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

Dr. Alanah Fitch
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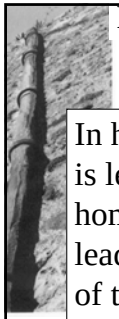
Office Hours Th&F 2-3:30 pm

**Module #19:**
**Precipitation Reactions**

Introduction/
Context



Roman pipes at Pompei

Solution Equilibria: Solubility

In homes older than 1980 most of the plumbing is lead pipe (Pb = **plumbous)**. 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/$10^9$ g water
< 5 x$10^{-9}$ g Pb/g water
< 5 ppb

What to do?

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 do you think the average homeowner prefers?

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

= insoluble salt

What makes insoluble salts?
hint: same concepts as govern what ions are or are not spectators.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**Module #19:**
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**Review Charge Density**

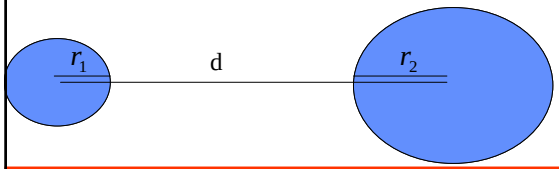
$k = 8.99x10^9 \frac{J\ m}{C^2}$

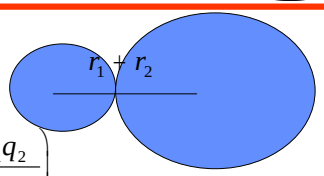
It's all about charge

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

Charge on object 1 or 2, in coulombs

Distance between the objects




$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$

Coulomb's Law

Review: Module 5

**Are there differences in predicted electrostatic effect?**

| ion | Symbol | Charge | Radius (pm) | Charge/radius |
|---|---|---|---|---|
| hydrogen | D+ | 1 | 4 | 0.25 |
| lithium | Li+ | 1 | 89.66666667 | 0.011152416 |
| sodium | Na+ | 1 | 127.4285714 | 0.007847534 |
| potasium | K+ | 1 | 164 | 0.006097561 |
| cesium | Cs+ | 1 | 192.8333333 | 0.005185825 |
| beryllium | Be2+ | 2 | 59 | 0.033898305 |
| magnesium | Mg2+ | 2 | 85 | 0.023529412 |
| calcium | Ca2+ | 2 | 129.5 | 0.015444015 |
| strontium | Sr2+ | 2 | 143.3333333 | 0.013953488 |
| barium | Ba2+ | 2 | 149 | 0.013422819 |
| oxide | O2- | -2 | 124.2 | -0.01610306 |
| sulfide | S2- | -2 | 170 | -0.011764706 |
| selenide | Se2- | -2 | 184 | -0.010869565 |
| telluride | Te2- | -2 | 207 | -0.009661836 |
| fluoride | F- | -1 | 116.625 | -0.008574491 |
| chloride | Cl- | -1 | 167 | -0.005988024 |
| bromide | Br- | -1 | 182 | -0.005494505 |
| iodine | I- | -1 | 206 | -0.004854369 |

H+ should behave differently

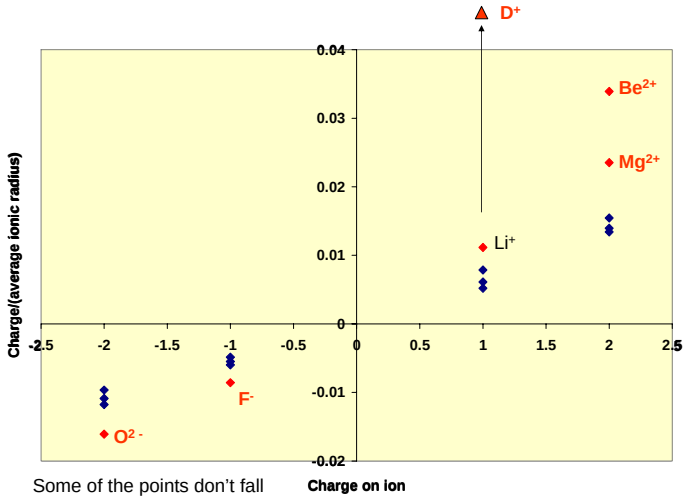
$Be^{2+}$ and $Mg^{2+}$ should behave differently

$O^{2-}$ and, maybe, $S^{2-}$ should behave differently

$F^-$ should behave differently

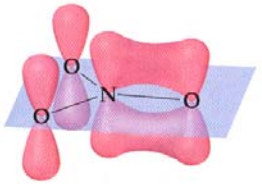
$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$

Review: Module 5

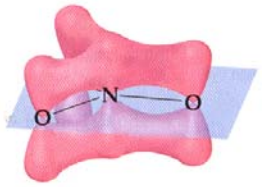



Some of the points don't fall Within a "cluster"

Review: Module 5



(a) N—O $\pi$ bond in one of the resonance structures of $NO_3^-$.



(b) Delocalization of the $\pi$ bonds in the $NO_3^-$ ion.

Low charge Density NOT an Alpha dog

Charge is Distributed Throughout The volume

Review: Module 5

**Who precipitates and who stays soluble?**
**Depends upon who reacts with whom?**

Low Charge Density
Intermediate Charge Density
High Charge Density

| | No Clean Socks | | | Oh | Card me PleeeeaSe!! | | |
|---|---|---|---|---|---|---|---|
| | $NO_3^-$ | $Cl^-$ | $SO_4^{2-}$ | OH- | $CO_3^{2-}$ | $PO_4^{3-}$ | $S^{2-}$ |
| Group 1 cations (1+) $NH_4^+$ | Weak Electrostatic Interaction = Soluble | | | | | | |
| Group 2 lg cations (2+) | | | $BaSO_4$ | $Mg(OH)_2$ | | | |
| 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
3. Intermediate – Intermediate – charge density ion interactions – generally weak electrostatic energy: soluble with exceptions

**Who gives up and who holds onto a hydroxide?**

Low Charge Density
Intermediate Charge Density
High Charge Density

| | No Clean Socks | | | Oh | Card me PleeeeaSe!! | | |
|---|---|---|---|---|---|---|---|
| | $NO_3^-$ | $Cl^-$ | $SO_4^{2-}$ | OH- | $CO_3^{2-}$ | $PO_4^{3-}$ | $S^{2-}$ |
| H+ | STRONG acids | | | | WEAK acids | | |
| Group 1 cations (1+) | | | | ~~Strong Bases~~ | | | |
| Group 2 cations (2+) | | | | | | | |

**Weak bases are produced by an alternative manner**

Review Acid Base Definitions: Module 6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**Module #19: Precipitation Reactions**

**Solubility Product, $K_{sp}$**

Mathematically Express These Concepts:
(Memorization Table is a short hand)

$$MX_s + H_2O_\ell \rightleftarrows M^+_{aq} + X^-_{aq}$$

$$K_{eq} = \frac{\left[M^+_{aq}\right]\left[X^-_{aq}\right]}{\left[MX_s\right]\left[H_2O_\ell\right]}$$

Didn't we learn
A trick about this?

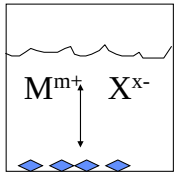
$$K_{solubility\ product} = K_{eq}\left[H_2O_\ell\right] = 55K_{eq} = \frac{\left[M^+_{aq}\right]\left[X^-_{aq}\right]}{\left[MX_s\right]} = \left[M^+_{aq}\right]\left[X^-_{aq}\right]$$

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

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

Solubility Constants

Numbers are determined from measuring the amount of stuff in solution.




**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?

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.

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?

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

Gain two e:

S $s^2p^4$

$S^{2-}$ $s^2p^6$

Formula?: $Bi^{3+}$ with $S^{2-}$

$Bi_2S_3$

Calculate the Ksp of Bismuth sulfide if there is $1.0x10^{-15}$ mol/L of the compound in solution at 25C.

Reaction?:

$$Bi_2S_s \rightleftarrows 2Bi^{3+}_{aq} + 3S^{2-}_{aq}$$

$$K_{sp} = [A]^a[B]^b$$

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

Now What?

What do we know/don't know/want?

$$solubility\ of\ solid \equiv s = 1.0x10^{-15}\ \frac{mole}{L}$$

Calculate the Ksp of Bismuth sulfide if there is $1.0x10^{-15}$ mol/L of the compound in solution at 25C.

| | $Bi_2S_{3(solid)}$ | $2Bi^{3+}_{aquated}$ | + $3S^{2-}_{aquated}$ |
|---|---|---|---|
| stoic | 1 | 2 | 3 |
| **I**nit | solid | 0 | 0 |
| **C**hange | -x | +2x | +3x |
| **E**quil. | $1.0x10^{-15}$ | $2.0x10^{-15}$ | $3.0x10^{-15}$ |

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

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

$$K_{sp} = 4x^2\,27x^3 = 108x^5$$

$$K_{sp} = 108\left(1.0x10^{-15}\right)^5 = 1.08x10^{-73}$$

OJO!

Or you can do it:

$$K_{sp} = \left[2.0x10^{-15}\right]^2\left[3.0x10^{-15}\right]^3$$

$$K_{sp} = 1.08x10^{-73}$$

Calculate the Ksp of Bismuth sulfide if there is $1.0x10^{-15}$ mol/L of the compound in solution at 25C.

For an enormous list of Ksp:

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?

| | $K_{sp}$ |
|---|---|
| $PbF_2$ | $4x10^{-8}$ |
| $PbCl_2$ | $1.6x10^{-5}$ |
| $PbI_2$ | $1.4x10^{-8}$ |
| $PbSO_4$ | $1.3x10^{-8}$ |
| $PbCrO_4$ | $2x10^{-16}$ |
| $PbCO_3$ | $1.5x10^{-15}$ |
| $Pb(OH)_2$ | $1.2x10^{-15}$ |
| $PbS$ | $7x10^{-29}$ |
| $Pb_3(PO_4)_2$ | $1x10^{-54}$ |

Criteria you will use?

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

Do our "rules" clue us to Ksp values?

| | $Pb_3(PO_4)_2 \rightleftharpoons$ | $3Pb^{2+}$ + | $2PO_4^{3-}$ |
|---|---|---|---|
| stoic | 1 | 3 | 2 |
| Init | solid | 0 | 0 |
| Change | -x | 3x | 2x |
| Equil? | - | 3x | 2x |

$$K_{sp} = 1.0x10^{-54} = \left[Pb^{2+}_{aq}\right]^3\left[PO^{3-}_{aq}\right]^2$$

$$K_{sp} = 1.0x10^{-54} = [3x]^3[2x]^2$$ OJO!

$$K_{sp} = 1.0x10^{-54} = 27x^3 4x^2 = 108x^5$$

$$\sqrt[5]{\frac{1.0x10^{-54}}{108}} = x = s$$

$$\sqrt[5]{9.27x10^{-57}} = x = s$$

$x = s = 6.2x10^{-12}$

Are we done?

No, need $[Pb^{2+}]$

$$\left[Pb^{2+}_{aq}\right] = 3x = 3\left(6.2x10^{-12}\right)$$

$$\left[Pb^{2+}_{aq}\right] = 1.8x10^{-11}$$

Is this below the federal standards (5 ppb)?

Yes: $\left[Pb^{2+}_{aq}\right] = 1.8x10^{-11}$

$$\left(1.8x10^{-11}\frac{molePb}{L}\right)\left(\frac{1L}{10^3\,gwater}\right)\left(\frac{207\,gPb}{mole}\right) = 3.85x10^{-12}\frac{gPb}{gwater}$$

$$\left(3.85x10^{-12}\frac{gPb}{gwater}\right)\left(\frac{10^9}{10^9}\right) = \frac{3.85x10^{-3}\,gPb}{10^9\,gwater} = 3.85x10^{-3}\,ppb$$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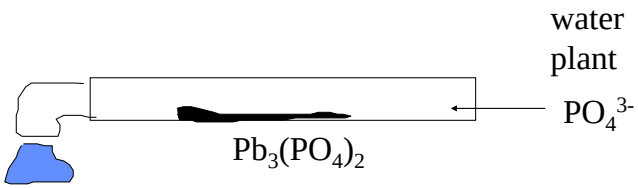
**Module #19: Precipitation Reactions**

**Common Ion Effects**

Will the actual amount of lead be more or less than this value?




LeC principle: **Common ion effect**

*add continuously* $PO_4^{3-}$

$$Pb_3(PO_4)_{2,s} \rightleftarrows 3Pb^{2+}_{aq} + 2PO^{3-}_{aq}$$

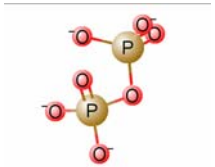
Constant flow of phosphate will suppress lead dissociation, value should be even lower.

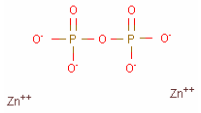
http://www.caruschem.com/phosphate_zpoly.htm

| *Name* | *formula* | *MM* | |
|---|---|---|---|
| *Zinc orthophosphate* | $Zn_3(PO_4)_2$ | 386.05 | $K_{spZn_3(PO_{aq}^{3-})_2} = 9.0x10^{-33}$ |

$$Zn_3\left(PO_{aq}^{3-}\right)_2 = Zn_3P_2O_6$$

| | | | |
|---|---|---|---|
| *Zinc pyrophosphate* | $Zn_2P_2O_7$ | 304.685 | $s_{Zn_2P_2O_7} = \frac{3lbs}{1gal}$ |






$$s = \left[\frac{3lb}{gal}\right]\left[\frac{1gal}{3.785L}\right]\left[\frac{453.6g}{1lb}\right]\left[\frac{1mole}{386.05}\right] = \frac{0.9336moles}{L} = 0.9336M$$

Water quality plants use either polyphosphate Or pyrophosphate (NOT orthophosphate)

$$P_3O_{10}^{5-} \xrightarrow{H_2O} P_2O_7^{4-} + 2H^+ + PO_4^{3-}$$ polyphosphate

$$P_2O_7^{4-} \xrightarrow{H_2O} 2PO_4^{3-} + 2H^+$$ pyrophosphate

$$P_3O_{10}^{5-} \xrightarrow{H_2O} 3PO_4^{3-} + 4H^+$$

**Example Calculation 3Common 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)

| | $Zn_2P_2O_7$ | $2Zn^{2+}$ | $2PO_4^{3-}$ |
|---|---|---|---|
| | | | 0.001 |
| | $Pb_3(PO_4)_2$ | $3Pb^{2+}$ | $+ 2PO_4^{3-}$ |
| 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?

| | $Zn_2P_2O_7$ | $2Zn^{2+}$ | $2PO_4^{3-}$ |
|---|---|---|---|
| | | | 0.001 |
| | $Pb_3(PO_4)_2$ | $3Pb^{2+}$ | $+ 2PO_4^{3-}$ |
| stoic | 1 | 3 | 2 |
| Init | solid | 0 | 0.001 |
| Change | -x | 3x | 2x |
| Equil? | - | 3x | 0.001+2x |
| Assume | | 3x | 0.001 |

$$K_{sp} = 1x10^{-54} = \left[Pb^{2+}\right]^3\left[PO_{aq}^{3-}\right]^2$$

$$K_{sp} = 1x10^{-54} = [3x]^3\left(10^{-3}\right)^2$$

$$K_{sp} = 1x10^{-54} = 27x^3\left(10^{-6}\right)$$

$$\sqrt[3]{\frac{1x10^{-54}}{27x10^{-6}}} = x$$

$$\sqrt[3]{3.7x10^{-50}} = x$$

$$x = 3.47x10^{-17}$$

$$2x = 2\left(3.47x10^{-17}\right) < 0.001?$$

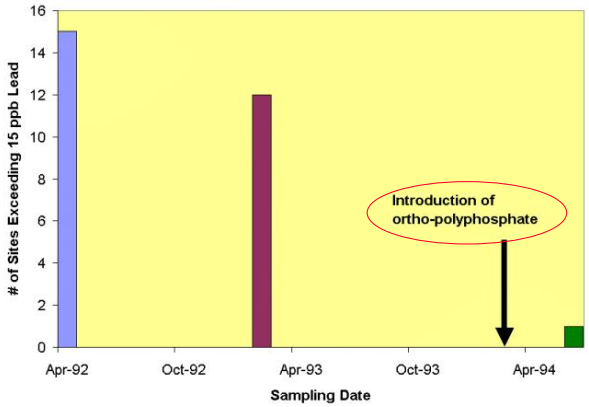
$$\left[Pb_{aq}^{2+}\right] = 3x$$

$$\left[Pb_{aq}^{2+}\right] = 3\left(3.47x10^{-17}\right)$$

$$\left[Pb_{aq}^{2+}\right] = 1.04x10^{-16}$$

$$\left[Pb_{aq}^{2+}\right]_{no\ phosphate} = 1.8x10^{-11}$$

Wilmette, Ill.




Proprietary license

Western suburbs Chicago Tribune, 2001

Phosphate coating

1. lowers total volume
2. Creates friction
3. Increases energy cost
4. Lowers life span

Suburbs want compensation from Chicago

LeC principle: Common ion effect

Can help ppt

Can prevent ppt

Addition of phosphate should suppress solubility

$$add\ continuously \rightarrow Zn_2P_2O_7 \xrightarrow{complete} 2Zn^{2+}_{aq} + 2PO^{3-}_{aq} + 2H^+$$

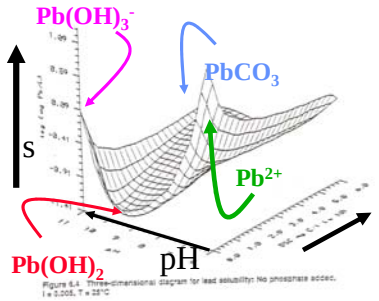
$$Pb_3(PO_4)_{2,s} \rightleftarrows 3Pb^{2+}_{aq} + 2PO^{3-}_{aq}$$

$$PO^{3-}_{aq} + H_3O^+ \rightleftarrows HPO^{2-}_{aq} + H_2O_\ell$$

Removal of phosphate
Under acidic conditions
Should enhance solubility

$$Pb^{2+}_{aq} + OH^-_{aq} \rightleftarrows Pb(OH)^+_{aq}$$

Removal of lead
Under basic conditions
Should also enhance solubility




American Waterworks Association

Hydroxide (pH) vs Carbonate

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!


The Washington Post

METRO

Saturday, March 20, 2004

2 School Districts Restrict Water Use

Lead Tests Expand In Montgomery, Prince George's

D.C. to Examine 60 Service Pipes

Lines Listed as Copper, Brass May Be Lead

The Washington Post

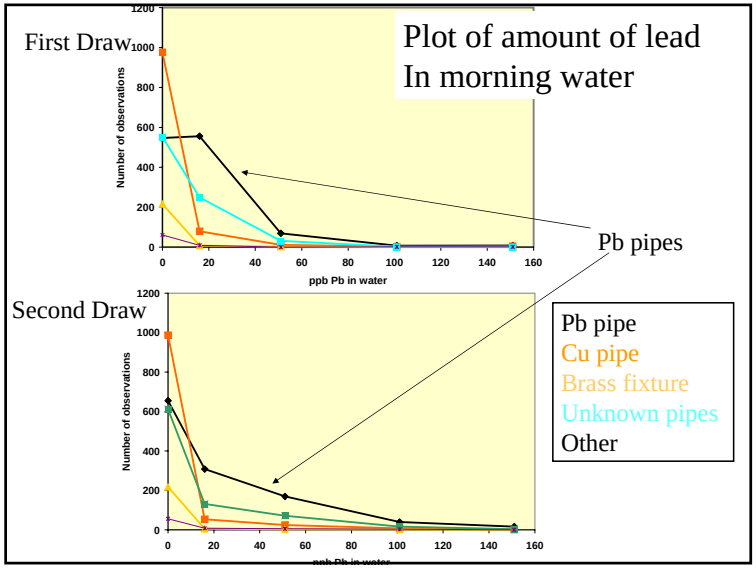
METRO

Deluge of Tap Water Tests Hits Labs

Technicians Work Long Hours to Handle Influx of Sampling Requests

MARCH 20/21, 2004

260 ppb Lead.




Plot of amount of lead
In morning water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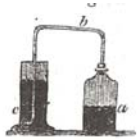
**Module #19:**
**Precipitation Reactions**

## Qualitative Analysis: Intro

METHOD OF DETECTING LEAD, WHEN CONTAINED IN WATER.

One of the most delicate tests for detecting lead, is water impregnated with sulphuretted hydrogen gas, which instantly imparts to the fluid containing the minutest quantity of lead, a brown or blackish tinge.

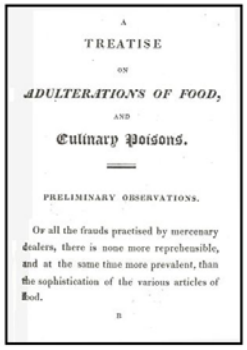
PbS




take one part of sulphuret of antimony of commerce, break it into pieces of half the size of split pease, put it into the flask, and pour upon it four parts of common concentrated muriatic acid (spirit of salt of commerce). Sulphuretted hydrogen gas will become disengaged from the materials in abundance, and pass through the water in the vial (c). Let the extrication of the gas

Muriatic acid
"of or pertaining to brine
Or salt" HCl

## Qualitative Analysis



A TREATISE ON ADULTERATIONS OF FOOD, AND Culinary Poisons.

PRELIMINARY OBSERVATIONS.

Of all the frauds practised by mercenary dealers, there is none more reprehensible, and at the same time more prevalent, than the sophistication of the various articles of food.

1820
Frederick Acum
London


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

## Qualitative Analysis

| | | |
|---|---|---|
| Oh Card me | hydroxide<br>Carbonate | $OH^-$<br>$CO_3^{-2}$ |
| Plea S | Phosphate<br>Sulfide | $PO_4^{3-}$<br>$S^{2-}$ |

$$M^{2+} + X^{x-} \leftarrow precipitate$$

$$+$$

$$nL^{x-}$$

$$\downarrow$$

$$ML^b_{n,aq}$$

$Cl^-$
$NH_3$
$OH^-$

$M(OH)_{2,s}$
$MS$
$MCO_3$
$M_3(PO_4)_2$

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:

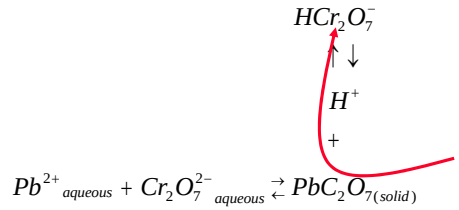
How to bring it back into solution

a. With acid

b. With a ligand

## Dissolving Precipitates

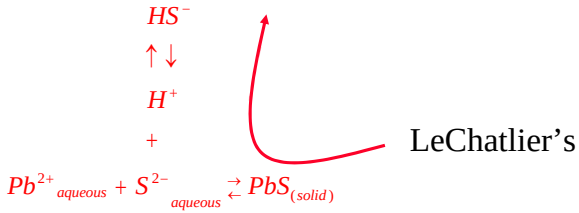
1. Strong acid




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

## Dissolving Precipitates

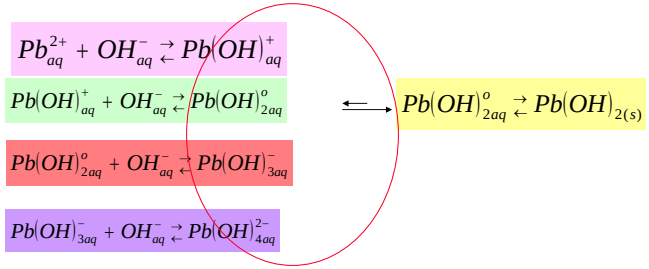
1. Strong acid




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

## Dissolving Precipitates

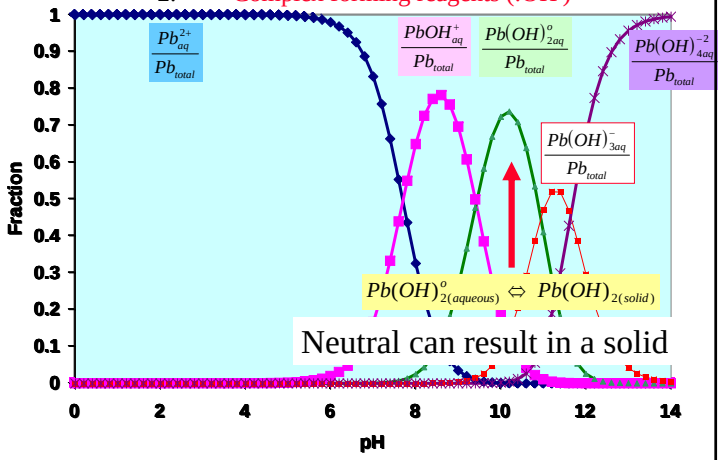
1. Strong acid
2. Complex forming reagents (:$NH_3$, :$OH^-$)




Complexes

Dissolving Precipitates

1. Strong acid
2. Complex forming reagents ($:OH^-$)




Ligands like :$NH_3$ and
:$OH^-$ can bring various precipitates into solution

| Complex | $K_f$ | Complex | $K_f$ |
|---|---|---|---|
| $Ag(NH_3)_2^+$ | $1.8x10^7$ | | |
| $Cu(NH_3)_4^{2+}$ | $2x10^{12}$ | | |
| $Zn(NH_3)_4^{2+}$ | $3.6x10^8$ | $Zn(OH)_4^{2-}$ | $3x10^{14}$ |
| $Cd(NH3)_4^{2+}$ | $2.8x10^7$ | $Cd(OH)_4^{2-}$ | $1.2x10^9$ |
| $Ni(NH_3)_6^{2+}$ | $9x10^8$ | | |
| | | $Al(OH)_4^-$ | $1x10^{33}$ |
| | | $Sb(OH)_4^-$ | |
| | | $Sn(OH)_6^{2-}$ | |

Hold Coordination Number constant

What do you observe?

Size matters: the larger The cation (less charge dense) the smaller the $K_f$

ligand: :$NH_3$

LeChatlier's Principle

Bring Silver Into solution

$$Ag^+_{aqueous} + Cl^-_{aqueous} \rightleftarrows AgCl_{(solid)}$$
$$+$$
$$2\,NH_{3,aqueous}$$
$$\uparrow\downarrow$$
$$Ag(NH_3)^+_{2(aqueous)}$$

**Example 4:** Calculate moles AgCl dissolved in 1 L of **6.0 M** $NH_3$ at a temperature of 298 K

| Know | Don't Know | Red Herring |
|---|---|---|
| 6.0 M $NH_3$ | s | 298K |

reaction — $K_{rx}$

$AgCl_{(solid)} \rightleftarrows Ag^+_{aqueous} + Cl^-_{aqueous}$ — $K_{sp} = 1.8x10^{-10}$

$Ag^+_{aqueous} + 2\,NH_{3,aq} \rightleftarrows Ag(NH_3)^+_{2,aq}$ — $K_f = 1.7x10^7$

$$AgCl_{(solid)} + 2\,NH_{3,aq} \rightleftarrows Ag(NH_3)^+_{2,aq} + Cl^-_{aqueous}$$

$$K_{reaction} = K_{sp}K_f = (1.8x10^{-10})(1.7x10^7) = 3.1x10^{-3}$$

| | $AgCl_s$ | $[NH_3]$ | $[Ag(NH_3)_2^+]$ | $[Cl^-]$ |
|---|---|---|---|---|
| stoic | n.a. | 2 | 1 | 1 |
| **I**nit | | **6.0 M** | 0 | 0 |
| **C**hange | | -2x | x | x |
| **E**quil | | **6.0**-2x | x | x |

**Example:** Calculate moles AgCl dissolved in 1 L of **6.0 M** $NH_3$ at a temperature of 298 K

| | $AgCl_s$ | $[NH_3]$ | $[Ag(NH_3)_2^+]$ | $[Cl^-]$ |
|---|---|---|---|---|
| stoic | n.a. | 2 | 1 | 1 |
| init | | **6.0 M** | 0 | 0 |
| change | | -2x | x | x |
| equil | | **6.0**-2x | x | x |

$$K_{reaction} = 3.1x10^{-3} = \frac{\left[Ag(NH_3)_2^+\right][Cl^-]}{[NH_3]^2}$$

$$3.1x10^{-3} = \frac{x[x]}{[6.0-2x]^2}$$

$$\sqrt{3.1x10^{-3}} = \frac{x}{6.0-2x}$$

X= moles complex
= 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

$$K_{reaction} = 3.1x10^{-3} = \frac{\left[Ag(NH_3)_2^+\right][Cl^-]}{[NH_3]^2}$$

$$K_{rx} = \frac{x[x]}{\left[[NH_3]_{init} - 2x\right]^2}$$

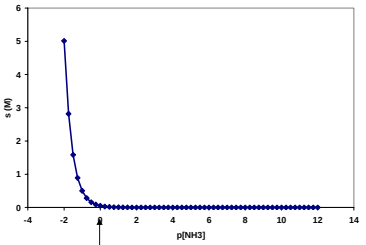
$$\sqrt{K_{rx}} = \frac{x}{\left[[NH_3]_{init} - 2x\right]}$$

$$\left(\sqrt{K_{rx}}\right)\left[[NH_3]_{init} - 2x\right] = x$$

$$\left(\sqrt{K_{rx}}\right)[NH_3]_{init} = x + 2x\left(\sqrt{K_{rx}}\right)$$

$$\left(\sqrt{K_{rx}}\right)[NH_3]_{init} = x\left(1 + 2\sqrt{K_{rx}}\right)$$

$$\frac{\left(\sqrt{K_{rx}}\right)[NH_3]_{init}}{\left(1 + 2\sqrt{K_{rx}}\right)} = x$$




AgCl becomes soluble
Around 1 M ammonia


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

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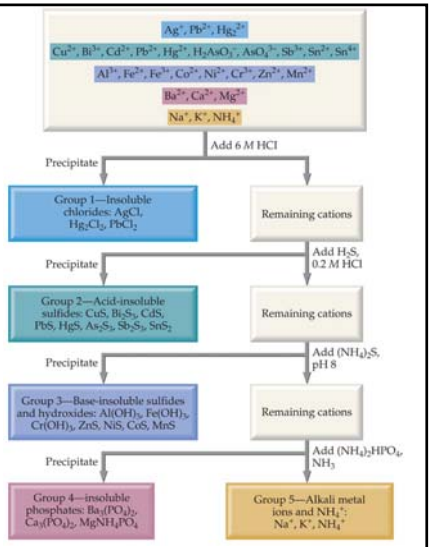
**Module #19:**
**Precipitation Reactions**

**Qualitative Analysis:**
**Cl to separate Pb, $Hg_2^{2+}$, Ag**

Using pH and complexation to Separate Ions For Qualitative Analysis

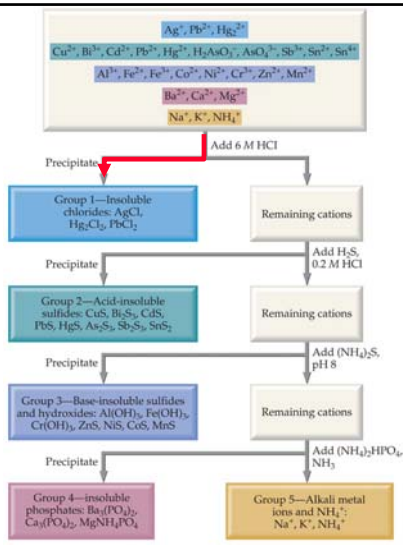


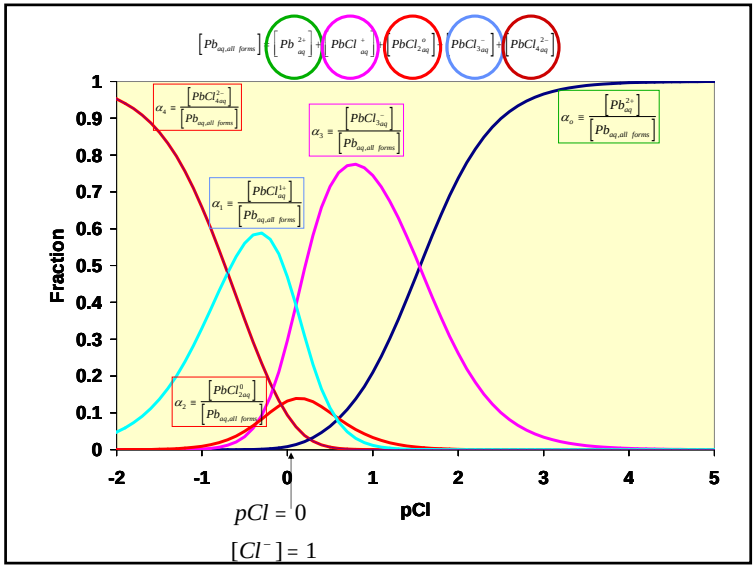
Separation in lab is not always the same
As in the text.

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

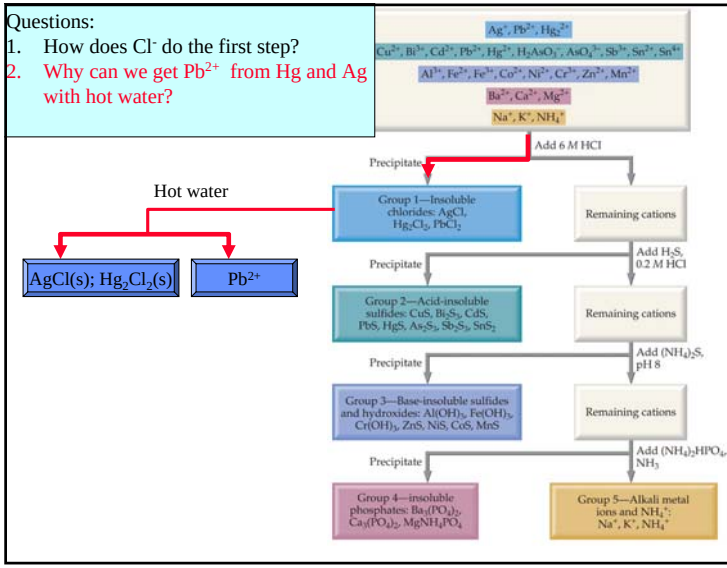
The separation below
Corresponds to
What goes on in lab

Questions:
1. **How does $Cl^-$ do the first step?**



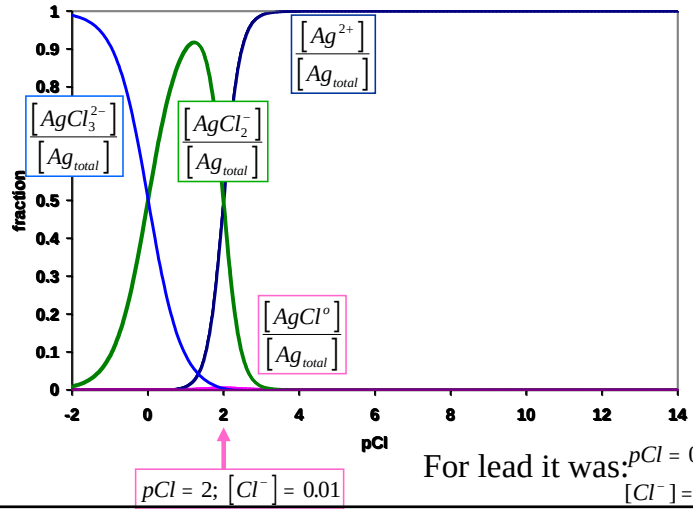




Questions:
1. How does $Cl^-$ do the first step?
2. Why can we get $Pb^{2+}$ from Hg and Ag with hot water?



$$Pb^{2+}_{aq} + Cl^{-}_{aq} \rightleftarrows PbCl^{+}_{aq} \qquad K_{f1}$$
$$PbCl^{+}_{aq} + Cl^{-}_{aw} \rightleftarrows PbCl^{0}_{2,aq} \qquad K_{f2} \longleftrightarrow PbCl^{0}_{2,s}$$
$$PbCl^{0}_{2,aq} + Cl^{-}_{aq} \rightleftarrows PbCl^{-}_{3,aq} \qquad K_{f3}$$
$$PbCl^{-}_{3,aq} + Cl^{-}_{aq} \rightleftarrows PbCl^{2-}_{4,aq} \qquad K_{f4}$$

$$Ag^{+}_{aq} + Cl^{-}_{aq} \rightleftarrows AgCl^{0}_{,aq} \qquad K_{f1}$$
$$AgCl^{0}_{,aqs} + Cl^{-}_{aq} \rightleftarrows AgCl^{1-}_{2,aq} \qquad K_{f2} \longleftrightarrow AgCl^{0}_{,s}$$
$$AgCl^{-}_{2,aqs} + Cl^{-}_{aq} \rightleftarrows AgCl^{2-}_{3,aq} \qquad K_{f3}$$

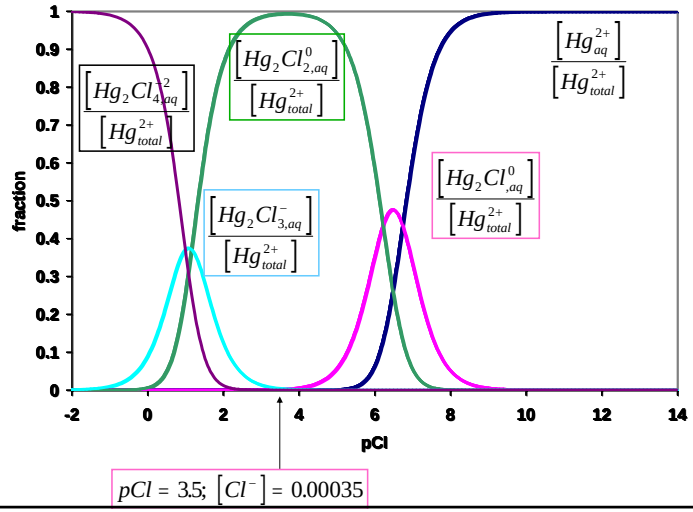


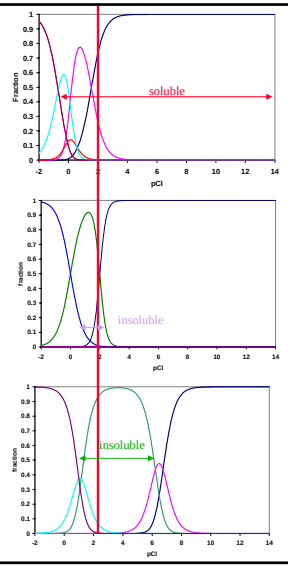

For lead it was: $pCl = 0$, $[Cl^-] = 1$

$$Pb^{2+}_{aq} + Cl^{-}_{aq} \rightleftarrows PbCl^{+}_{aq} \qquad K_{f1}$$
$$PbCl^{+}_{aq} + Cl^{-}_{aw} \rightleftarrows PbCl^{0}_{2,aq} \qquad K_{f2} \longleftrightarrow PbCl^{0}_{2,s}$$
$$PbCl^{0}_{2,aq} + Cl^{-}_{aq} \rightleftarrows PbCl^{-}_{3,aq} \qquad K_{f3}$$
$$PbCl^{-}_{3,aq} + Cl^{-}_{aq} \rightleftarrows PbCl^{2-}_{4,aq} \qquad K_{f4}$$

$$Ag^{+}_{aq} + Cl^{-}_{aq} \rightleftarrows AgCl^{0}_{,aq} \qquad K_{f1}$$
$$AgCl^{0}_{,aqs} + Cl^{-}_{aq} \rightleftarrows AgCl^{1-}_{2,aq} \qquad K_{f2} \longleftrightarrow AgCl^{0}_{,s}$$
$$AgCl^{-}_{2,aqs} + Cl^{-}_{aq} \rightleftarrows AgCl^{2-}_{3,aq} \qquad K_{f3}$$

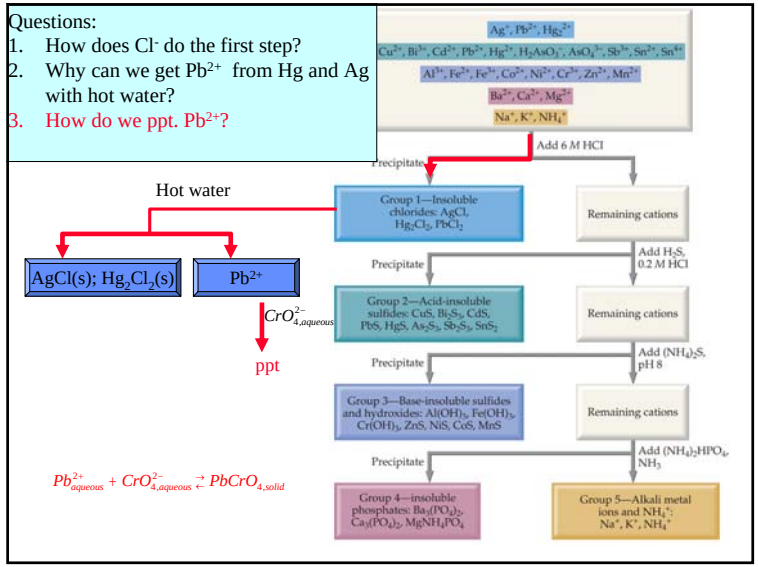
$$2Hg^{+}_{aq} + Cl^{-}_{aq} \rightleftarrows Hg_2Cl^{+}_{aq} \qquad K_{f1}$$
$$Hg_2Cl^{+}_{aq} + Cl^{-}_{aq} \rightleftarrows Hg_2Cl_2 \qquad K_{f2} \longleftrightarrow Hg_2Cl_{2(solid)}$$
$$Hg_2Cl_2 + Cl^{-}_{aq} \rightleftarrows Hg_2Cl^{-}_{3,aq} \qquad K_{f3}$$
$$Hg_2Cl^{-}_{3,aq} + Cl^{-}_{aq} \rightleftarrows Hg_2Cl^{-2}_{4,aq} \qquad K_{f4}$$






Lower chloride concentration by placing ppt in hot water.
$PbCl_2$ dissolves;
AgCl and $Hg_2Cl_2$ remain insoluble

Questions:
1. How does $Cl^-$ do the first step?
2. Why can we get $Pb^{2+}$ from Hg and Ag with hot water?
3. How do we ppt. $Pb^{2+}$?




$Pb^{2+}_{aqueous} + CrO^{2-}_{4,aqueous} \rightleftarrows PbCrO_{4,solid}$

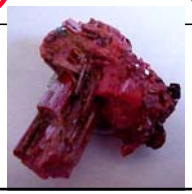
## Candidates for precipitating $Pb^2$ from supernatent?

| | $K_{sp}$, Pb | Cd | Zn |
|---|---|---|---|
| $PbF_2$ | $4x10^{-8}$ | - | - |
| $PbCl_2$ | $1.6x10^{-5}$ | - | - |
| $PbI_2$ | $1.4x10^{-8}$ | - | |
| $PbSO_4$ | $1.3x10^{-8}$ | - | |
| $PbCrO_4$ | $2x10^{-16}$ | - | – |
| $PbCO_3$ | $1.5x10^{-15}$ | $5.5x10^{-13}$ | – |
| $Pb(OH)_2$ | $1.2x10^{-15}$ | $6.45x10^{-6}$ | $6.3x10^{-17}$ |
| PbS | $7x10^{-29}$ | – | $1.99x10^{-25}$ |
| $Pb_3(PO_4)_2$ | $1x10^{-54}$ | | $3.8x10^{-36}$ |

**$OH^-$, $CO_3^{2-}$ bring $Cd^{2+}$**

**$S^{2-}$, $PO_4^{3-}$ bring $Zn^{2+}$**

Need very insoluble species, that doesn't bring along Cd or Zn



**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

$P > K_{sp}$; *ppt forms*

$$P = \left[Pb^{2+}\right]\left[CrO_4^{2-}\right] > K_{sp}(2x10^{-16})?$$

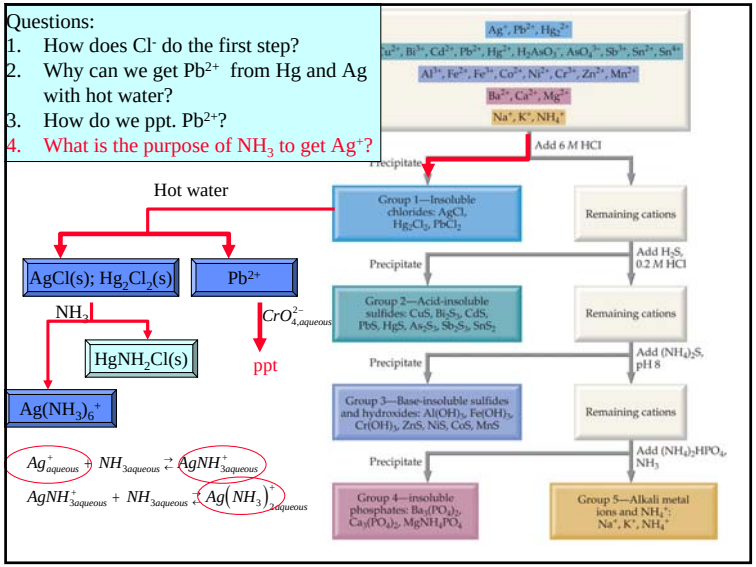
$$\frac{\left[\frac{mole}{331gPb(NO_3)_2}\right]\left(0.50mgPb(NO_3)_2\right)\left(\frac{1g}{10^3mg}\right)}{1L} = 1.51x10^{-6}\,MPb^{2+}$$

$$\frac{\left[\frac{mole}{194.2gK_2CrO_4}\right]\left(0.020mgK_2CrO_4\right)\left(\frac{1g}{10^3mg}\right)}{1L} = 1.029x10^{-7}\,MCrO_4^{2-}$$

$$P = (1.51x10^{-6})(1.029x10^{-7}) = 1.554x10^{-13} > K_{sp}(2x10^{-16})$$

Questions:

1. How does $Cl^-$ do the first step?
2. Why can we get $Pb^{2+}$ from Hg and Ag with hot water?
3. How do we ppt. $Pb^{2+}$?
4. What is the purpose of $NH_3$ to get $Ag^+$?




$Ag^+_{aqueous} + NH_{3aqueous} \rightleftarrows AgNH^+_{3aqueous}$

$AgNH^+_{3aqueous} + NH_{3aqueous} \rightleftarrows Ag(NH_3)^+_{2aqueous}$

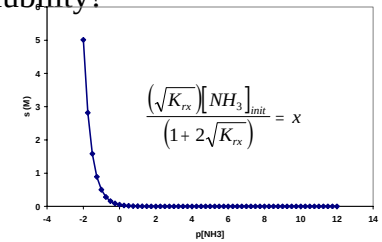
We did an example in which we calculated the Solubility of AgCl in the presence of ammonia

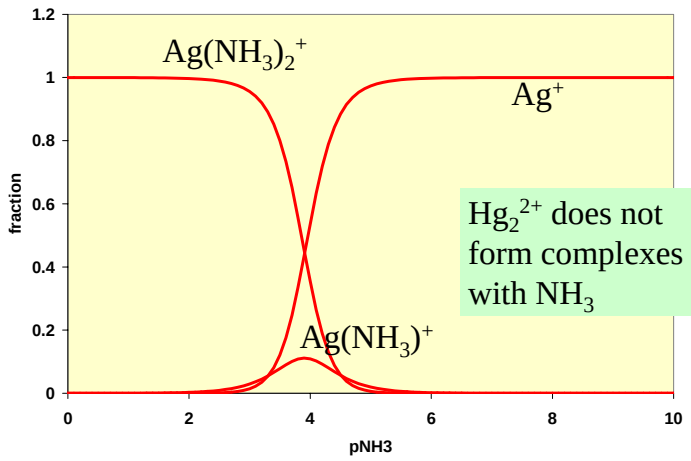
$$AgCl_{(solid)} \rightleftarrows Ag^+_{aqueous} + Cl^-_{aqueous} \qquad K_{sp} = 1.8x10^{-10}$$

$$Ag^+_{aqueous} + 2NH_{3,aq} \rightleftarrows Ag(NH_3)^+_{2} \qquad K_f = 1.7x10^{7}$$

$$AgCl_{(solid)} + 2NH_{3,aq} \rightleftarrows Ag(NH_3)^+_{2,aq} + Cl^-_{aqueous} \qquad K_{reaction} = 3.1x10^{-3}$$

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




$Hg_2^{2+}$ does not form complexes with $NH_3$


"A" students work (without solutions manual)
~ 10 problems/night.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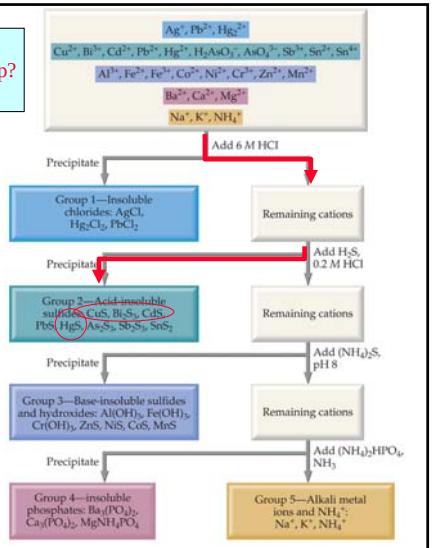
**Module #19: Precipitation Reactions**

**Qualitative Analysis: S to separate Cu $^{2+}$, $Hg^+$, $Bi^{3+}$, $Cd^{2+}$**

Questions:

1. How does $H_2S$ do the second step?




| | $\log K_{sp}$ $S^{2-}$ |
|---|---|
| $Cu^{2+}$ | -48.5 |
| $Bi^{3+}$ | |
| $Hg^{2+}$ | -52.7 |
| $Cd^{2+}$ | -27.0 |
| $Al^{3+}$ | |
| $Fe^{3+}$ | |
| $Cr^{3+}$ | |
| $Mn^{2+}$ | -10.5 |
| $Zn^{2+}$ | -24.7 |
| $Ba^{2+}$ | - |
| $Ca^{2+}$ | - |

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

Weak Precipitators with $[S^{2-}]$ Will ppt only at higher $[S^{2-}]$

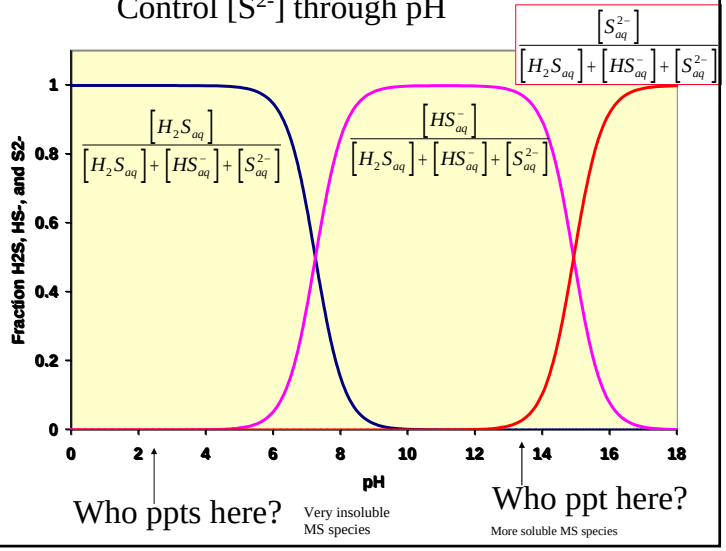
How can we control [S2-] Easily?

$$H_2S_{aq} \rightleftarrows H^+_{aq} + HS^-_{aq} \qquad K_{a1}$$

$$HS^-_{aq} \rightleftarrows H^+_{aq} + S^{2-}_{aq} \qquad K_{a2}$$

$$H_2S_{aq} \rightleftarrows 2H^+_{aq} + S^{2-}_{aq} \qquad K_{a1}K_{a2}$$

Control $[S^{2-}]$ through pH





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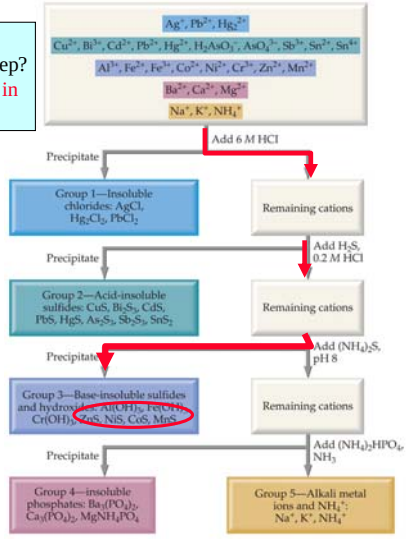
**Module #19: Precipitation Reactions**

**Qualitative Analysis: S to separate $Zn^{2+}$, $Co^{+2}$, $Mn^{2+}$, $Ni^{2+}$**

Questions:
1. How does $(NH_4)_2S$ do the first step?
2. Why is the solution basic (pH 8) in next step?




| | $\log K_{sp}$ $S^{2-}$ |
|---|---|
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| $Hg^{2+}$ | -52.7 |
| $Cd^{2+}$ | -27.0 |
| $Al^{3+}$ | |
| $Fe^{3+}$ | |
| $Cr^{3+}$ | |
| $Mn^{2+}$ | -10.5 |
| $Zn^{2+}$ | -24.7 |
| $Ba^{2+}$ | - |
| $Ca^{2+}$ | - |

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 $[S^{2-}]$

$2M\ NH_4^+;\ 5\ MNH_3;\ (NH_4)_2S$ } Ppt out sulfides

Buffer pH to basic solution of 9.599 to ppt hydroxides

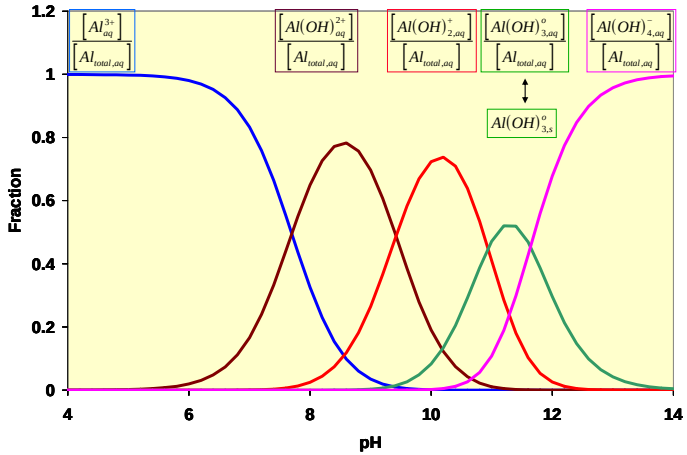
$NH_4^+ \rightleftarrows NH_3 + H^+$ $\qquad K_a = 5.6x10^{-10}$

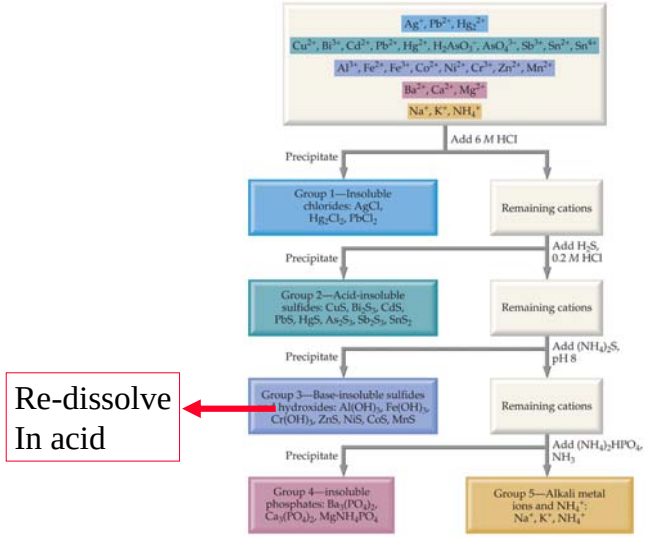
$$pH = pK_a + \log\frac{[A]}{[HA]}$$

$$pH = -\log(5.6x10^{-10}) + \log\frac{5M}{2M}$$

$pH = 9.25 + 0.397 = 9.65$

$Al^{3+}$, $Cr^{3+}$ $Fe^{3+}$ come along as a hydroxides

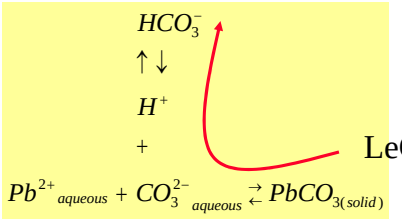





Re-dissolve
In acid

## Dissolving Precipitates

1. Strong acid
2. Complex forming reagents ($:NH_3$, $:OH^-$)




LeChatlier's

Acid dissolves: carbonates; sulfides, hydroxides


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

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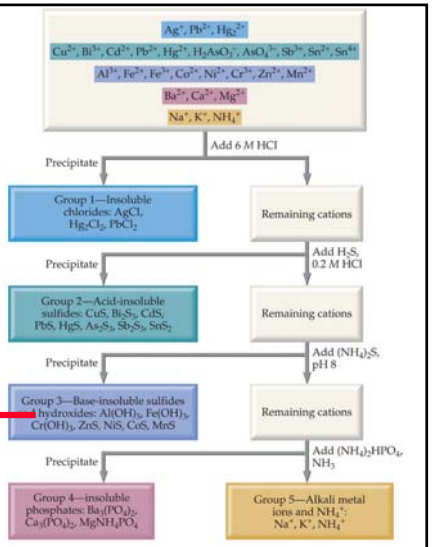
**Module #19:**
**Precipitation Reactions**

**Qualitative Analysis:**
**Separating $Zn^{2+}$,**
**And $Al^{3+}$, from the sulfides**
**By OH complexation**




Re-dissolve
In acid

Increase pH

## Example Calculation 6:

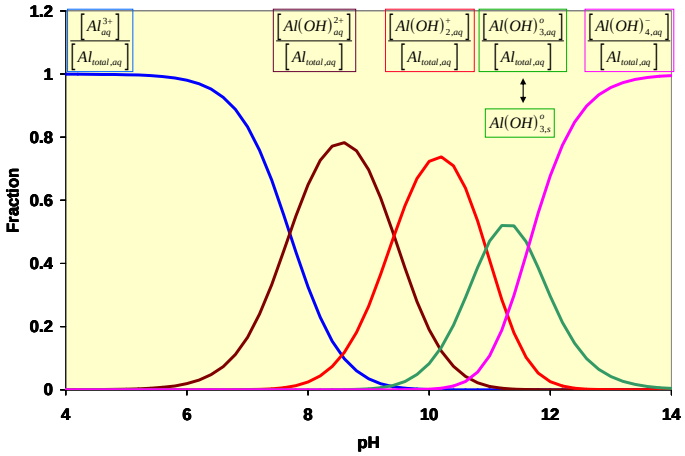
| | | $K_f$ | | $K_{sp}$ | $K_{sp}K_f$ |
|---|---|---|---|---|---|
| $Ag^+$ | $Ag(OH)_2^-$ | $1x10^4$ | Ag(OH) | $1.99x10^{-9}$ | $1.99x10^{-5}$ |
| $Zn^{2+}$ | $Zn(OH)_4^{2-}$ | $4.6x10^{17}$ | $Zn(OH)_2$ | $3.16x10^{-16}$ | 145 |
| $Mn^{2+}$ | $Mn(OH)^+$ | $2.51x10^3$ | $Mn(OH)_{2(s)}$ | $1.58x10^{-13}$ | $3.96x10^{-10}$ |
| $Cr^{3+}$ | $Cr(OH)^{2+}$ | $6.3x10^3$ | $Cr(OH)_{3(s)}$ | $6.3x10^{-31}$ | 1.28 |
| $Al^{3+}$ | $Al(OH)_4^-$ | $1x10^{33}$ | $Al(OH)_{3(s)}$ | $4.6x10^{-33}$ | 4.6 |
| $Fe^{3+}$ | $Fe(OH)_2^+$ | $1.99x10^{22}$ | $Fe(OH)_3(s)$ | $4x10^{-38}$ | $7.96x10^{-16}$ |
| $Sn^{2+}$ | $Sn(OH)_3^-$ | $2.5x10^{25}$ | $Sn(OH)_{2(s)}$ | $1.2x10^{-17}$ | $3.0x10^8$ |

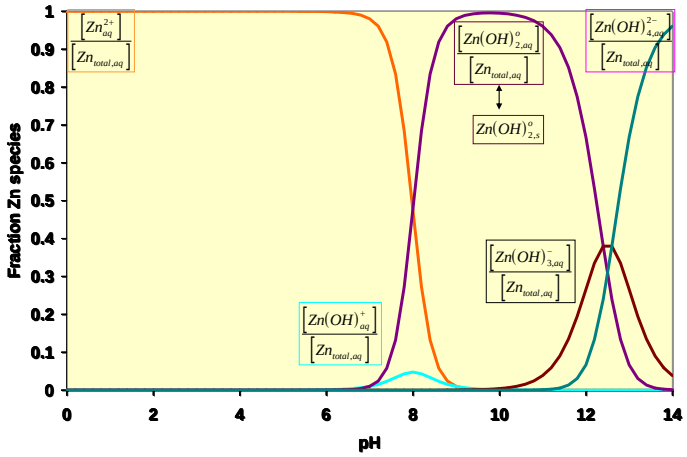
$AgOH_s \Leftrightarrow Ag^+_{aq} + OH^-_{aq} \qquad K_{sp} = 1.99x10^{-9}$

$Ag^+_{aq} + 2OH^-_{aq} \Leftrightarrow ag(OH)^-_{2,aq} \qquad K_f = 1x10^4$

$AgOH_s + OH^-_{aq} \Leftrightarrow Ag(OH)^-_{2,aq} \qquad K_{net} = K_{sp}K_f = (1.99x10^{-9})(1x10^4) = 1.99x10^{-5}$

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




How do we distinguish Zn from Al?

Between $Al(OH)_4^-$ and $Zn(OH)_4^-$ only Zn has complexation with :$NH_3$

**Drop pH** to re-ppt $Al(OH)_3$, while simultaneously forming soluble $Zn(NH_3)_4^{2+}$

$NH_4^+ \rightleftarrows NH_3 + H^+ \qquad K_a = 5.6x10^{-10}$

$pH = pK_a + \log\frac{[A]}{[HA]}$

$pH = -\log(5.6x10^{-10}) + \log\frac{3M}{12M}$

$pH = 9.25 + -0.602 = 8.65$

| | |
|---|---|
| 3 | M $NH_4^+$ |
| 12 | M $NH_3$ |

## Dissolving Precipitates

1. Strong acid
2. Complex forming reagents (:$NH_3$, :$OH^-$)

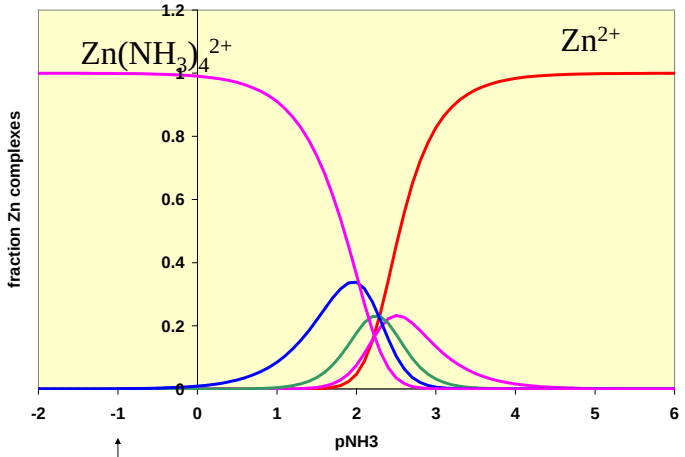
$$Zn^{2+}{}_{aqueous} + 2OH^-{}_{aqueous} \rightleftarrows Zn(OH)_{2(solid)}$$

$$+$$

$$4NH_3$$

$$\uparrow\downarrow$$

$$Zn(NH_3)^{2+}_{4(aqueous)}$$





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

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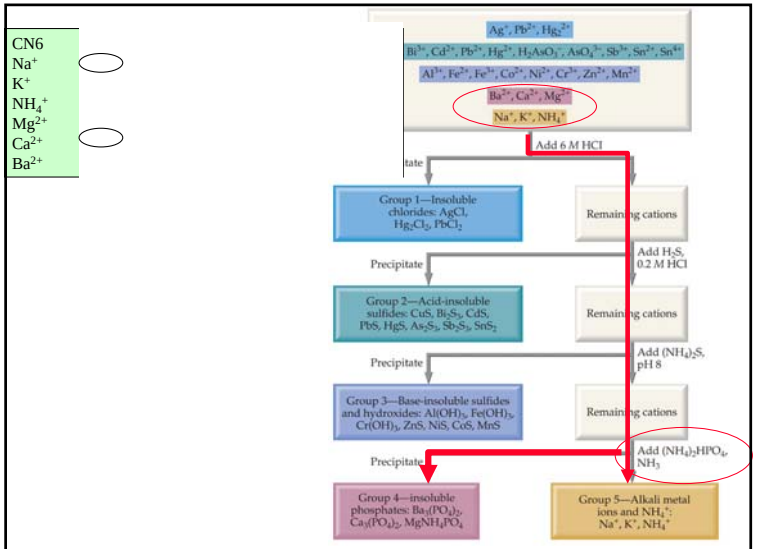
**Module #19: Precipitation Reactions**

**Qualitative Analysis: $PO_4^{3-}$ to separate Ba $^{2+}$, $Ca^{+2}$, $Mg^{2+}$**




"A" students work
(without solutions manual)
~7 problems/night.

Solubility

What you need
To know

## 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

$Ba_3(PO_4)_2$


"A" students work
(without solutions manual)
~7 problems/night.

END