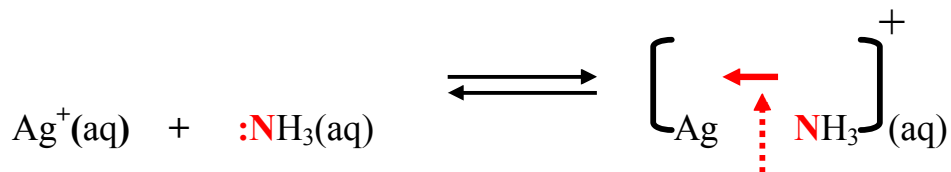


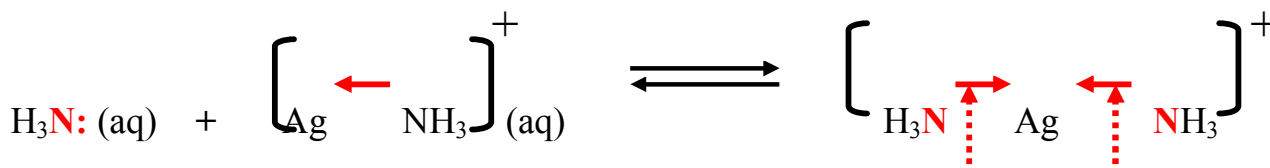
## COMPLEX-ION EQUILIBRIA

- Complex ions are ions that form from transition metal ions attached to molecules or anions by coordinate covalent bonds



Lewis base  
(electron pair donor)

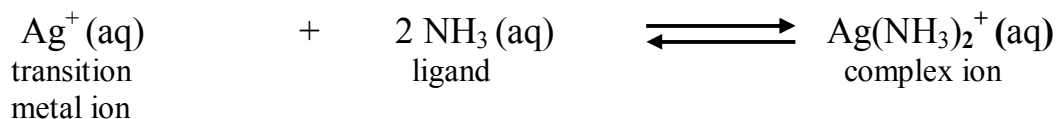
coordinate covalent bond



Lewis base  
(electron pair donor)

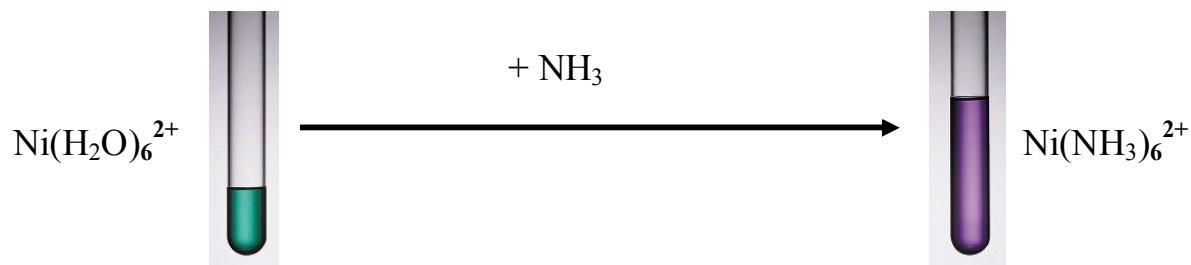
coordinate covalent bonds

### Overall



- Ligand is a Lewis base (electron pair donor) that bonds to a metal ion by a coordinate covalent bond to form a complex ion (ex:  $\text{NH}_3$ )

Note: Different ligands usually impart different colors to the complex ions in solution:



<b>COMPLEX-ION FORMATION</b>
------------------------------

$\text{Ag}^+(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$	
$K_d$ <b>The Dissociation Constant</b>	$K_f$ <b>The Formation Constant</b>
$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$	$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$
<ul style="list-style-type: none"> <li>• <b>The equilibrium constant for the dissociation of the complex ion into a metal ion and the ligands</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>The dissociation constant for the formation of the complex ion from the aqueous metal ion and the ligands</b></li> <li>• <b>Also called “the stability constant”</b></li> </ul>
$K_d$ is the reciprocal of $K_f$	$K_f$ is the reciprocal of $K_d$
$K_d = \frac{1}{K_f}$	$K_f = \frac{1}{K_d}$

**EQUILIBRIUM CALCULATIONS WITH  $K_f$** 

What is the concentration of  $\text{Cu}^{2+}(\text{aq})$  in a solution that was originally **0.015 M  $\text{Cu}(\text{NO}_3)_2$**  and 0.100 M  $\text{NH}_3$  ? The  $\text{Cu}^{2+}$  ion forms the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$  ( $K_f = 4.8 \times 10^{12}$ ).

**Step 1: Stoichiometry Calculation:**

	$\text{Cu}^{2+}(\text{aq})$	+ $4 \text{NH}_3(\text{aq})$	→ $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$
<b>Amounts present in 1L:</b>	0.015 mol	0.100 mol	0
<b>Amounts reacting:</b>	0.015 mol	4 (0.015) mol	0
<b>Amount present at equil.</b>	0	(0.100 – 0.060) = <b>0.040 mol</b>	<b>0.015 mol</b>

**Step 2: Equilibrium Calculation:**

	$\text{Cu}^{2+}(\text{aq})$	+ $4 \text{NH}_3(\text{aq})$	⇌ $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$
<b>Initial</b>	0	0.040	0.015
<b>Change</b>	+ x	+4 x	– x
<b>Equilibrium</b>	x	0.040 + x	0.015 – x

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{(0.015 - 4x)}{(x)(0.040 + 4x)^4}$$

← negligible compared to 0.015  
← negligible compared to 0.040

$$K_f = \frac{0.015}{(x)(0.040)^4} = 4.8 \times 10^{12} \quad x = [\text{Cu}^{2+}] = 1.2 \times 10^{-9} \text{ M}$$

- Check assumptions:  $0.015 - 0.0000000012 = 0.015$   
 $0.040 + 4 \times 0.0000000012 = 0.040 + 0.0000000048 = 0.040$
- Both assumptions are valid!

## AMPHOTERIC HYDROXIDES

### Solubility Rule of the Day:

- Metallic Hydroxides are insoluble.**

Exceptions: Hydroxides of Group IA metals (LiOH, NaOH, KOH)  
 Hydroxides of Group IIA metals: Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>

Amphoteric Hydroxides is a metal hydroxide that reacts with both:	
<b>Acids</b>	and <b>Bases</b>
$\text{Zn(OH)}_2(\text{s}) + 2 \text{HCl}(\text{aq}) \longrightarrow \text{ZnCl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	$\text{Zn(OH)}_2(\text{s}) + 2 \text{NaOH}(\text{aq}) \longrightarrow \text{Na}_2[\text{Zn(OH)}_4](\text{aq})$ <p style="text-align: right; margin-right: 20px;">sodium zincate</p>
$\text{Zn(OH)}_2(\text{s}) + 2 \text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$ <p style="text-align: center; margin-left: 20px;">zinc cation</p>	$\text{Zn(OH)}_2(\text{s}) + 2 \text{OH}^-(\text{aq}) \longrightarrow \text{Zn(OH)}_4^{2-}(\text{aq})$ <p style="text-align: right; margin-right: 20px;">zincate ion</p>
$\text{Al(OH)}_3(\text{s}) + 3 \text{HCl}(\text{aq}) \longrightarrow \text{AlCl}_3(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$	$\text{Al(OH)}_3(\text{s}) + \text{NaOH}(\text{aq}) \longrightarrow \text{Na}[\text{Al(OH)}_4](\text{aq})$ <p style="text-align: right; margin-right: 20px;">sodium aluminate</p>
$\text{Al(OH)}_3(\text{s}) + 3 \text{H}^+(\text{aq}) \longrightarrow \text{Al}^{3+}(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$ <p style="text-align: center; margin-left: 20px;">aluminum cation</p>	$\text{Al(OH)}_3(\text{s}) + \text{OH}^-(\text{aq}) \longrightarrow \text{Al(OH)}_4^-(\text{aq})$ <p style="text-align: right; margin-right: 20px;">aluminate ion</p>

### Laboratory Applications of Amphoteric Hydroxides

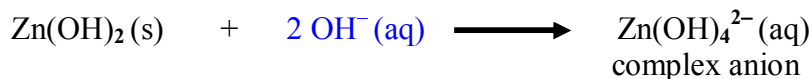
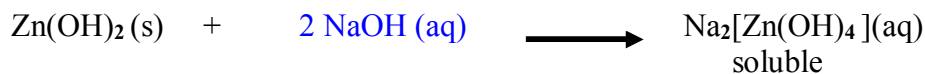
- The identity of some metallic cations can be established by knowing that they can form amphoteric hydroxides.

Example: Consider an aqueous solution of **ZnCl<sub>2</sub>(aq)**

1. If a strong base is added to this solution a precipitate forms:



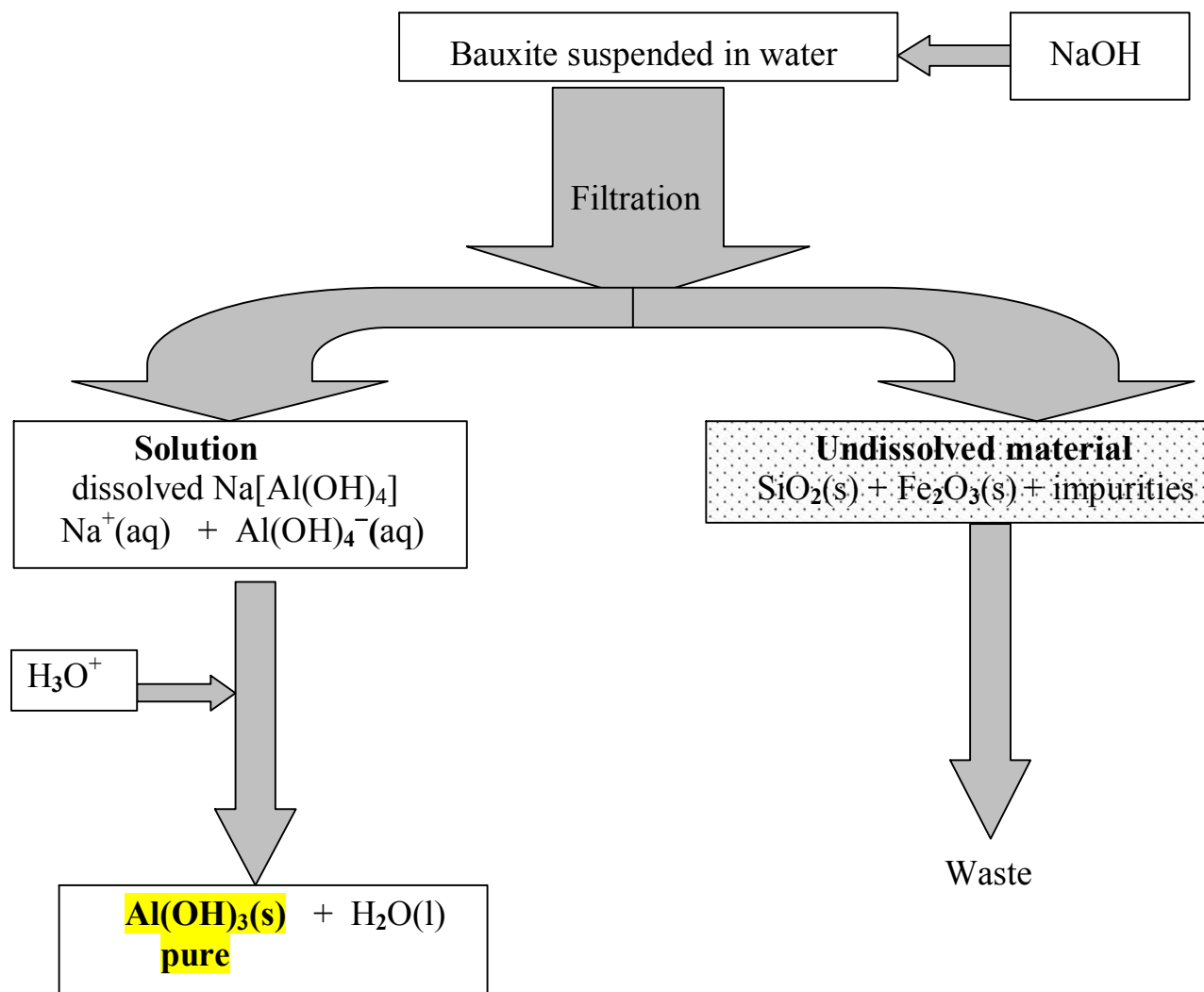
2. If more of the strong base is added, the precipitate dissolves:



- Other metallic cations that form insoluble hydroxides that dissolve in excess of strong base added:  
 $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Sn}^{4+}$

**AN INDUSTRIAL APPLICATION OF AN AMPHOTERIC HYDROXIDE**

- The amphoterism of  $\text{Al}(\text{OH})_3$  is used in the industrial process by which Aluminum metal is obtained.
- Aluminum ore: Bauxite (hydrated  $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{impurities}$ )
- Goal: to obtain pure  $\text{Al}(\text{OH})_3$  from which Al is extracted by electrolysis.



**COMPLEX IONS AND SOLUBILITY**

- The formation of a complex ion reduces the concentration of the metallic ion in solution.
- Consider a 0.010 M AgNO<sub>3</sub> solution.
  - In pure water:  $[Ag^+](aq) = 0.010 \text{ M}$
  - In 1.00 M NH<sub>3</sub>  $[Ag^+](aq) = 6.1 \times 10^{-10} \text{ M}$

**Consequences:**

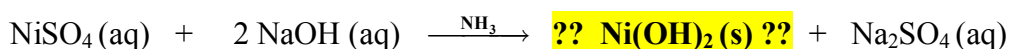
1. The ion product for a slightly soluble salt could be decreased by complexation below the K<sub>sp</sub> value.
2. A slightly soluble salt that:
  - would precipitate in an aqueous solution
  - might not precipitate in a solution that provides ligands for complexation

**Example:**

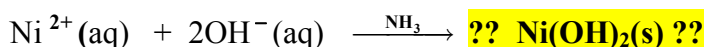
Predict whether nickel(II) hydroxide, Ni(OH)<sub>2</sub>, will precipitate from a solution that is 0.0020 M NiSO<sub>4</sub>, 0.010 M NaOH, and 0.100 M NH<sub>3</sub>.

Note that the nickel(II) ion forms the Ni(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> complex ion with a K<sub>f</sub> = 5.6 × 10<sup>8</sup>.

The K<sub>sp</sub> for Ni(OH)<sub>2</sub> is 2.0 × 10<sup>-15</sup>



Net Ionic:



- Will a precipitate of Ni(OH)<sub>2</sub> form or not?

**Step 1: Stoichiometry Calculation:**

	Ni(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup> (aq) ←	Ni <sup>2+</sup> (aq) +	6 NH <sub>3</sub> (aq)
<b>Amounts present in 1L:</b>	0	0.0020 mol	0.100 mol
<b>Amounts reacting:</b>	0	0.0020 mol	6 (0.0020) mol
<b>Amount present at equil.</b>	<b>0.0020 mol</b>	<b>0</b>	(0.100 – 0.012) <b>0.088 mol</b>

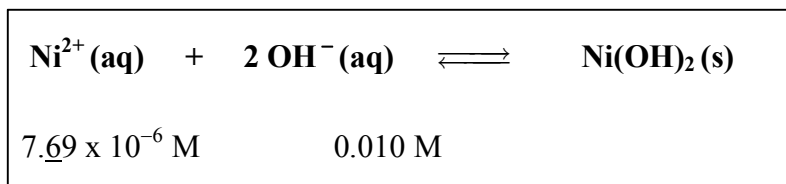
**Step 2: Equilibrium Calculation:**

	$\text{Ni}(\text{NH}_3)_6^{2+}(\text{aq}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + 6 \text{NH}_3(\text{aq})$		
<b>Initial</b>	0.0020	0	0.088
<b>Change</b>	- x	+ x	+ 6x
<b>Equilibrium</b>	0.0020 - x	x	0.088 + 6x

$$K_f = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^4} = \frac{(0.0020 - x)}{(x)(0.0088 + 6x)^4}$$

← negligible compared to 0.0020  
← negligible compared to 0.088

$$K_f = \frac{0.0020}{(x)(0.088)^6} = 5.6 \times 10^8 \quad x = [\text{Ni}^{2+}] = 7.69 \times 10^{-6} \text{ M}$$

**Step 3: Calculation of Ion Product for Ni(OH)<sub>2</sub>**Actual  
Conc's:

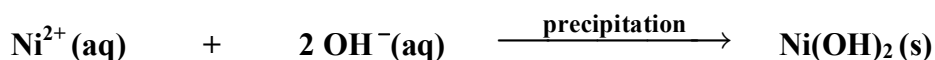
**$K_{sp} = 2.0 \times 10^{-15}$**

**$Q_c = [\text{Ni}^{2+}][\text{OH}^{-}]^2 = (7.69 \times 10^{-6})(0.010)^2 = 7.69 \times 10^{-10}$**

Note:  **$7.69 \times 10^{-10} > 2.0 \times 10^{-15}$**

**$Q_c > K_{sp}$**

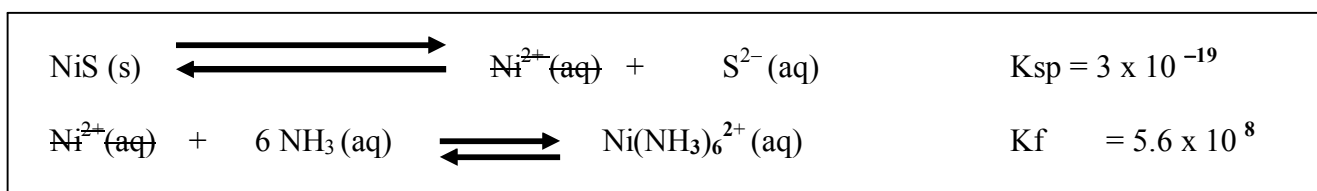
- The solution is supersaturated before equilibrium.
- At equilibrium a precipitate of Ni(OH)<sub>2</sub>(s) will form and the solution will become saturated



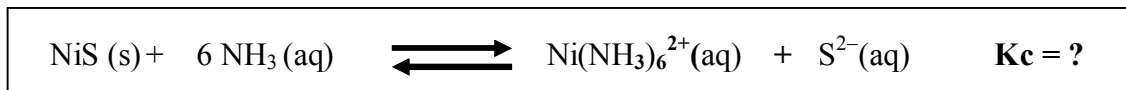
**CALCULATING THE SOLUBILITY OF A SLIGHTLY SOLUBLE IONIC COMPOUND IN A SOLUTION OF A COMPLEX ION**

What is the molar solubility of NiS in 0.10 M NH<sub>3</sub>?

(K<sub>sp</sub> for NiS = 3 × 10<sup>-19</sup> and K<sub>f</sub> for Ni(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> = 5.6 × 10<sup>8</sup>)

**Step 1: Write the solubility equilibrium and the complex-ion equilibrium:**


If you add the two equilibria the overall equilibrium for dissolving the NiS in NH<sub>3</sub> is obtained:



- Recall: K<sub>c</sub> for the overall equilibrium is the product of the two equilibrium constants:

$$K_{\text{c}} = K_{\text{sp}} \times K_{\text{f}} = (3 \times 10^{-19}) (5.6 \times 10^8) = \mathbf{1.7 \times 10^{-10}}$$

**Step 2: Equilibrium Calculation:**

	$\text{NiS (s)} + 6 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$			
<b>Initial</b>	-----	0.10	0	0
<b>Change</b>	-----	- 6x	+ x	+ x
<b>Equilibrium</b>	-----	0.10 - 6x	x	x

$$K_{\text{c}} = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}][\text{S}^{2-}]}{[\text{NH}_3]^6} = \frac{x^2}{(0.10 - 6x)^6} = 1.7 \times 10^{-10}$$

Taking the square root of both sides :  $\frac{x}{(0.10 - 6x)^3} = 1.3 \times 10^{-5}$   
←..... negligible

$$\frac{x}{(0.10)^3} = 1.3 \times 10^{-5}$$

**x = Molar Solubility of NiS in 0.10 M NH<sub>3</sub>**

$$x = \mathbf{1.3 \times 10^{-8} \text{ M} = 1 \times 10^{-8} \text{ M}}$$

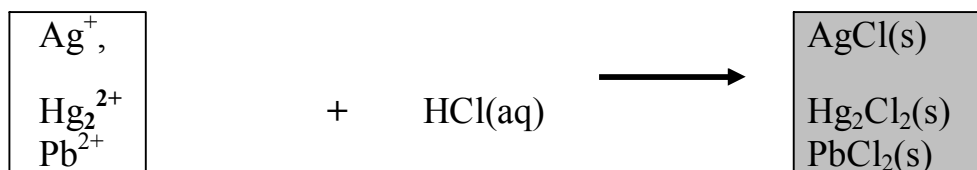
## QUALITATIVE ANALYSIS OF METAL IONS

- Qualitative analysis is the determination of the presence of a metallic ion in the mixture by which a cation is detected by the presence of a characteristic precipitate

### The Sulfide Scheme

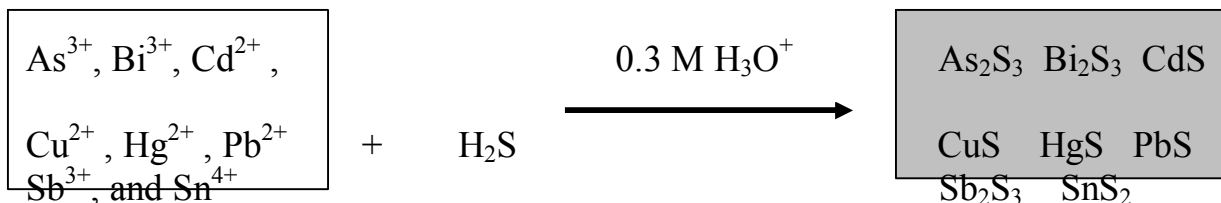
Divides metallic ions into 5 analytical groups:

- Analytical Group I ions:**  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$  [mercurous, or mercury (I)], and  $\text{Pb}^{2+}$ 
  - These ions are separated from a solution of other ions by adding dilute hydrochloric acid



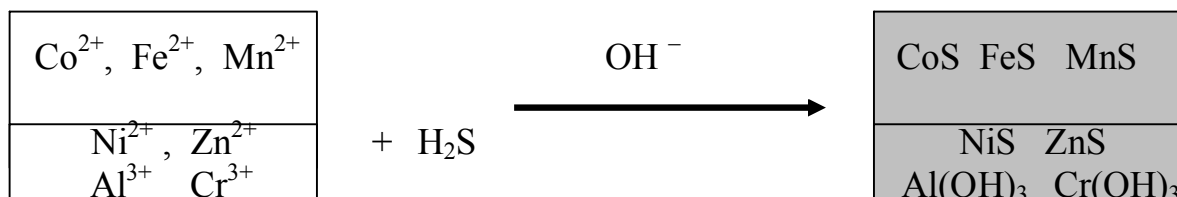
chloride precipitates  
that can be filtered off

- Analytical Group II ions:**  $\text{As}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sb}^{3+}$ , and  $\text{Sn}^{4+}$ 
  - These ions are separated from a solution by precipitation with an acidic solution of  $\text{H}_2\text{S}$



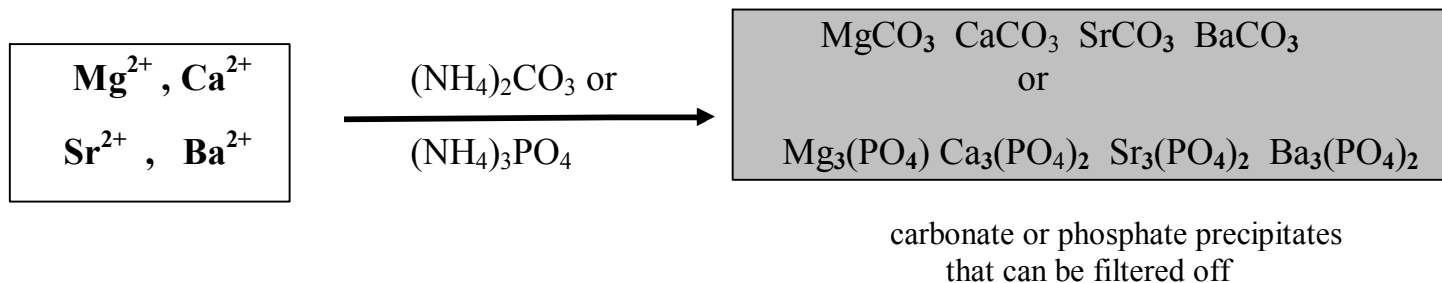
sulfide precipitates  
that can be filtered off

- Analytical Group III ions:**  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$   $\text{Cr}^{3+}$ 
  - These ions are separated from a solution by precipitation with a weakly basic solution of  $\text{H}_2\text{S}$



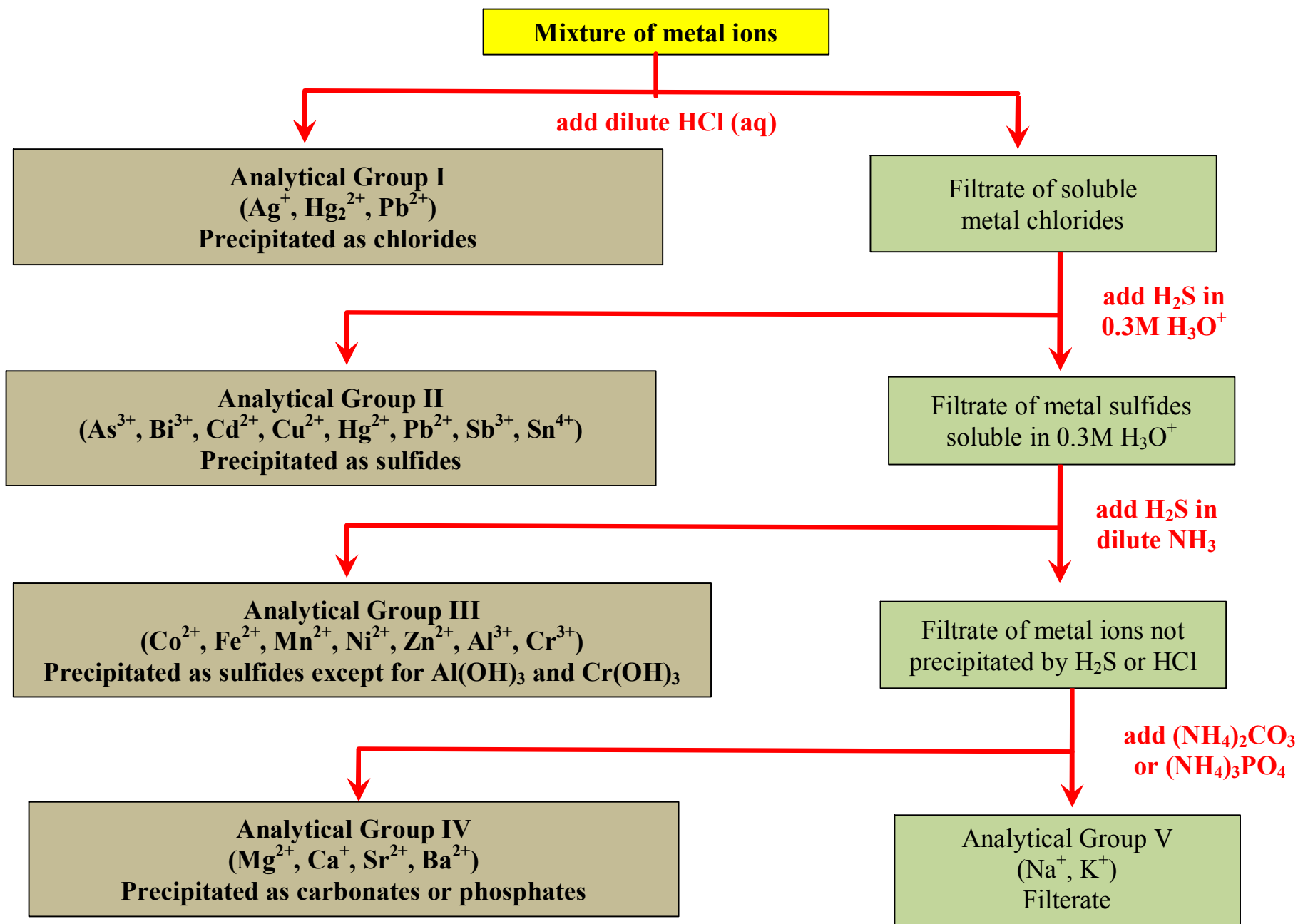
sulfide or hydroxide precipitates  
that can be filtered off

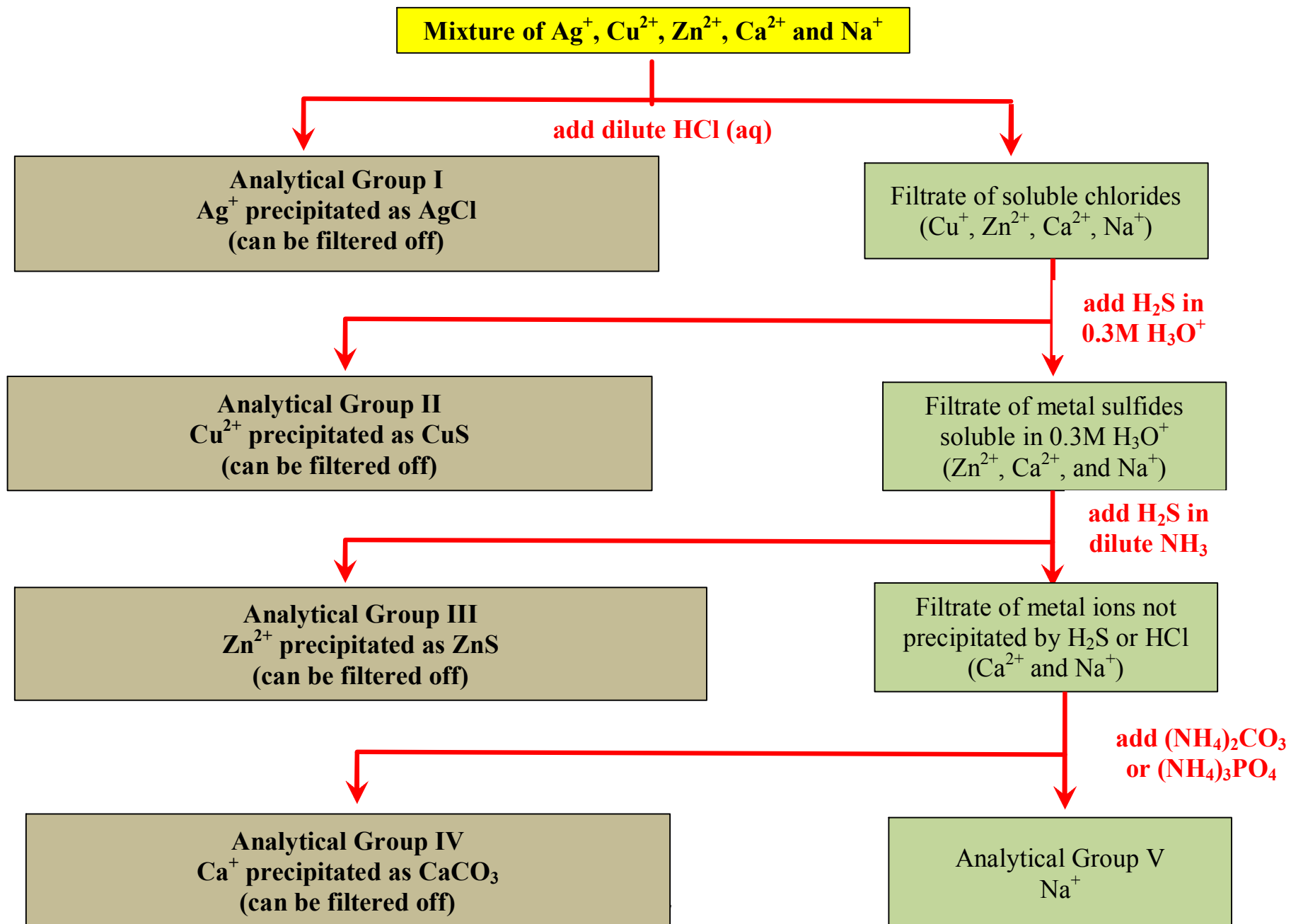
- **Analytical Group IV ions:** Alkaline earth metals (Group IIA):  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  
 ➤ These ions are separated from a solution by precipitation with a solution of  $(\text{NH}_4)_2\text{CO}_3$  or  $(\text{NH}_4)_3\text{PO}_4$



- **Analytical Group V ions:** Alkaline metals (Group IA):  $\text{Na}^+$  and  $\text{K}^+$   
 ➤ These ions remain in the filtrate after filtering off all of the precipitates  
 ➤ These ions do not form any precipitates since all their compounds are soluble

## SEPARATION FLOW CHART



**EXAMPLE OF SEPARATION OF A MIXTURE OF FIVE METALLIC CATIONS**

## SEPARATION OF A MIXTURE OF GROUP I METALLIC CATIONS

