align*}
\]

Strong precipitators with \(S^{2-}\), will ppt at very low \([S^{2-}]\)

Intermediate: need relatively larger values of \([S^{2-}]\) to ppt

Do not ppt at any value of \([S^{2-}]\)
**Dissolving Precipitates**

1. **Strong acid**

2. Complex forming reagents (:NH₃, :OH⁻)

   LeChatlier’s

   Acid dissolves: carbonates; sulfides, hydroxides

---

“**A**” students work
(without solutions manual)
~ 10 problems/night.

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**Module #19: Precipitation Reactions**

Qualitative Analysis:
Separating Zn²⁺, And Al³⁺, from the sulfides
By OH complexation

---

Re-dissolve
In acid

Increase pH
Example Calculation 6:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Compound 1</th>
<th>Compound 2</th>
<th>K_f</th>
<th>K_sp</th>
<th>K_f/K_sp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>Ag(OH)_2⁻</td>
<td>Ag(OH)⁻</td>
<td>1x10⁴</td>
<td>1.99x10⁻⁹</td>
<td>1.99x10⁻⁵</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Zn(OH)₂⁻</td>
<td>Zn(OH)₂⁺</td>
<td>4.6x10¹⁷</td>
<td>1.58x10⁻¹³</td>
<td>1.58x10⁻¹⁰</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Mn(OH)₃⁻</td>
<td>Mn(OH)₃²⁻</td>
<td>2.51x10³</td>
<td>3.96x10⁻¹⁰</td>
<td>3.96x10⁻¹⁰</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>Cr(OH)₄²⁻</td>
<td>Cr(OH)₃⁻</td>
<td>6.3x10⁵</td>
<td>6.3x10⁻³⁴</td>
<td>1.28</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>Al(OH)₄⁻</td>
<td>Al(OH)₃⁻</td>
<td>1x10³⁷</td>
<td>4.6x10⁻⁸</td>
<td>4.6</td>
</tr>
<tr>
<td>Sn²⁺</td>
<td>Sn(OH)₃⁻</td>
<td>Sn(OH)₂⁻</td>
<td>2.5x10⁻⁵</td>
<td>7.96x10⁻¹⁶</td>
<td>3.0x10⁸</td>
</tr>
</tbody>
</table>

\[
\text{AgOH} \rightleftharpoons \text{Ag}^{+} + \text{OH}^{-}, \quad K_f = 1.99 \times 10^{-9} \\
\text{Ag}^{+} + 2\text{OH}^{-} \rightleftharpoons \text{Ag(OH)}_{2}^{+}, \quad K_f = 1 \times 10^{4} \\
\text{AgOH} + \text{OH}^{-} \rightleftharpoons \text{Ag(OH)}_{2}^{+}, \quad K_{aq} = K_f \times K_f = (1.99 \times 10^{-9})(1 \times 10^{4}) = 1.99 \times 10^{-5}
\]

Which compounds can be brought into solution by raising the pH?

How do we distinguish Zn from Al?

Between Al(OH)₃⁻ and Zn(OH)₄²⁻ only Zn has complexation with :NH₃

**Drop pH** to re-ppt Al(OH)₃, while simultaneously forming soluble Zn(NH₃)₄²⁺

\[ \text{NH}_4^+ + \text{NH}_3 + \text{H}^+ \rightleftharpoons K_a = 5.6 \times 10^{-10} \]

\[ p\text{H} = pK_a + \log \left[ \text{HA} \right] \]

\[ p\text{H} = -\log(5.6 \times 10^{-10}) + \log \frac{3M}{12M} \]

\[ p\text{H} = 9.25 + (-0.602) = 8.65 \]

| 3 M NH₄⁺ | 12 M NH₃ |
Dissolving Precipitates

1. Strong acid
2. Complex forming reagents (:NH₃, :OH⁻)

\[ \text{Zn}^{2+} \text{aqueous} + 2 \text{OH}^- \text{aqueous} \rightarrow \text{Zn(OH)}_2\text{solid} \]
+ 
\[ 4 \text{NH}_3 \]

\[ \uparrow \downarrow \]

\[ \text{Zn(NH}_3)_4^{2+} \text{aqueous} \]

“\(A\)” students work (without solutions manual)

~ 10 problems/night.

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Module #19: Precipitation Reactions

Qualitative Analysis:
PO₄³⁻ to separate Ba²⁺, Ca²⁺, Mg²⁺
“A” students work (without solutions manual) ~7 problems/night.

What you need To know

Solubility

Summary Points
Complexation vs Solubility
  - Complexation based on electrostatic attraction
  - Lone pairs for central cation
  - Size matters!; Charge matters!
  - Can result in multiple points of binding
  - Can result in charge -, o, +
  - Based on charge can result in precipitation
Use to manipulate and separate elements (biology too!)
Ksp = solubility product; large - # implies not soluble
Kf = formation constant; large +# implies strong binding
Calculations proceed similarly to Ka
EXCEPT – STOICHIOMETRY is trickier
  \[ \text{Ba}_3(\text{PO}_4)_2 \]

END