

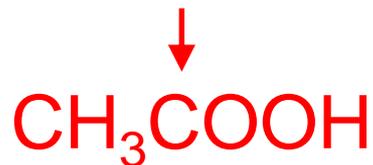
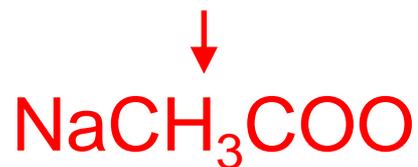
AP Chemistry

Aqueous Equilibria, Part Two



The Common-Ion Effect

Consider a mixture of a “weak” and a “common-ion,”
soluble salt.



Since NaCH_3COO is strong, adding it to the solution...

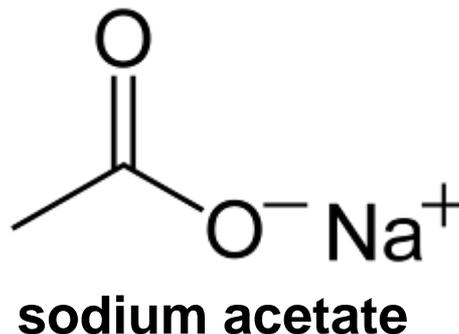
greatly \uparrow $[\text{CH}_3\text{COO}^-]$.

By Le Chatelier...

shift ←

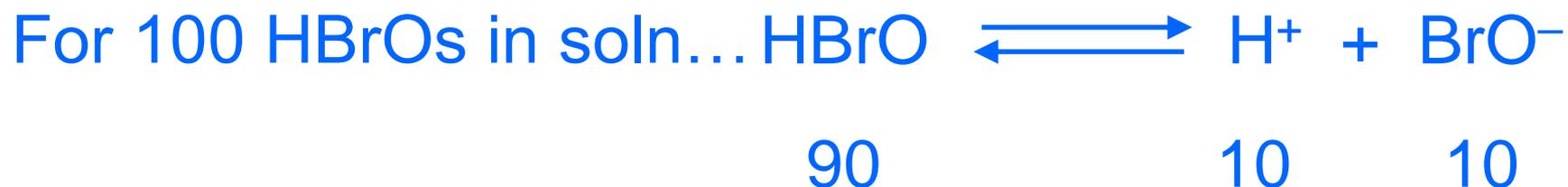
The result is that...

$[\text{H}^+] \downarrow$ and $\text{pH} \uparrow$



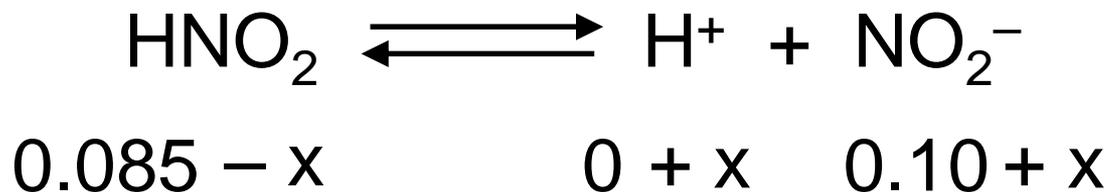
This illustrates the common-ion effect:

“The dissociation of a ‘weak’ DECREASES when a strong, common-ion salt is added to the solution.”



If we add a “strong,” BrO^- salt (like KBrO), the amount of BrO^- goes up, and the amount of HBrO that dissociates goes down (by Le Chatelier).

Find the pH of a solution containing 0.085 M nitrous acid ($K_a = 4.5 \times 10^{-4}$) and 0.10 M potassium nitrite.



$$K_a = 4.5 \times 10^{-4} = \frac{0.10x}{0.085 - x}$$

So... $x = [\text{H}^+] = 3.825 \times 10^{-4} \text{ M} \implies \text{pH} = 3.42$

Find the pH of 0.085 M nitrous acid, on its own.

$$4.5 \times 10^{-4} = \frac{x^2}{0.085 - x}$$

So... $x = [\text{H}^+] = 6.185 \times 10^{-3} \text{ M} \implies \text{pH} = 2.21$

HNO₂ DID dissociate less when the common-ion salt was present.

Buffered Solutions (“buffers”)

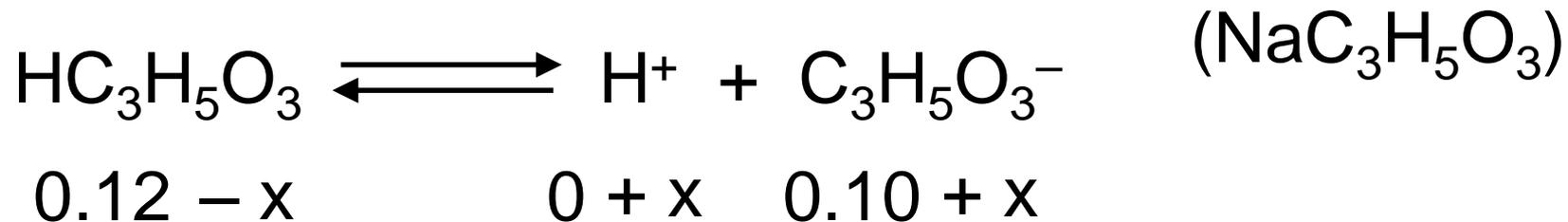
- solns based on the common-ion effect
- they resist ΔpH
- a mixture of...a “weak” (either acid or base) and a common-ion salt

e.g., HOAc and NaOAc NH_3 and NH_4Cl
HF and KF HBrO_2 and $\text{Ca}(\text{BrO}_2)_2$

buffer capacity: the amount of acid or base the buffer can “neutralize” before the pH begins to change appreciably

- buffer capacity increases with... greater amounts of acid/base AND common-ion salt

Find the pH of a buffer that is 0.12 M lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$ ($K_a = 1.4 \times 10^{-4}$) and 0.10 M sodium lactate.



$$1.4 \times 10^{-4} = \frac{0.10x + \cancel{x^2}}{0.12 \cancel{x}}$$

“Shortcut OK?”

“You betcha.”

$$x = [\text{H}^+] = 1.68 \times 10^{-4} \text{ M} \quad \Rightarrow$$

$$\text{pH} = 3.77$$

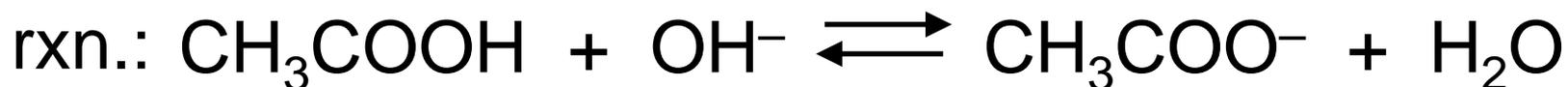
Addition of Strong Acids or Bases to Buffers

- Reactions between strong acids/bases and weak bases/acids proceed to completion.
- We assume that the strong acid/base is completely consumed.
- When adding a “strong” to buffered solutions...
 - (1) Calc. []s after rxn, using stoichiometry
 - (2) Calc. eq. []s using K_a or K_b

2.00-L of a buffered solution of pH 4.74 contains 0.30 mol of acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.30 mol of sodium acetate. Calculate the pH after 0.040 mol of sodium hydroxide is added. Ignore volume changes.

(1) Calc. []s after rxn, using stoichiometry

(Use mol for rxn, M for ICE!)



Init. 0.30 0.04 0.30 w.c?

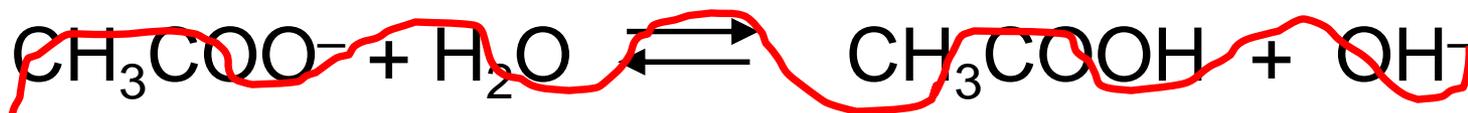
Δ - 0.04 - 0.04 + 0.04

After rxn. 0.26 mol 0 mol + 0.34 mol

(2) Calc. eq. []s using K_a or K_b

(Since $K_a > K_b$,
use K_a equation.)

?



ICE

$$0.13 - x$$

$$0.17 + x$$

$$0 + x$$

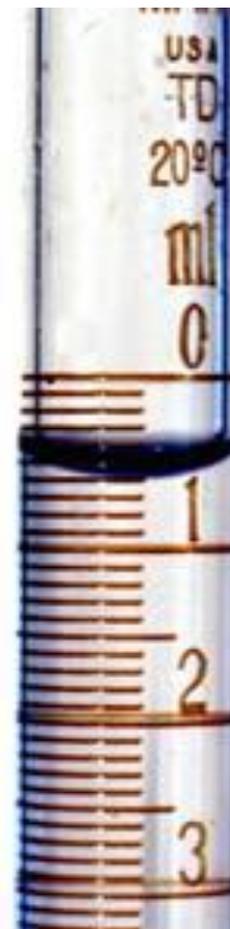
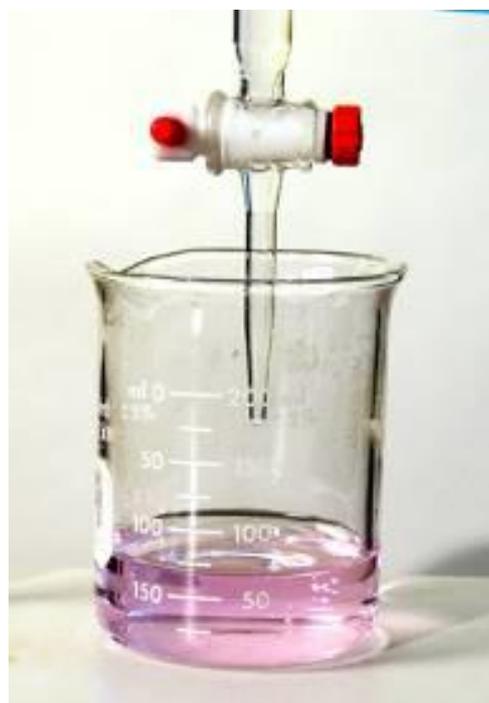
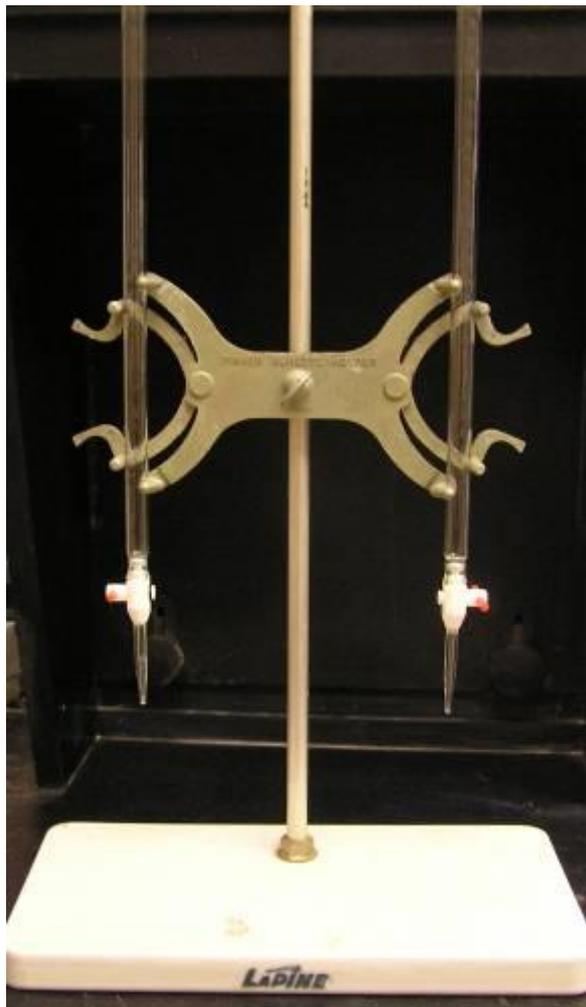
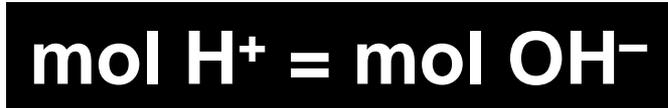
$$1.8 \times 10^{-5} = \frac{0.17x + \cancel{x^2}}{0.13 \cancel{x}}$$

$$x = [\text{H}^+] = 1.376 \times 10^{-5} \text{ M} \quad \Rightarrow$$

$$\text{pH} = 4.86$$

Acid-Base Titrations

equivalence point: the pt. at which equivalent amounts of acid and base have been mixed

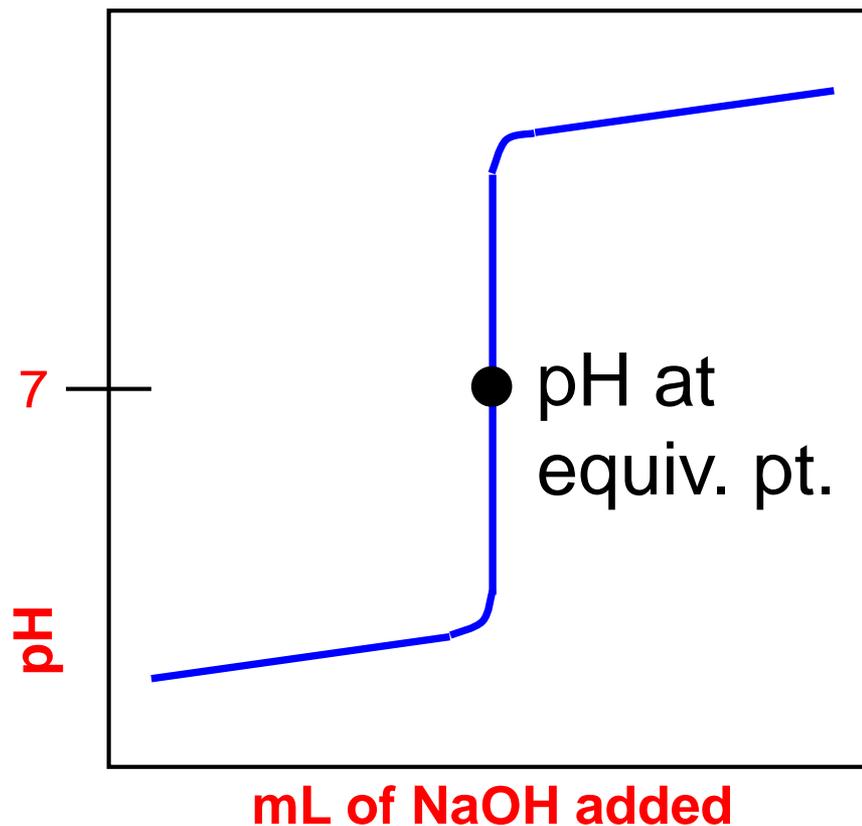


Strong Acid – Strong Base Titrations



Any indicator whose color change begins and ends along the vertical line is okay.

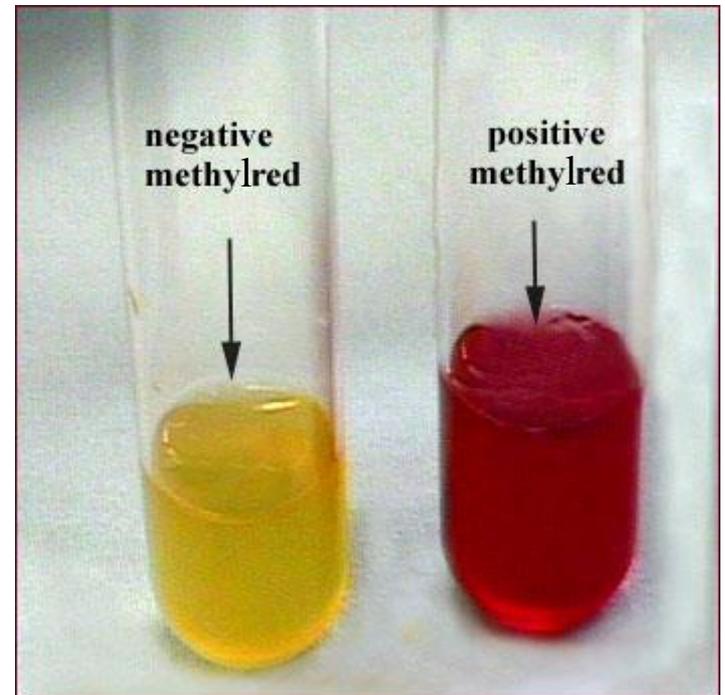
pH curve for HCl titrated with NaOH



Strong Acid – Strong Base Titrations (cont.)

-- phenolphthalein
colorless (pH 8.3-10.0) pink

-- methyl red
yellow (pH 4.2-6.0) red



Find pH when 24.90 mL of 0.10 M nitric acid are mixed with 25.00 mL of 0.10 M potassium hydroxide.

For strong-strong...

(HNO₃ and KOH)

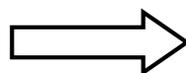
Rxn. goes to completion;
excess determines pH.

$$\text{mol H}^+ = 0.10 \text{ M} (0.0249 \text{ L}) = 0.00249 \text{ mol H}^+$$

$$\begin{aligned} \text{mol OH}^- &= 0.10 \text{ M} (0.0250 \text{ L}) = \underline{0.00250 \text{ mol OH}^-} \\ &= 0.00001 \text{ mol OH}^- \\ &\quad \text{excess} \end{aligned}$$

$$[\text{OH}^-] = \frac{1 \times 10^{-5} \text{ mol}}{\sim 0.0499 \text{ L}} = 2.004 \times 10^{-4} \text{ M OH}^-$$

$$\text{pOH} = 3.70$$



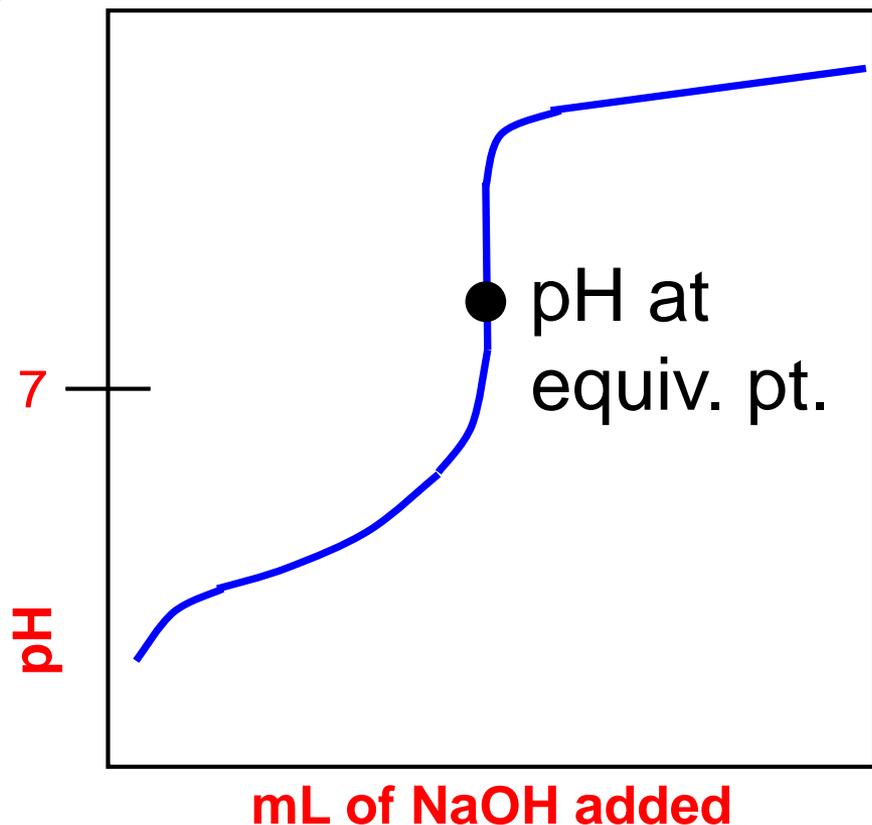
$$\text{pH} = 10.30$$

Weak Acid – Strong Base Titrations

The equivalence point is when, say, 50.0 mL of 0.10 M NaOH have been added to 50.0 mL of 0.10 M CH_3COOH , but pH is > 7 at that point because... the CH_3COO^- generated by the rxn acts as a



pH curve for CH_3COOH titrated with NaOH



Calculate the pH at the equivalence point if 40.0 mL of 0.0250 M benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, $K_a = 6.3 \times 10^{-5}$) are titrated with 0.050 M sodium hydroxide.

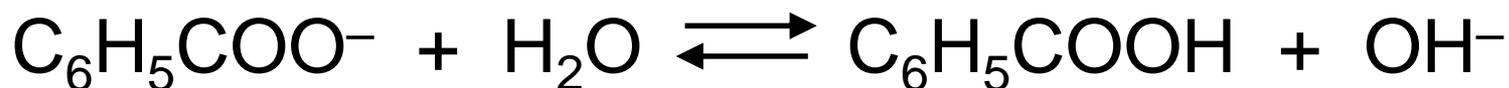
At equivalence pt., $\text{mol H}^+ = \text{mol OH}^-$

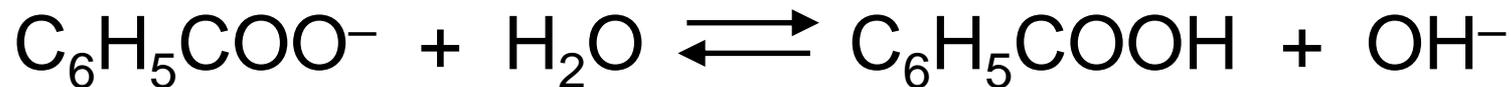
$$0.025 (0.04) = 0.05 (X \text{ L OH}^-)$$

$$X = 0.020 \text{ L NaOH}$$

$$\text{So } V_{\text{tot}} = (0.040 + 0.020) \text{ L} = 0.06 \text{ L}$$

We are at the eq. pt. from the rxn. btwn. a weak acid and a strong base. Strong wins. Use the K_b equation.





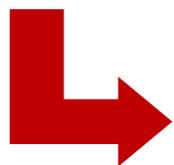
$$\frac{0.025(0.04)}{0.06} - x \quad \text{w.c?} \quad 0 + x \quad 0 + x$$

$$0.0167 - x \quad \text{w.c?} \quad x \quad x$$

Need "conjugatized" K_b for $\text{C}_6\text{H}_5\text{COO}^-$...

$$\frac{1 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.59 \times 10^{-10} = \frac{x^2}{0.0167 - x}$$

$$x = [\text{OH}^-] = 1.63 \times 10^{-6} \text{ M}$$



$$\text{pOH} = 5.79$$



$$\text{pH} = 8.21$$

Calculate the pH when 10.0 mL of 0.080 M sodium hydroxide are added to 40.0 mL of 0.0250 M benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, $K_a = 6.3 \times 10^{-5}$).

available $\text{OH}^- = 0.080 \text{ M} (0.01 \text{ L}) = 0.0008 \text{ mol OH}^-$

available $\text{H}^+ = 0.025 \text{ M} (0.04 \text{ L}) = 0.0010 \text{ mol H}^+$

So... 0.0008 mol OH^- rips 0.0008 mol H^+ off of $\text{C}_6\text{H}_5\text{COOH}$, leaving 0.0008 mol $\text{C}_6\text{H}_5\text{COO}^-$ and 0.0002 mol of unreacted $\text{C}_6\text{H}_5\text{COOH}$.

BEFORE: 100 kids w/IPhones 0.0010 mol $\text{C}_6\text{H}_5\text{COOH}$
80 bullies w/nothing 0.0008 mol OH^-

AFTER: 80 bullies w/IPhones 0.0008 mol H_2O
80 kids crying 0.0008 mol $\text{C}_6\text{H}_5\text{COO}^-$
20 kids w/IPhones 0.0002 mol $\text{C}_6\text{H}_5\text{COOH}$

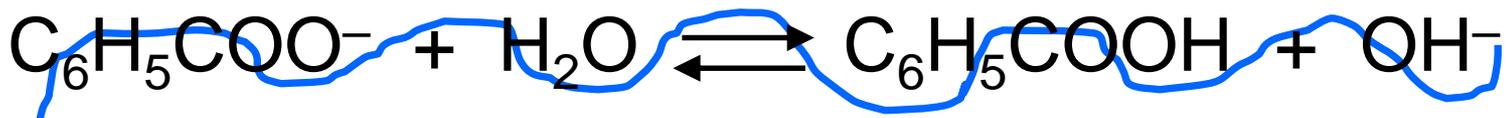
Now find pH:

Before eq., we have...

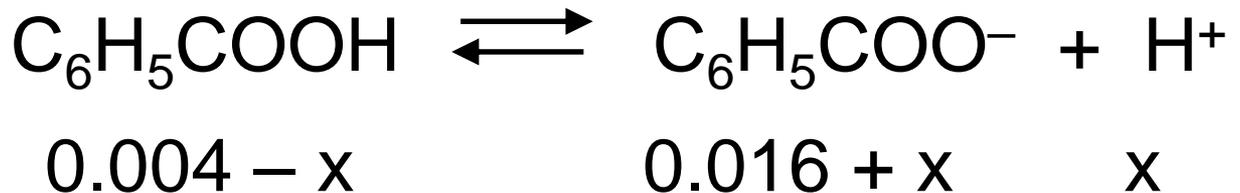
$$[\text{C}_6\text{H}_5\text{COOH}] = 0.0002 \text{ mol} / 0.05 \text{ L} = 0.004 \text{ M}$$

$$[\text{C}_6\text{H}_5\text{COO}^-] = 0.0008 \text{ mol} / 0.05 \text{ L} = 0.016 \text{ M}$$

?



**(H⁺ > OH⁻, so
use**



$$6.3 \times 10^{-5} = \frac{0.016x \cancel{+ x^2}}{0.004 \cancel{- x}}$$

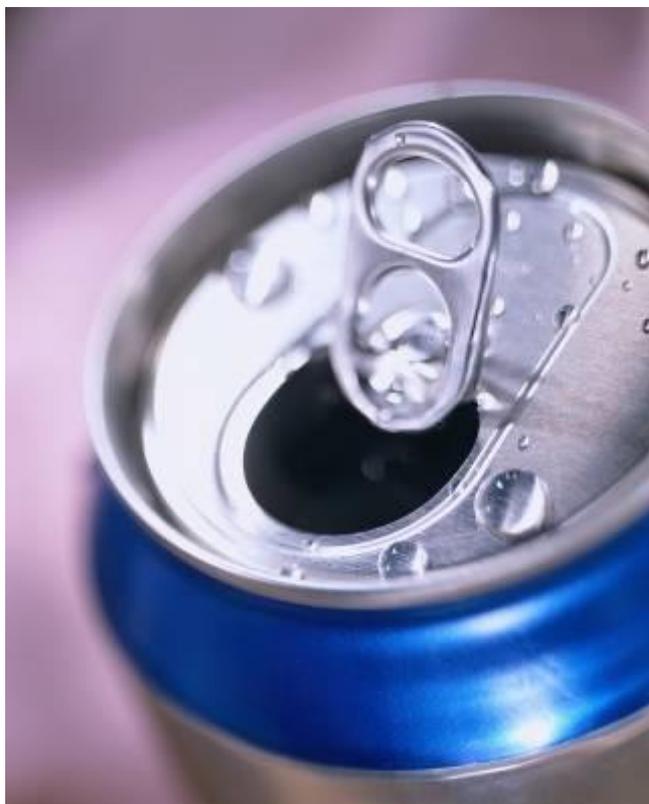
$$x = [\text{H}^+] = 1.575 \times 10^{-5} \text{ M} \implies$$

$$\text{pH} = 4.80$$

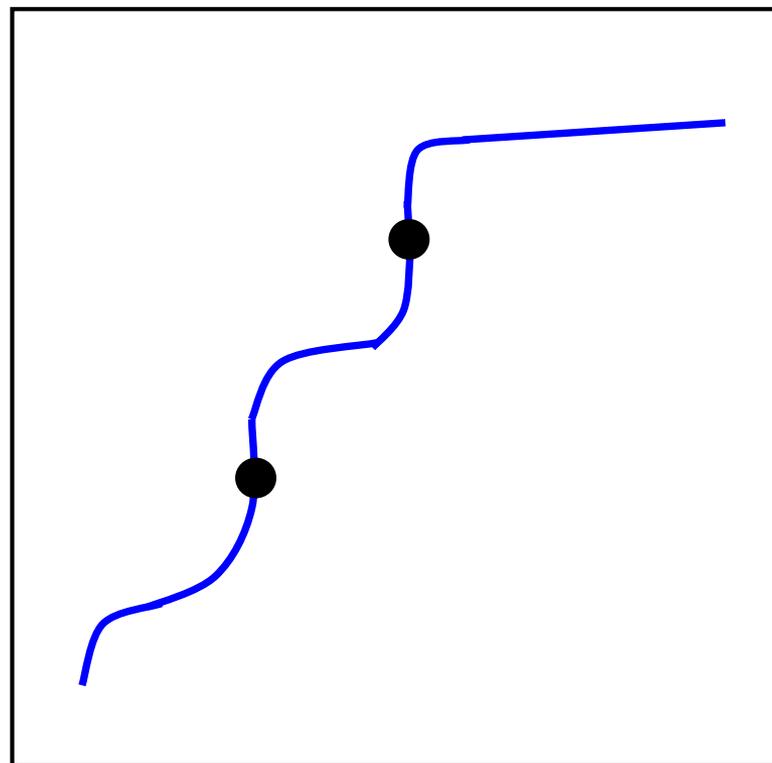
Titration curves for polyprotic acids (e.g., H_2CO_3) look something like

-- they have...

two equivalence points



pH curve for H_2CO_3

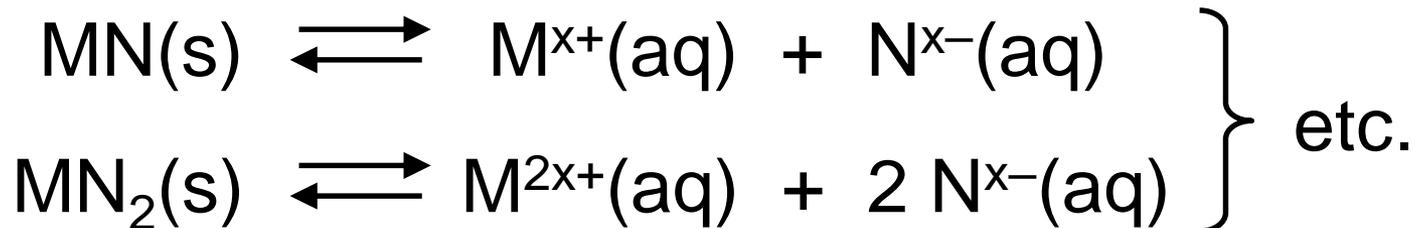


mL of base added

Solubility Equilibria

-- involve the dissolution or precipitation of “insoluble” salts

Consider a saturated solution of a typical salt:



For these cases, the solubility-product constant is equal to (respectively):

$$K_{\text{sp}} = [\text{M}^{\text{x}+}] [\text{N}^{\text{x}-}]$$

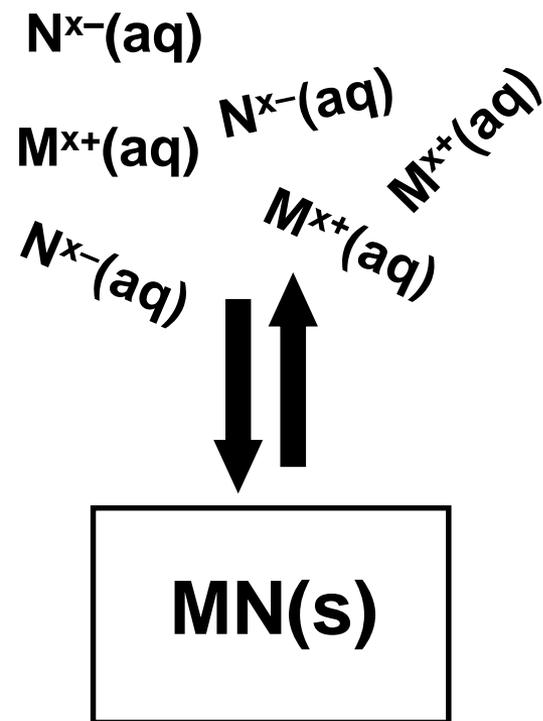
$$K_{\text{sp}} = [\text{M}^{2\text{x}+}] [\text{N}^{\text{x}-}]^2$$

K_{sp} expressions NEVER have denominators because... the “reactant” is always a solid, and we never write solids in equil. eqs.

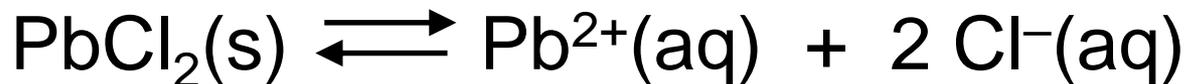
-- K_{sp} is the equilibrium constant between undissolved and dissolved ionic solute in a saturated aqueous solution.

small K_{sp} ... Not much dissolves.

large K_{sp} ... "Quite a bit" dissolves.



Write the solubility-product constant expression for lead(II) chloride.



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

Copper(II) azide has $K_{sp} = 6.3 \times 10^{-10}$. Find the solubility of $\text{Cu}(\text{N}_3)_2$ in water, in g/L.



$$K_{sp} = 6.3 \times 10^{-10} = [\text{Cu}^{2+}] [\text{N}_3^{-}]^2$$

(Let
[Cu^{2+}] = x)

** In “plain-old” $\text{Cu}(\text{N}_3)_2$,: $[\text{N}_3^{-}] = 2 [\text{Cu}^{2+}]$

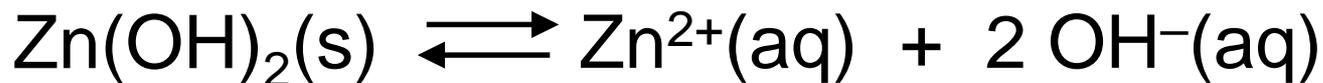
$$\text{So...} 6.3 \times 10^{-10} = x (2x)^2 = 4x^3$$

$$x = 5.40 \times 10^{-4} \text{ M} = [\text{Cu}^{2+}]$$

From eq. at top, $5.40 \times 10^{-4} \text{ M}$ is also the [] of $\text{Cu}(\text{N}_3)_2$ that dissolves.

$$5.40 \times 10^{-4} \frac{\text{mol } \text{Cu}(\text{N}_3)_2}{\text{L}} \left(\frac{147.5 \text{ g}}{1 \text{ mol}} \right) = 8.0 \times 10^{-2} \frac{\text{g}}{\text{L}}$$

Find the solubility of zinc hydroxide ($K_{sp} = 3.0 \times 10^{-16}$) in a soln buffered at pH = 11.43.



$$K_{sp} = 3.0 \times 10^{-16} = [\text{Zn}^{2+}] [\text{OH}^{-}]^2$$

from given pH...



$$3.0 \times 10^{-16} = [\text{Zn}^{2+}] (2.69 \times 10^{-3})^2$$

$$[\text{Zn}^{2+}] = 4.1 \times 10^{-11} \text{ M}$$

From eq. at top, $4.1 \times 10^{-11} \text{ M}$ is also the [] of Zn(OH)_2 that dissolves.

Factors That Affect Solubility

1. For solids, as temperature increases, solubility... 

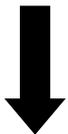
2. common-ion effect

Use Le Chatelier's principle.

For example, with...



If you add Ca^{2+} or F^{-} ,

(Sol. )

3. pH and solubility

Compounds with anions exhibiting basic properties
(e.g., $\text{Mg}(\text{OH})_2 / \text{OH}^{-}$, $\text{CaCO}_3 / \text{CO}_3^{2-}$, $\text{CaF}_2 / \text{F}^{-}$)

 in solubility as solution becomes more acidic.

4. presence of complex ions: metal ions and the Lewis bases bonded to them

e.g., In a soln of AgCl, we have the equilibrium:



If ammonia is added, we get...

complex ion

As Ag^+ forms the complex ion $^w/\text{NH}_3$, Le Chatelier dictates that more AgCl will dissolve into the soln to replenish the decreased [] of Ag^+ .

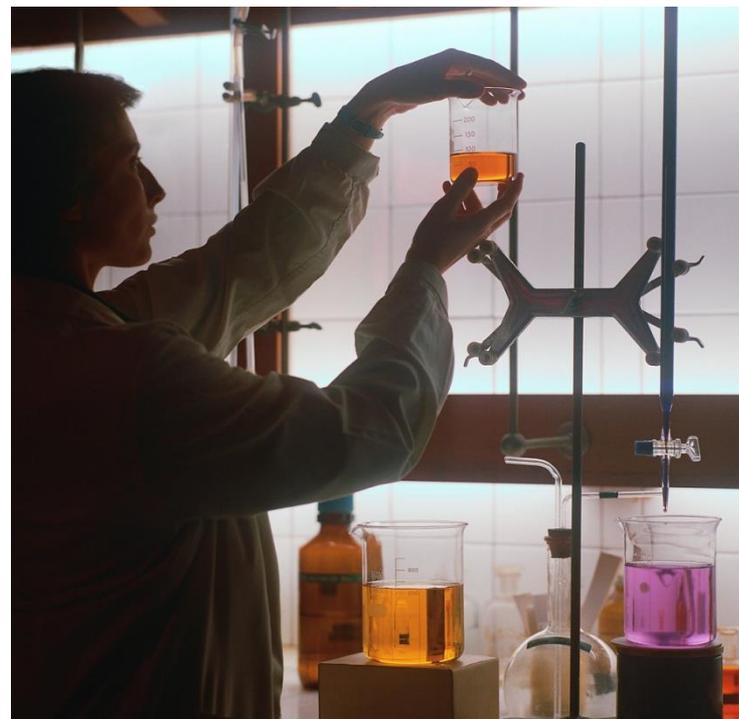
In general, the solubility of metal salts ↑ in the presence of suitable Lewis bases (e.g., NH_3 , CN^- , OH^-) if the metal forms a complex ion with the bases.

Qualitative Analysis for Metallic Elements

determines the presence or absence of a particular ion

Steps:

- (1) separate ions into broad groups by solubility
- (2) specific ions are then separated from the group and identified by specific tests



aqueous solution
containing “god-knows-
what” metal ions

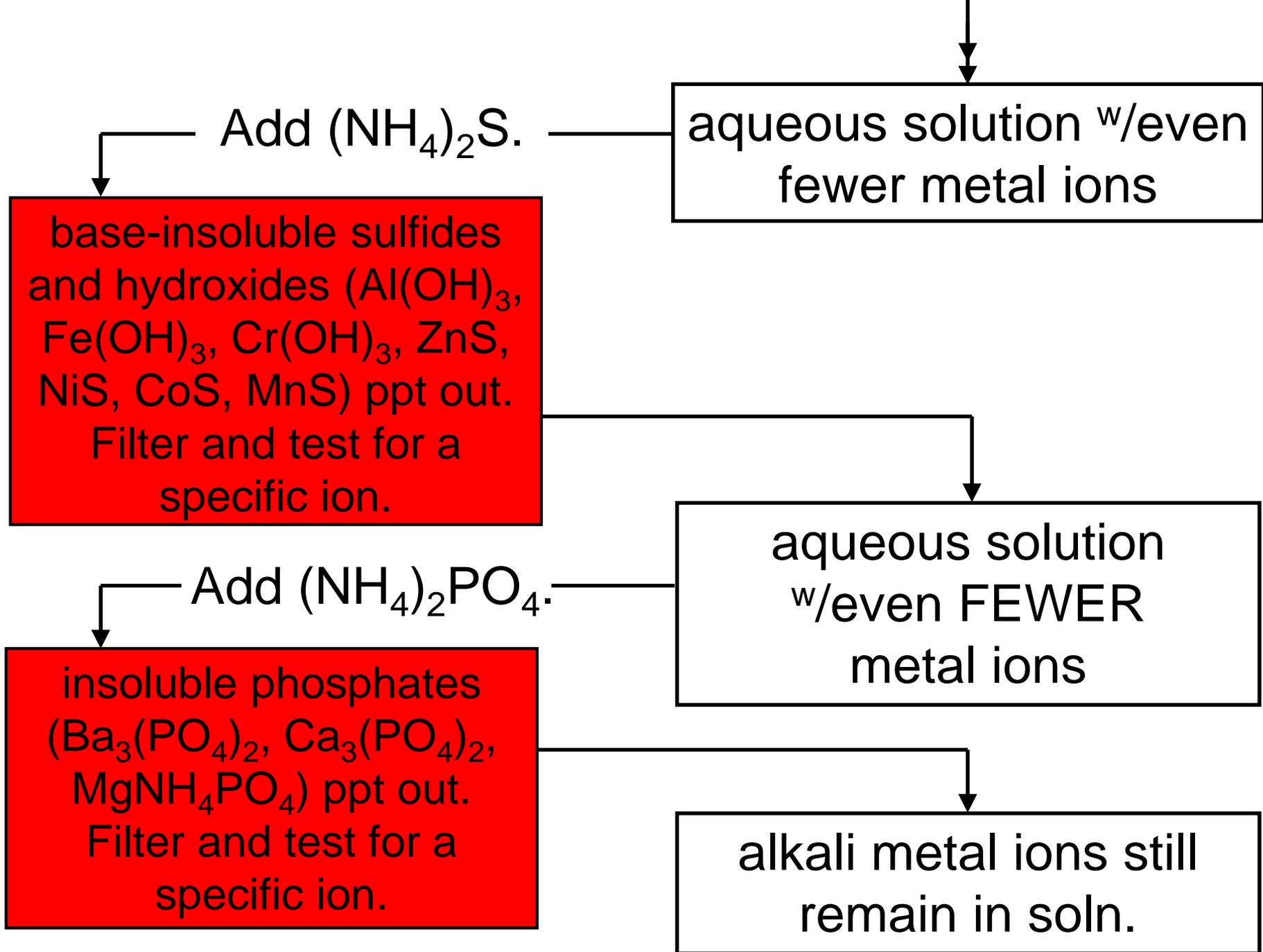
Add HCl.

insoluble chlorides
(AgCl, Hg₂Cl₂, PbCl₂)
ppt out. Filter and
test for a specific ion.

aqueous solution
containing “god-knows-
what” metal ions
(but not much Ag⁺,
Hg₂²⁺, or Pb²⁺)

Bubble H₂S(g) in.

acid-insoluble
sulfides (CuS, Bi₂S₃,
CdS, PbS, HgS,
As₂S₃, Sb₂S₃, SnS₂)
ppt out. Filter and
test for a specific ion.



		$\frac{\text{Hg}_2\text{Cl}_2}{\text{AgCl}}$ $\frac{\text{PbCl}_2}{\text{PbCl}_2}$	Group I Chlorides					
Hg_2^{2+} $\bullet \text{Ag}^+$ $\bullet \text{Pb}^{2+}$ $\bullet \text{Bi}^{3+}$ $\bullet \text{Cu}^{2+}$ Cd^{2+} Hg^{2+} As^{3+} $\bullet \text{Sb}^{3+}$ $\bullet \text{Sn}^{4+}$ Co^{2+} $\bullet \text{Ni}^{2+}$ $\bullet \text{Mn}^{2+}$ $\bullet \text{Fe}^{3+}$ $\bullet \text{Al}^{3+}$ $\bullet \text{Cr}^{3+}$ $\bullet \text{Zn}^{2+}$ Ba^{2+} Sr^{2+} Ca^{2+} Mg^{2+} NH_4^+ Na^+ K^+	$\xrightarrow{\text{HCl}}$	Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+} Hg^{2+} As^{3+} Sb^{3+} Sn^{4+} Co^{2+} Ni^{2+} Mn^{2+} Fe^{3+} Al^{3+} Cr^{3+} Zn^{2+} Ba^{2+} Sr^{2+} Ca^{2+} Mg^{2+} NH_4^+ Na^+ K^+	$\xrightarrow[0.3 \text{ M HCl}]{\text{H}_2\text{S}}$	PbS Bi_2S_3 CuS CdS HgS As_2S_3 Sb_2S_3 SnS_2 Co^{2+} Ni^{2+} Mn^{2+} Fe^{2+} Al^{3+} Cr^{3+} Zn^{2+} Ba^{2+} Sr^{2+} Ca^{2+} Mg^{2+} NH_4^+ Na^+ K^+	$\xrightarrow[\text{H}_2\text{S}]{\text{NH}_4\text{Cl}, \text{NH}_3 + \text{H}_2\text{O}}$	CoS NiS MnS FeS Al(OH)_3 Cr(OH)_3 ZnS Ba^{2+} Sr^{2+} Ca^{2+} Mg^{2+} NH_4^+ Na^+ K^+	Group II Sulfides	Group III Sulfides and Hydroxides

Group Separations Chart with Precipitates Underlined