

Qualitative inorganic analysis

part (II)

Cations

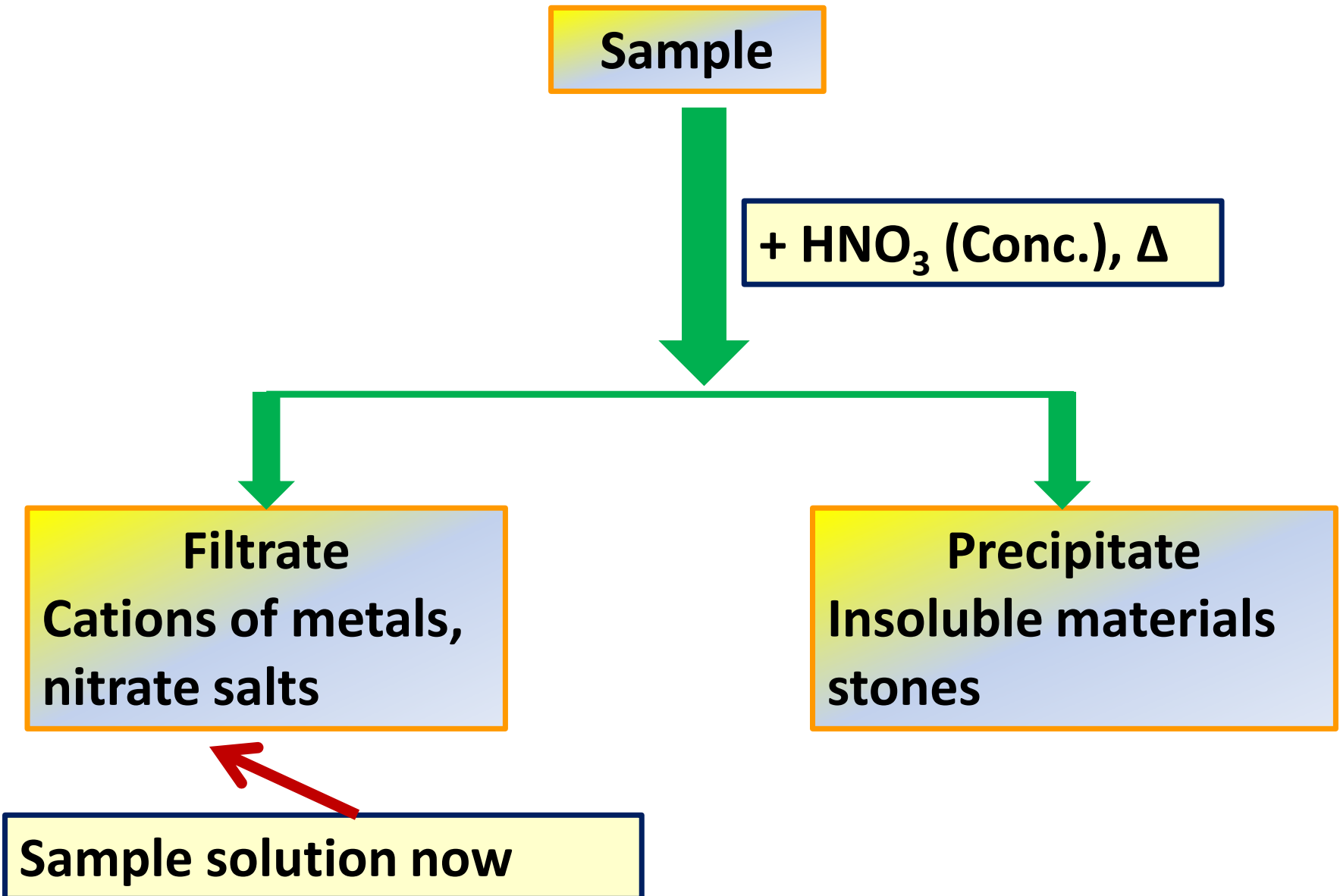
Classification of cations

If you have an alloy??? What are the components???

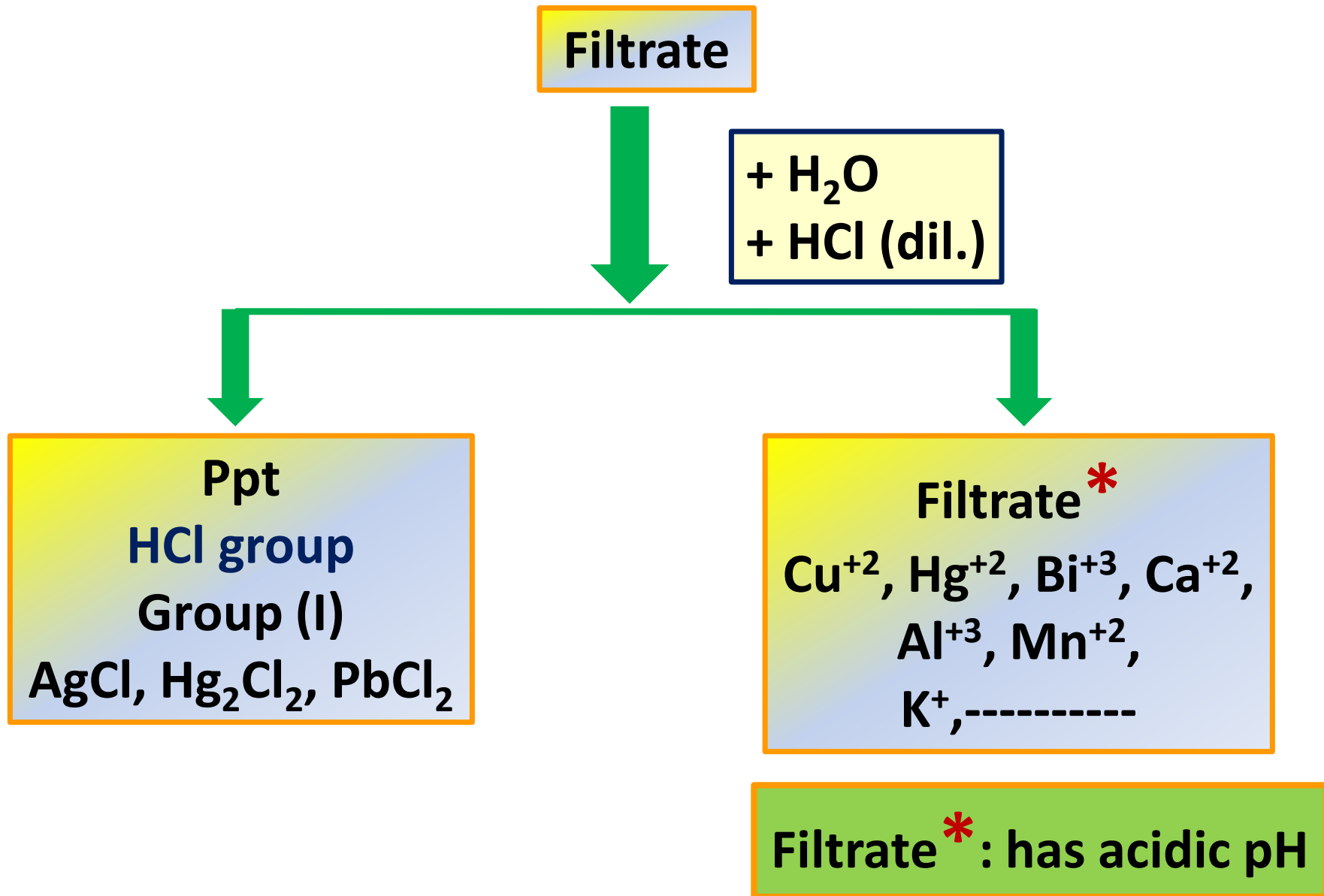


The first step is dissolution of metals and separation of any insoluble materials e.g. stones, wood,-----

Classification of cations



Classification of cations



Classification of cations

Filtrate *

+ H₂S

Ppt

H₂S group

Group (II)

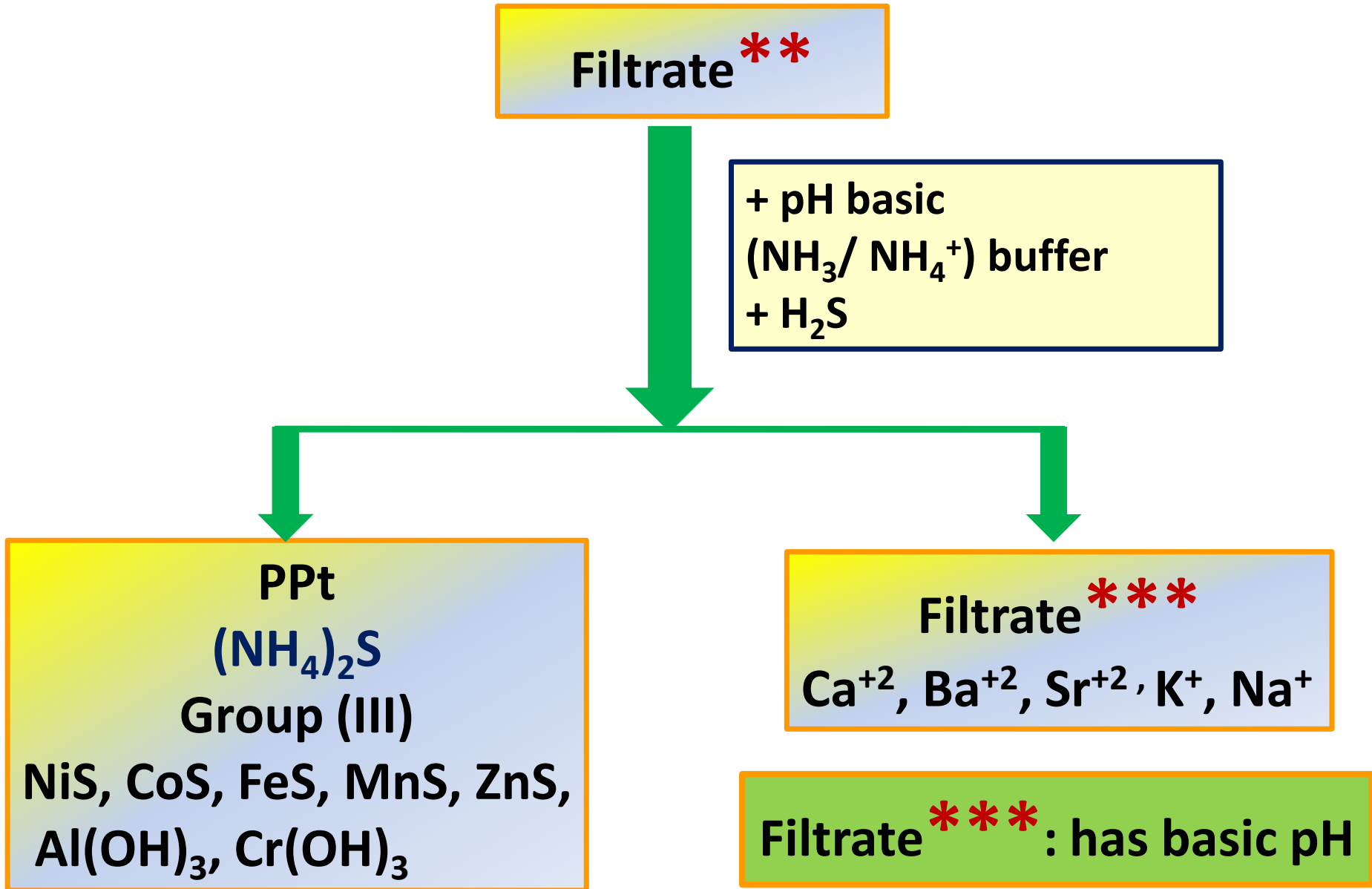
CuS, Bi₂S₃, CdS, PbS,
HgS, SnS, SnS₂, As₂S₃,
As₂S₅, Sb₂S₃, Sb₂S₅

Filtrate **

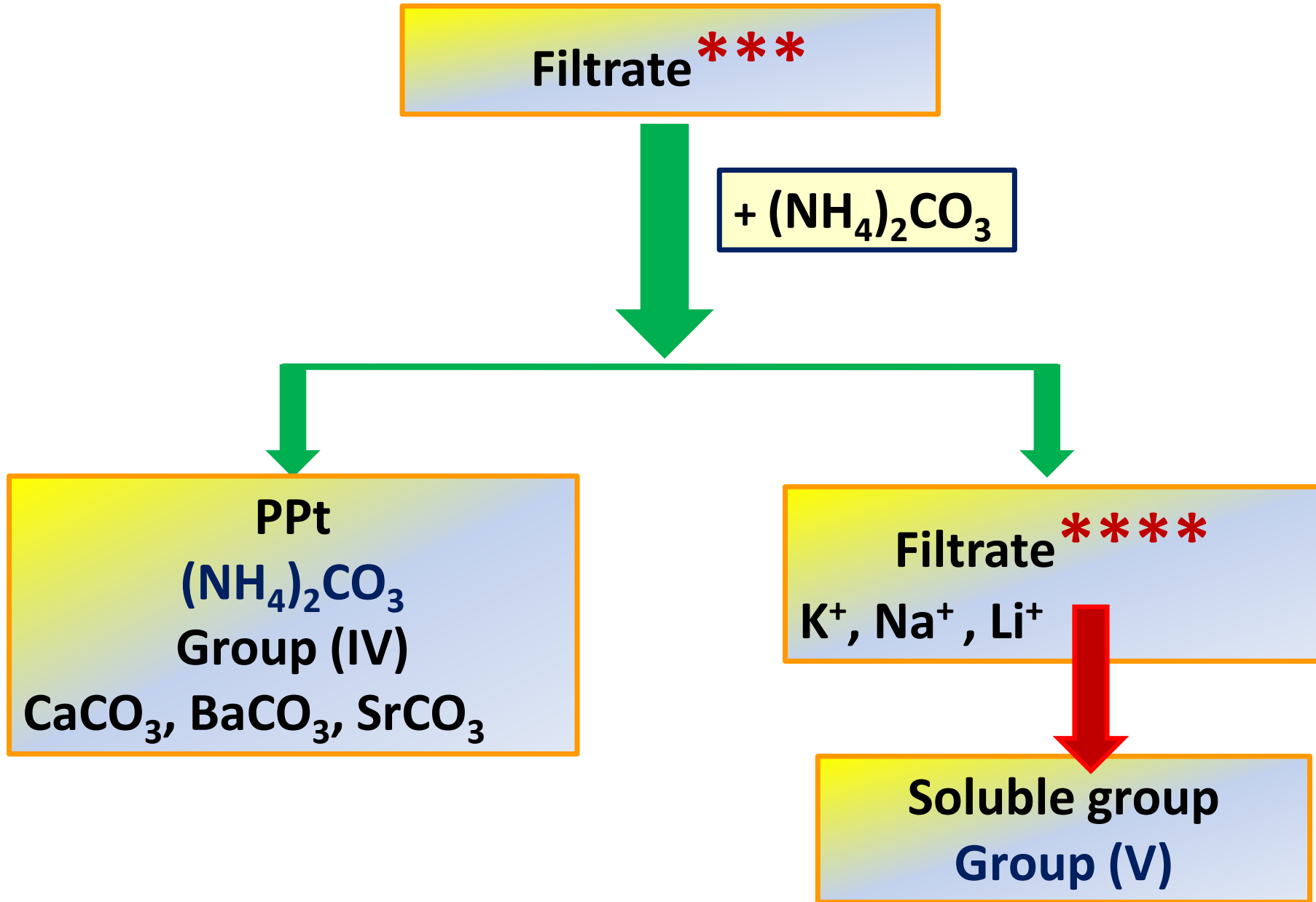
Co⁺², Ni⁺², Al⁺³,
Mn⁺², Ca⁺², Ba⁺²,
K⁺, Na⁺,-----

Filtrate **: has acidic pH

Classification of cations



Classification of cations



Classification of cations

Cations are classified in 5 groups:

Group	Common reagent	Examples
Group (I)	HCl group	Ag^+ , Pb^{+2} , Hg_2^{+2}
Group (II)	H_2S group	Cu^{+2} , Cd^{+2} , Pb^{+2} , Hg^{+2} , Bi^{+3} , As^{+3} , As^{+5} , Sb^{+3} , Sb^{+5} , Sn^{+2} , Sn^{+4}
Group (III)	$(\text{NH}_4)_2\text{S}$	Co^{+2} , Ni^{+2} , Mn^{+2} , Zn^{+2} , Fe^{+2} , Al^{+3} , Cr^{+3}
Group (IV)	$(\text{NH}_4)_2\text{CO}_3$	Ca^{+2} , Ba^{+2} , Sr^{+2}
Group (V)	Soluble group	K^+ , Na^+ , Li^+

HCl group

Cations precipitate in acidic media as chloride salts belong to this group. Group (I)

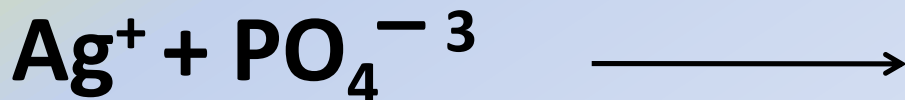
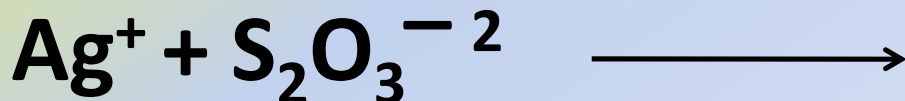
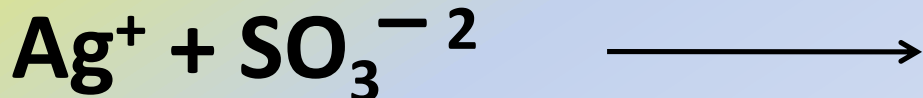
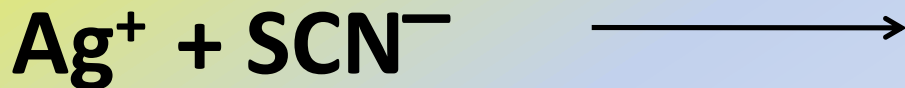
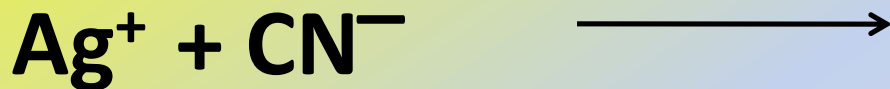
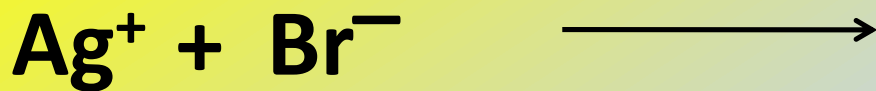


This means also chloride salts of cations of group (II) - (V) are soluble

HCl group

Detection of Ag^+ :

Complete, mention properties of ppt:



HCl group

Detection of Pb^{+2} :

With HCl:

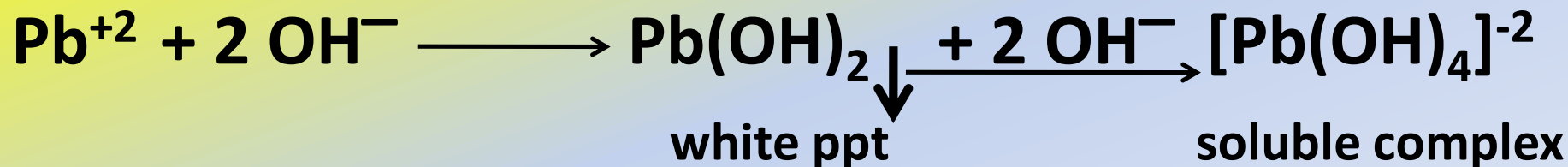


white ppt, soluble on heating ,
reformed on cooling [ppt has high K_{sp}]. Pb^{+2} is found again in
Group (II)

HCl group

Detection of Pb^{+2} :

With NaOH:

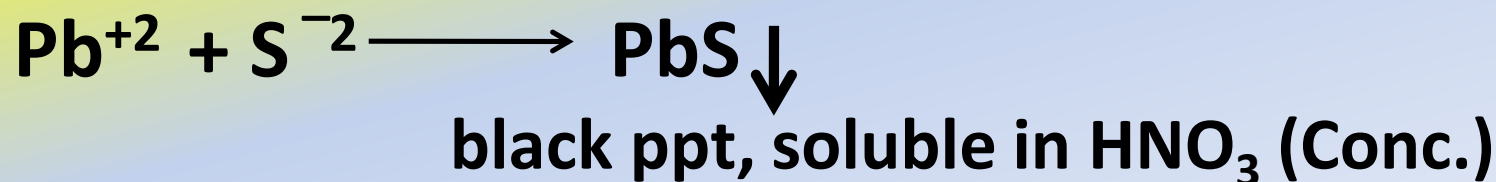


$[\text{Pb}(\text{OH})_4]^{-2}$: tetrahydroxoplumbate(II) ion

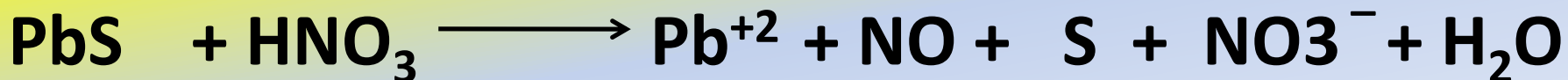
HCl group

Detection of Pb^{+2} :

With H_2S :



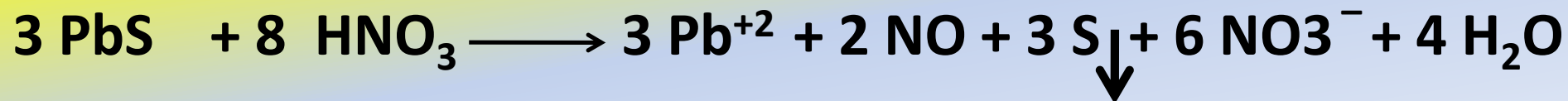
Redox reaction: Balance equation



HCl group

Detection of Pb^{+2} :

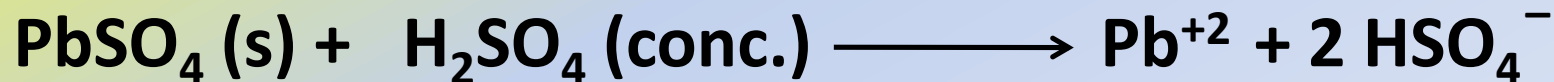
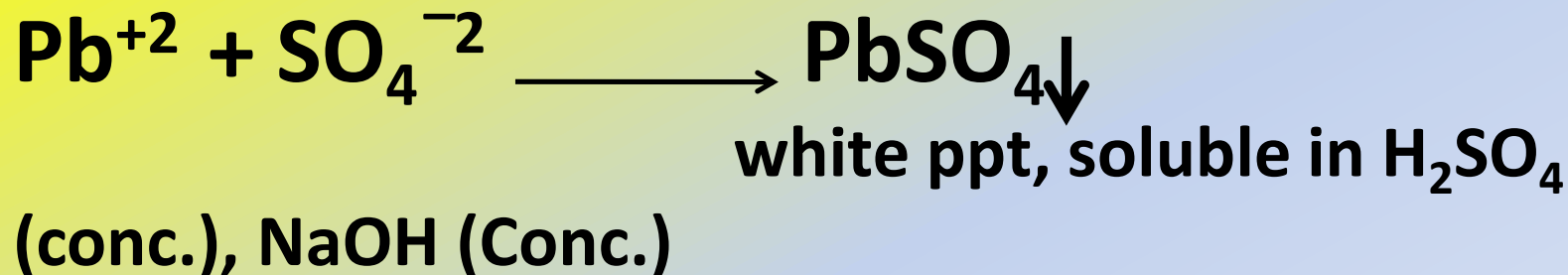
Redox reaction:



HCl group

Detection of Pb^{+2} :

With H_2SO_4 (dil.):



HCl group

Detection of Pb^{+2} :

With KI: Complete?????



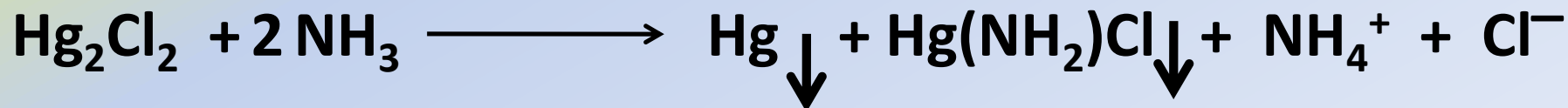
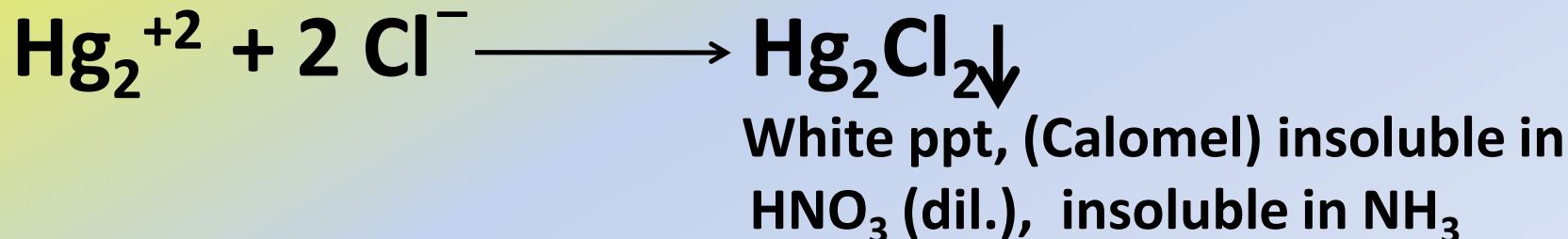
yellow ppt, soluble in boiling water, on cooling golden yellow plates are formed.

HCl group

Detection of Hg_2^{+2} :

Mercury is a silver-white liquid metal at 25 °C, it is 13 times heavier than water.

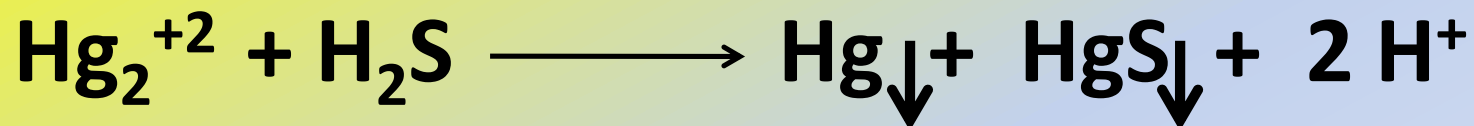
With HCl (dil.):



HCl group

Detection of Hg_2^{+2} :

With H_2S :



black ppt, dissolves

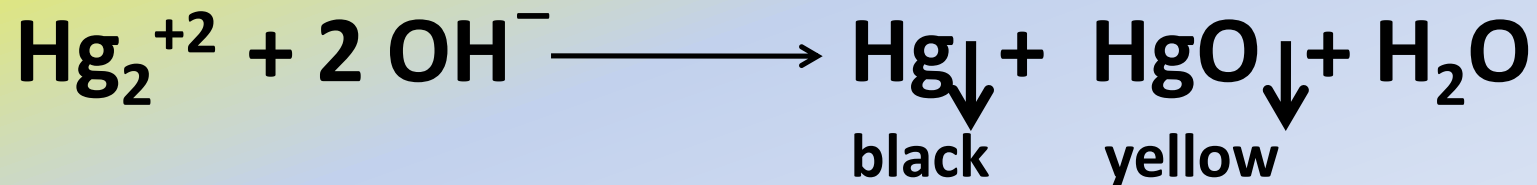
by adding sodium sulfide



HCl group

Detection of Hg_2^{+2} :

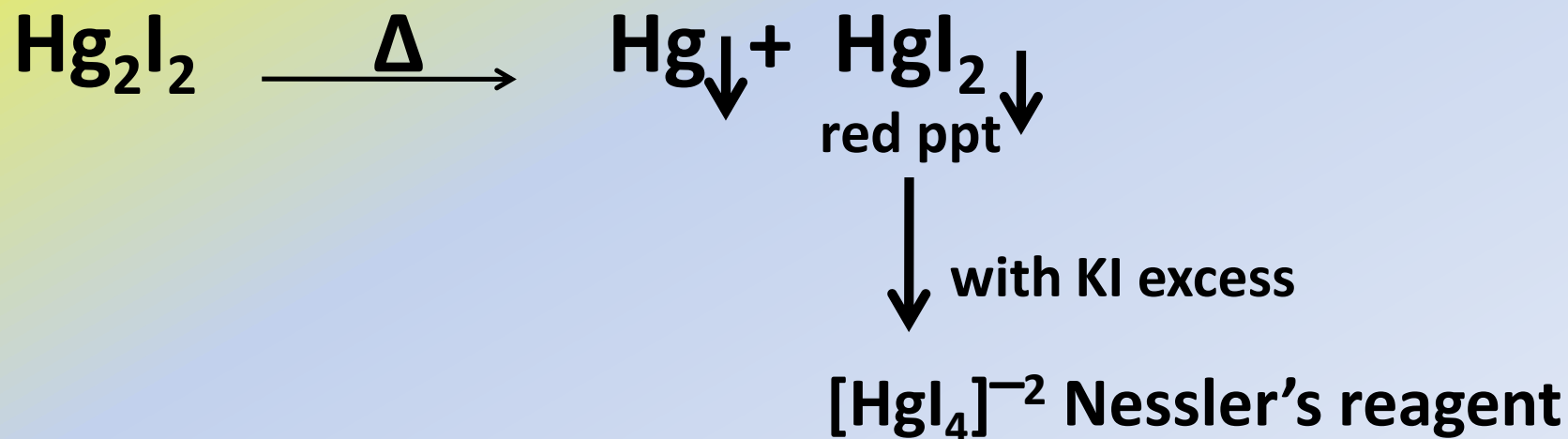
With NaOH:



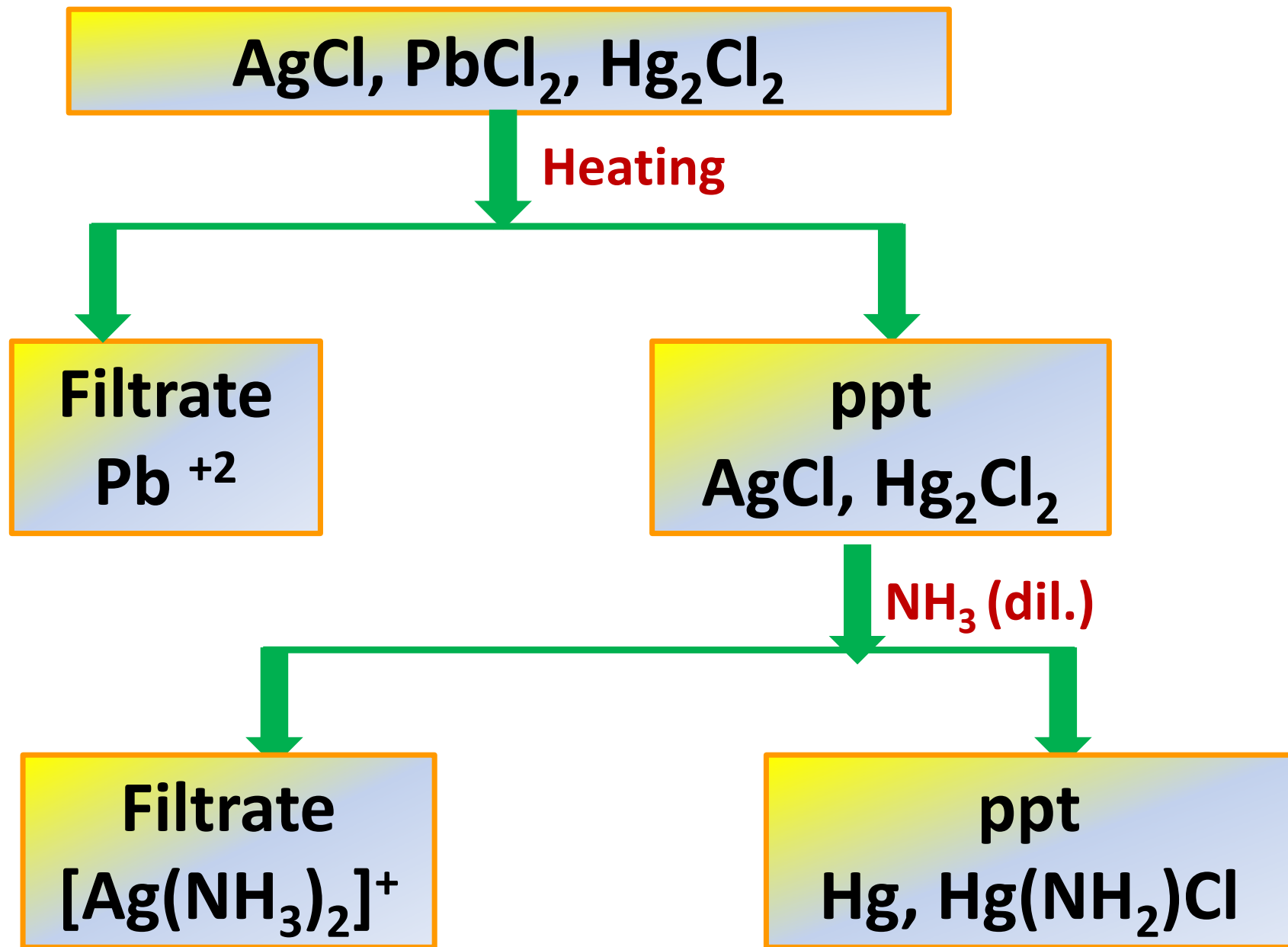
HCl group

Detection of Hg_2^{+2} :

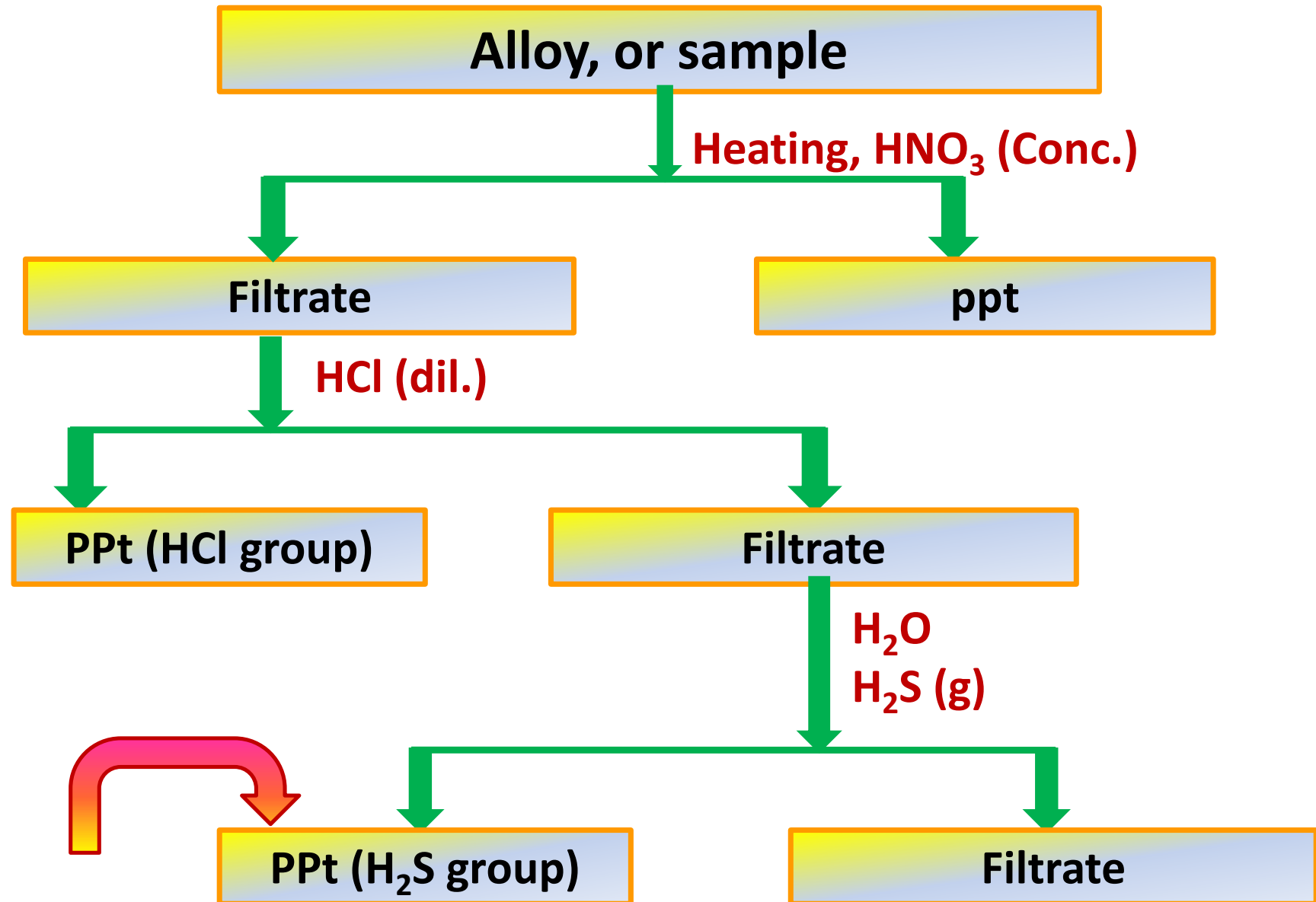
With KI:



HCl group



Group (II): H₂S group



Group (II): H₂S group

Ppt

H₂S group, Group (II)

**CuS, Bi₂S₃, CdS, PbS, HgS,
SnS, SnS₂, As₂S₃, As₂S₅, Sb₂S₃, Sb₂S₅**

H₂S group, Group (II)

**Cations form insoluble sulfide salts in acidic media
, since they have a very low K_{sp}.(?)**

**H₂S group is divided into two subgroups according
to solubility in ammonium polysulfide (NH₄)₂S_x**

Group (II): H₂S group

Ppt H₂S group

CuS, Bi₂S₃, CdS, PbS, HgS,
SnS, SnS₂, As₂S₃, As₂S₅, Sb₂S₃, Sb₂S₅

$\Delta, (\text{NH}_4)_2\text{S}_x$

Filtrate

Arsenic subgroup
(Thiosalts)

$\text{AsS}_4^{-3}, \text{SbS}_4^{-3}, \text{SnS}_3^{-2}$

ppt

Copper subgroup

CuS, Bi₂S₃, CdS, PbS, HgS

AsS_4^{-3} : Thioarsenate ion

SbS_4^{-3} : Thioantimonate ion

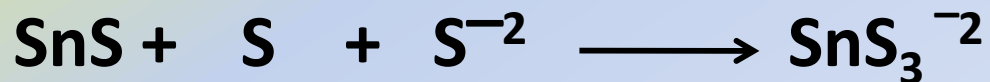
SnS_3^{-2} : Thiostannate ion

H₂S group: Arsenic subgroup

Arsenic subgroup: AsS_4^{-3} , SbS_4^{-3} , SnS_3^{-2}

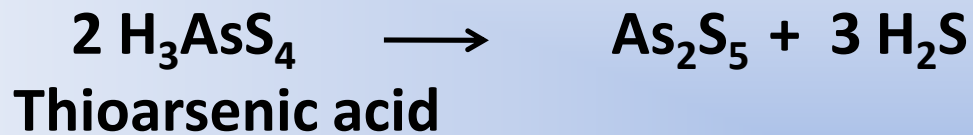
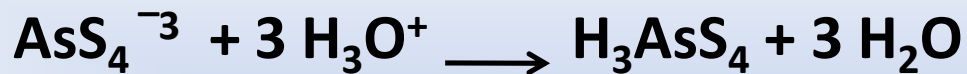
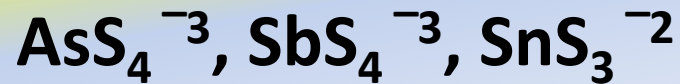
Dissolution of sulfide salts in ammonium polysulfide is due to formation of thiosalts.

Dissolution is accompanied by a **redox** reaction.



H₂S group: Arsenic subgroup

Filtrate Arsenic subgroup



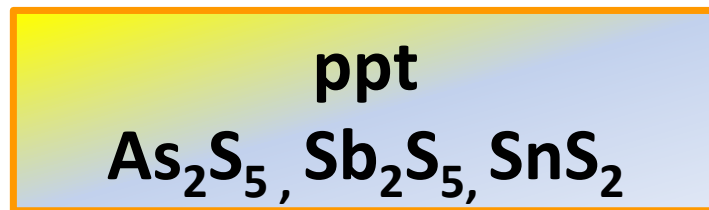
HCl (dil.)



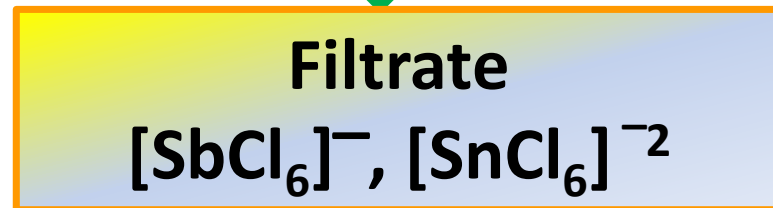
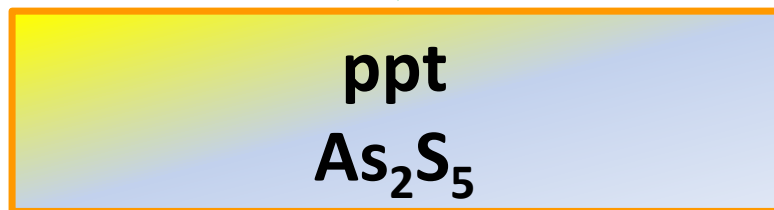
ppt



H₂S group: Arsenic subgroup

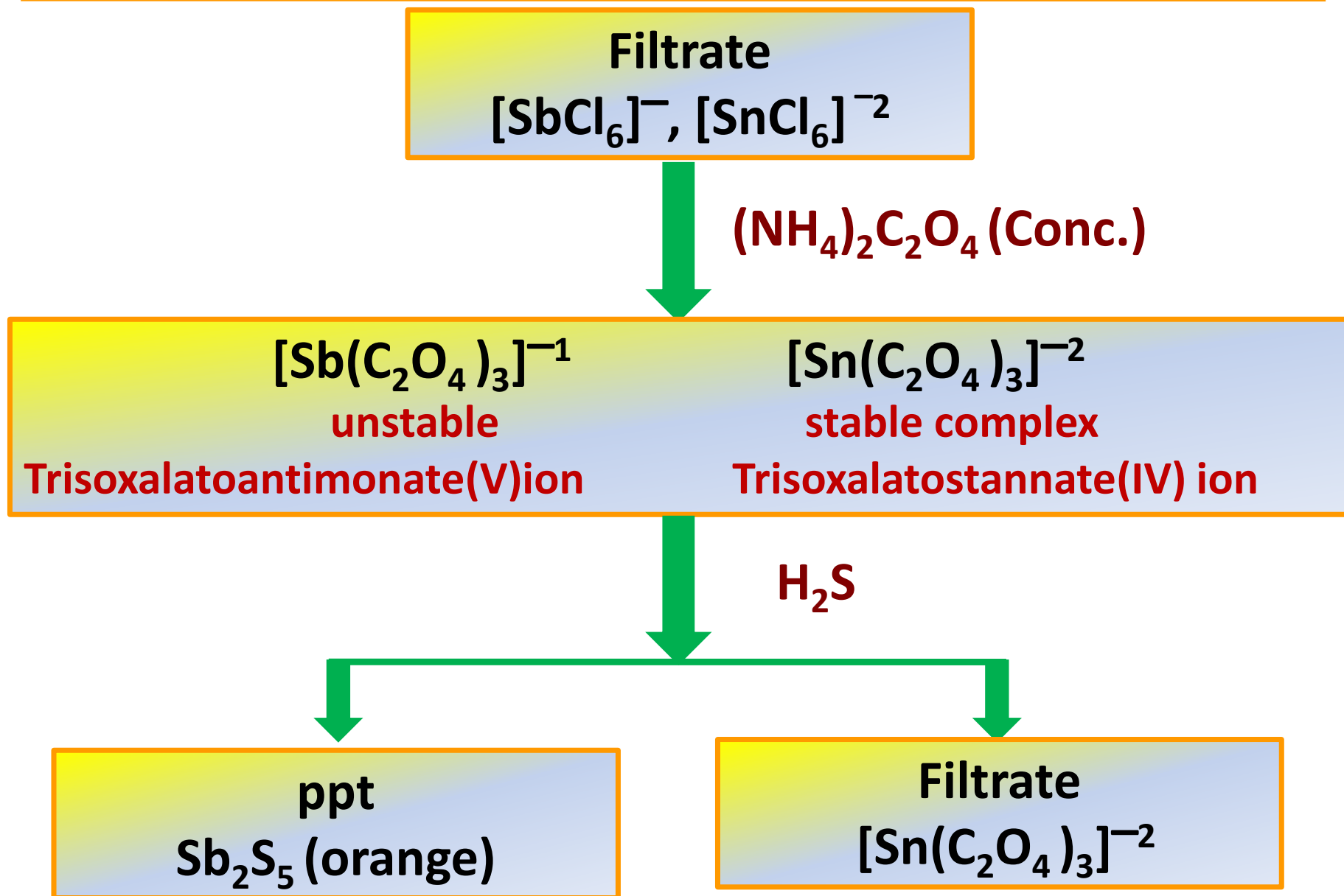


HCl (Conc.)



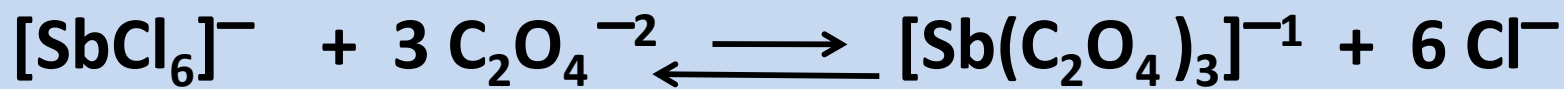
Hexachlorostannate(IV) ion

H₂S group: Arsenic subgroup

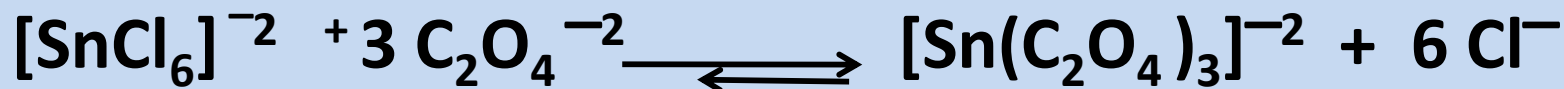
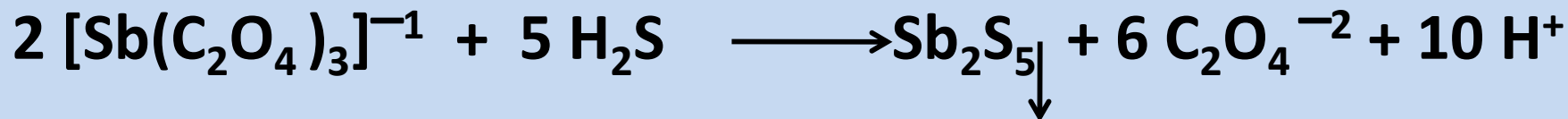


H₂S group: Arsenic subgroup

Equations and Explanation



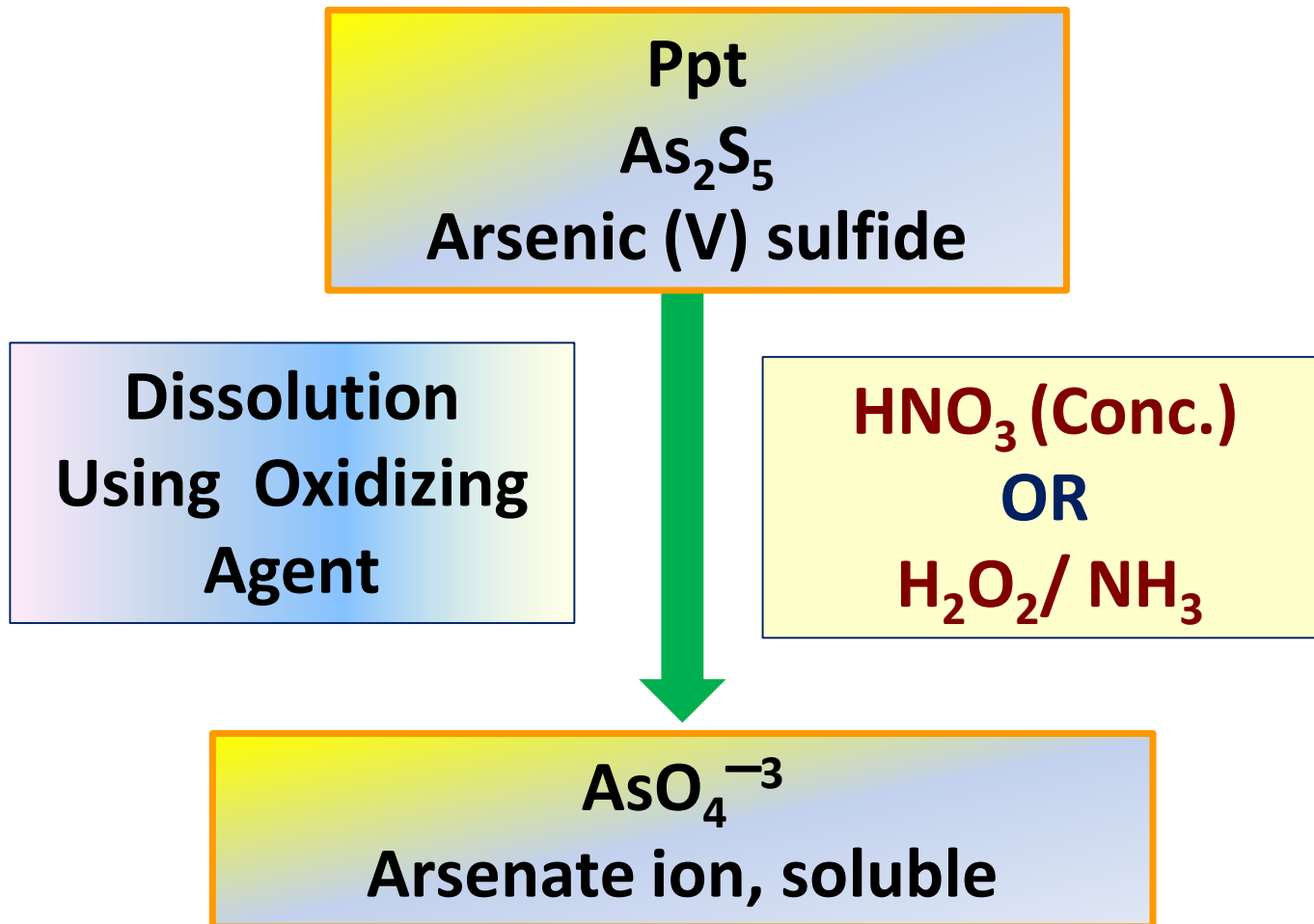
unstable Complex, dissociate rapidly



Stable Complex



H₂S group: Arsenic subgroup



Note: As_2S_5 is insoluble in acid, insoluble in HCl (Conc.), soluble in ammonium poly sulfide .

H₂S group: Arsenic subgroup

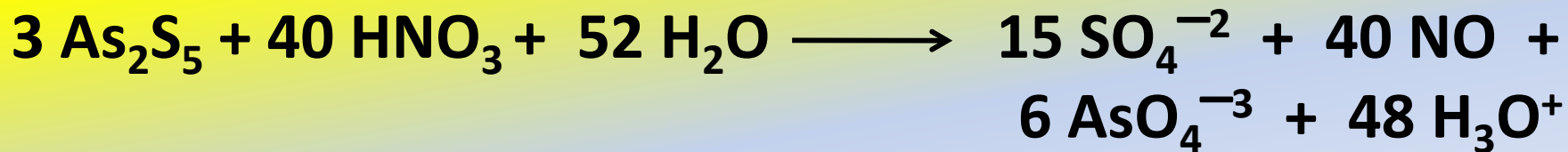
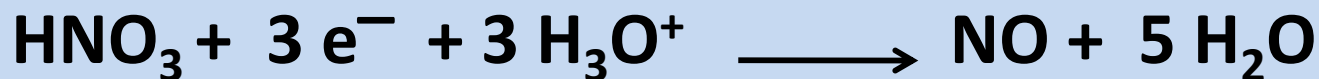
Equations and Explanation



Oxd. Half RXN:



Red. Half RXN:



H₂S group: Arsenic subgroup

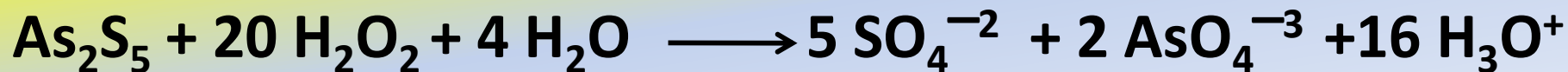
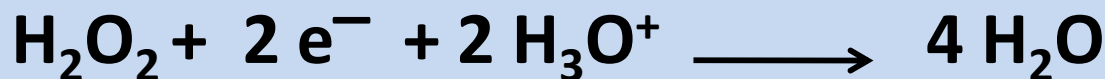
Equations and Explanation



Oxd. Half RXN:



Red. Half RXN:



H₂S group: Arsenic subgroup

Detection of AsO_4^{-3}

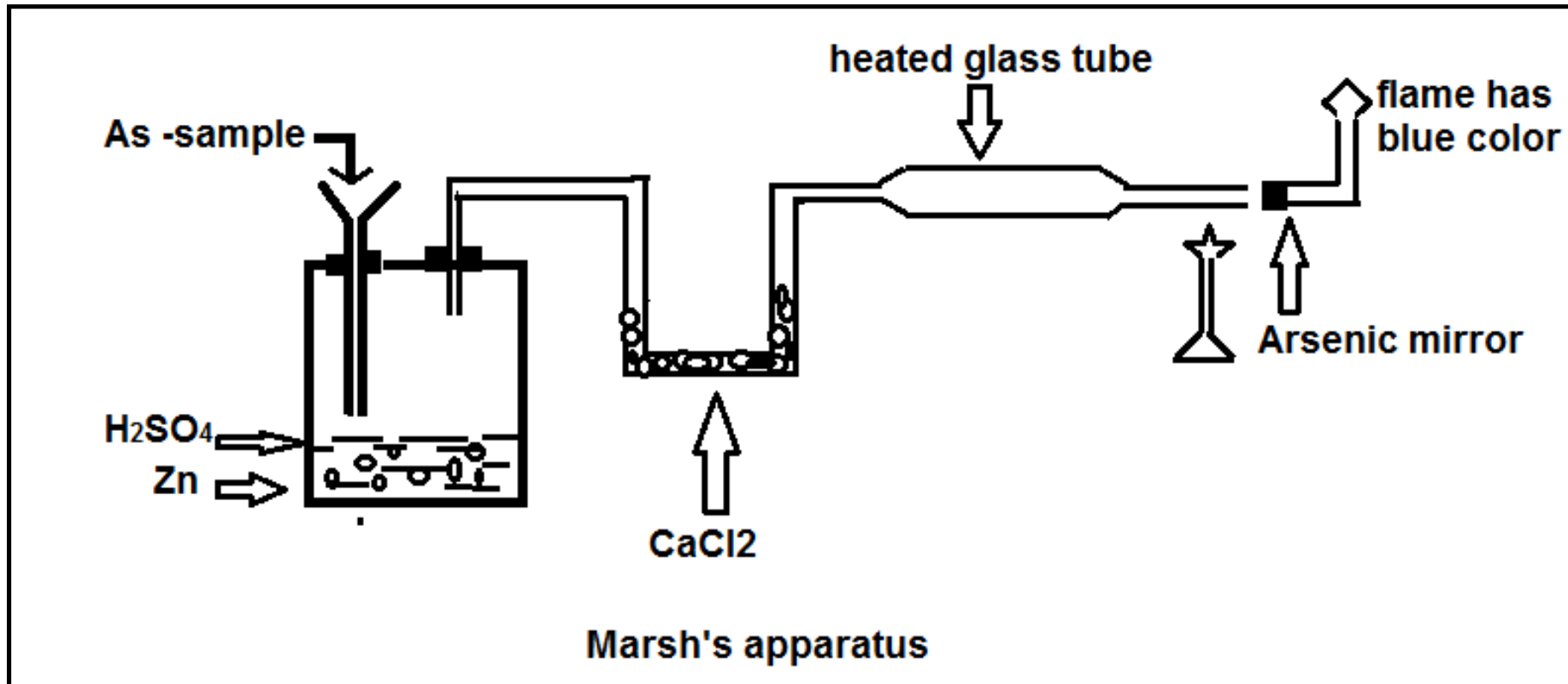
+ 3 Ag⁺

$\text{Ag}_3\text{AsO}_4 \downarrow$
brownish red ppt

H₂S group: Arsenic subgroup

Detection of Arsenic in very small amount
(Forensic medicine)

Marsh's Test



H₂S group: Arsenic subgroup

Marsh's Test

Equations:



Arseine gas (toxic, garlic like odor)



brownish black (Arsenic mirror)

$\text{AsH}_3 \xrightarrow{\text{ignition}}$ blue colored flame with white fumes

H₂S group: Arsenic subgroup

Marsh's Test

Malfunction is Sb.

To **distinguish** the results in Marsh's test

Arsenic mirror is **soluble** in H₂O₂/ NH₃

Antimony mirror is **insoluble** in H₂O₂/ NH₃

See the following video

Marsh's Test

Group (II): H₂S group

Ppt H₂S group

CuS, Bi₂S₃, CdS, PbS, HgS,
SnS, SnS₂, As₂S₃, As₂S₅, Sb₂S₃, Sb₂S₅

$\Delta, (\text{NH}_4)_2\text{S}_x$

Filtrate

**Arsenic subgroup
(Thiosalts)**

ppt

**Copper subgroup
CuS, Bi₂S₃, CdS, PbS, HgS**

H₂S group: Copper subgroup

ppt
Copper subgroup
CuS, Bi₂S₃, CdS, PbS, HgS

Dissolution
Using Oxidizing
Agent

+ HNO₃ (Conc.)
Δ



Filtrate
Cu²⁺, Cd²⁺, Pb²⁺, Bi³⁺

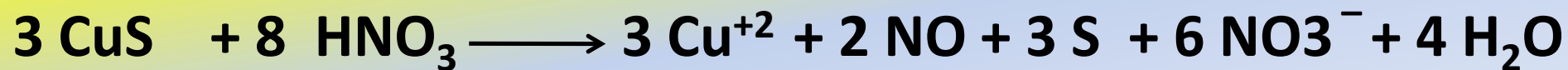
Ppt
HgS

H₂S group: Copper subgroup

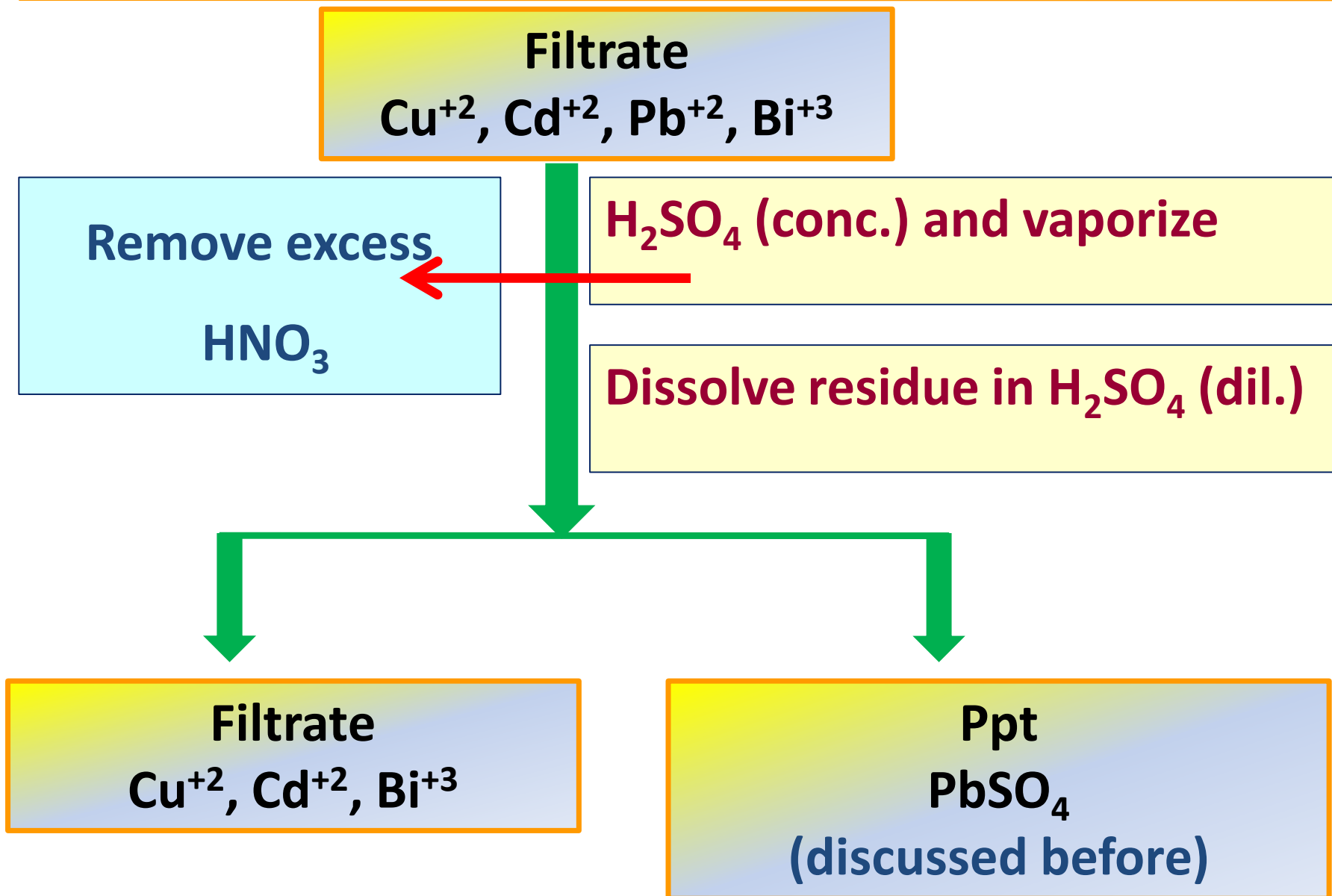
Remember:

**H₂S group are sulfide salts insoluble in acids.
Dissolution in HNO₃ (Conc.) due to its'
oxidizing agent property.**

Redox reaction:



H₂S group: Copper subgroup



H₂S group: Copper subgroup

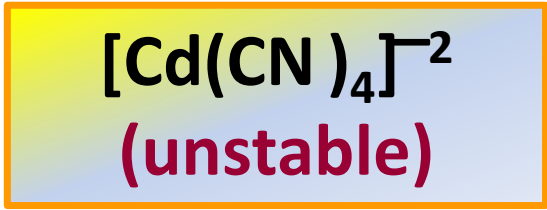
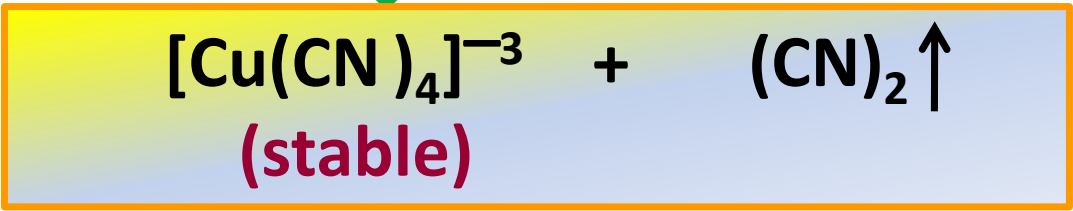
Filtrate
Cu⁺², Cd⁺², Bi⁺³

NH₃ (conc.)
Centrifugation

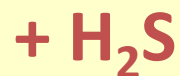
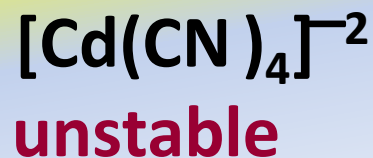
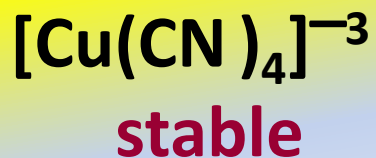
Filtrate
[Cu(NH₃)₄]⁺²
Tetraamminecopper(II) ion (blue color)
[Cd(NH₃)₄]⁺²
Tetraamminecadmium(II) ion

Ppt
Bi(OH)₃
White ppt

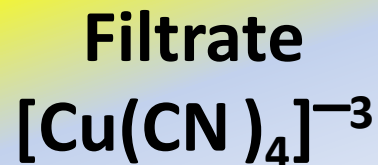
H₂S group: Copper subgroup



H₂S group: Copper subgroup



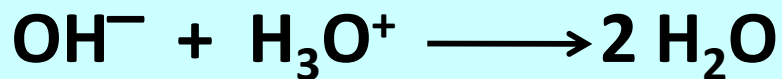
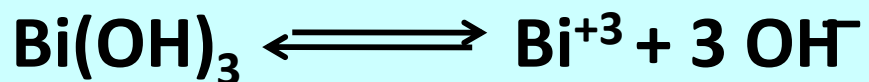
NO RXN



Ppt
CdS
Yellow ppt

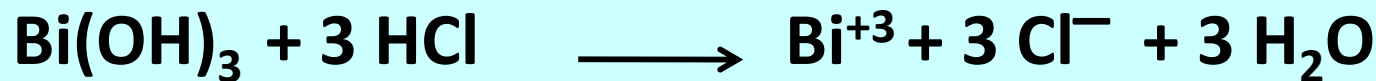
H₂S group: Copper subgroup

Ppt
Bi(OH)₃
White ppt

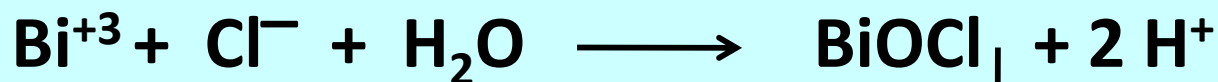
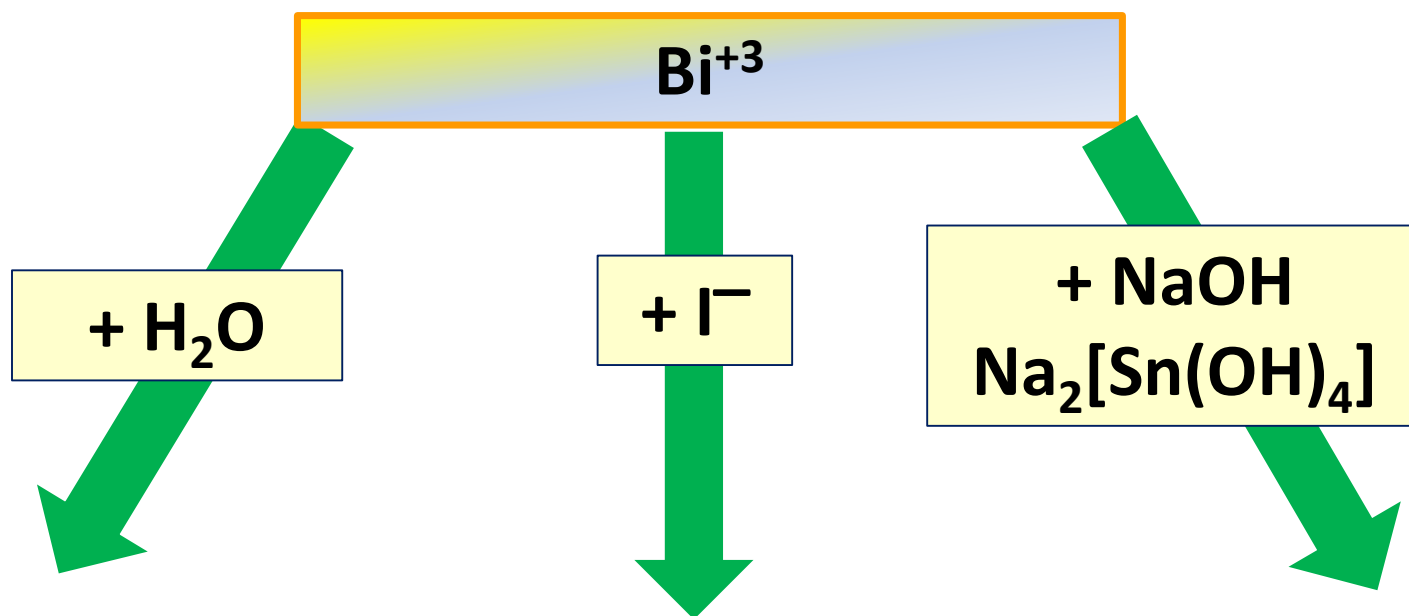


+ HCl for dissolution

Bi⁺³



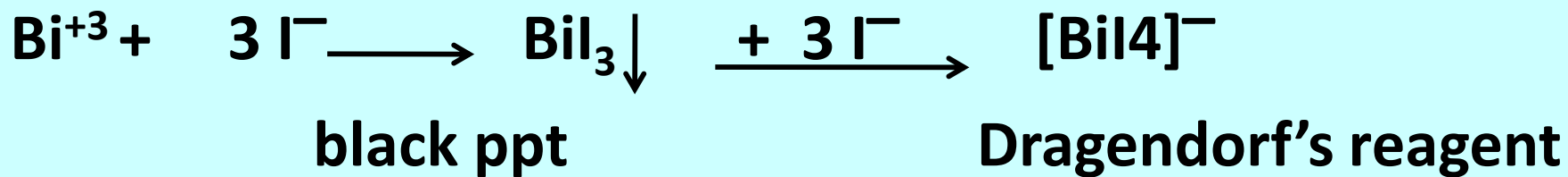
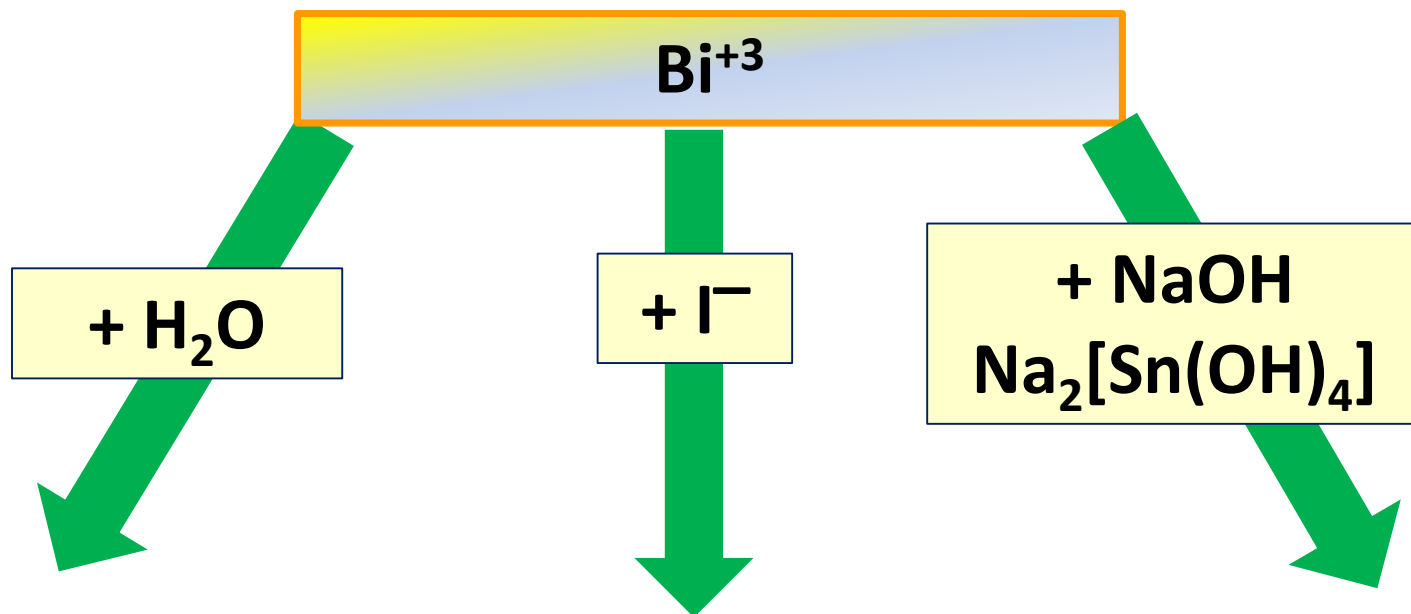
H₂S group: Copper subgroup



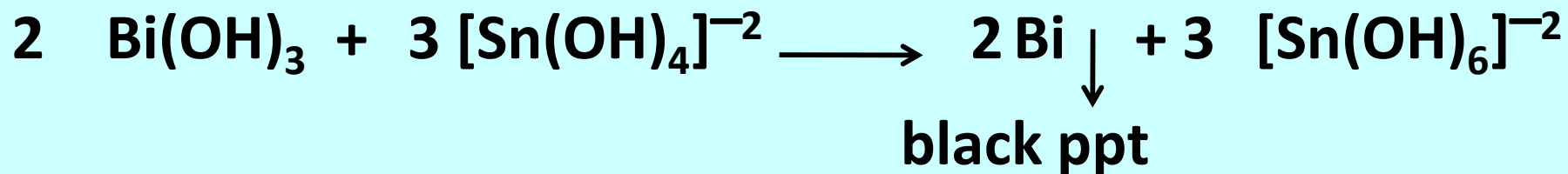
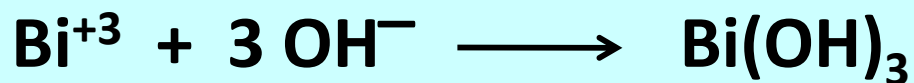
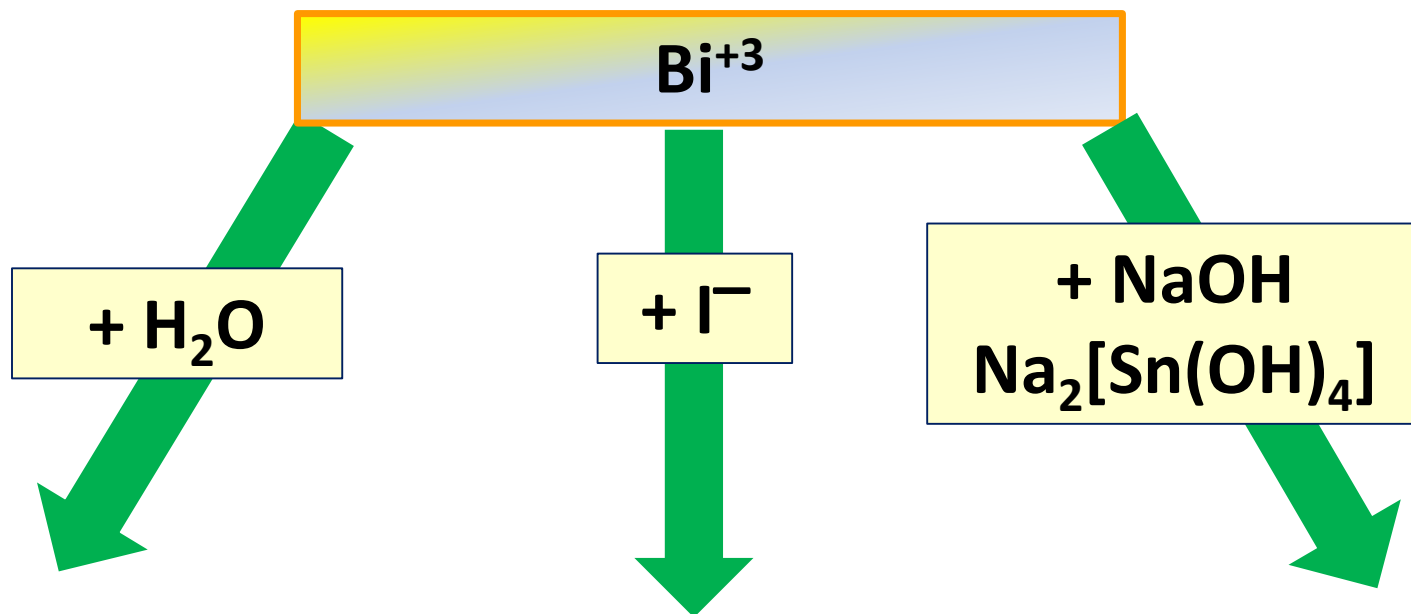
↓
Bismuthyl chloride

Upon dilution with water turbidity appears (BiOCl),
when mineral acid is added turbidity disappears.

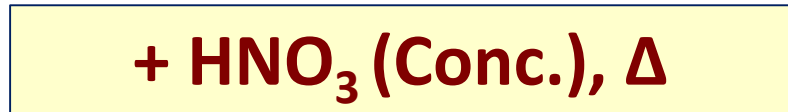
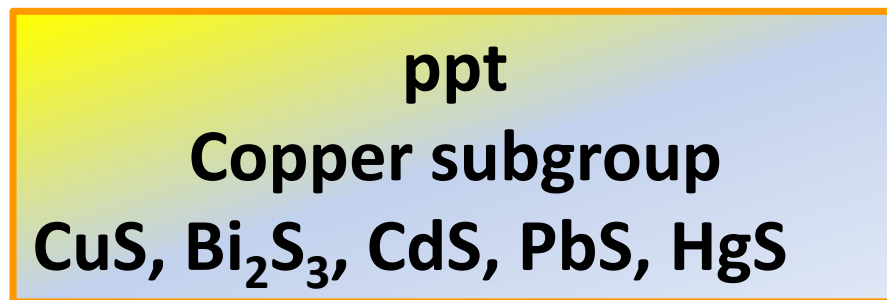
H₂S group: Copper subgroup



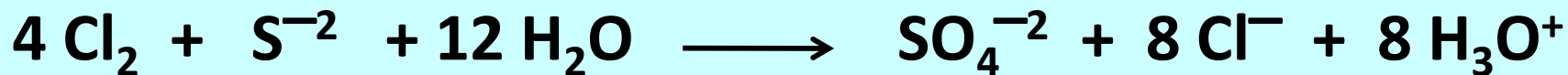
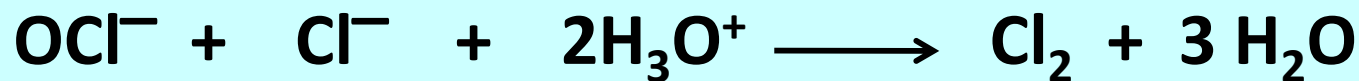
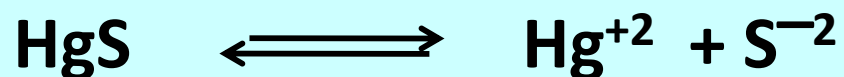
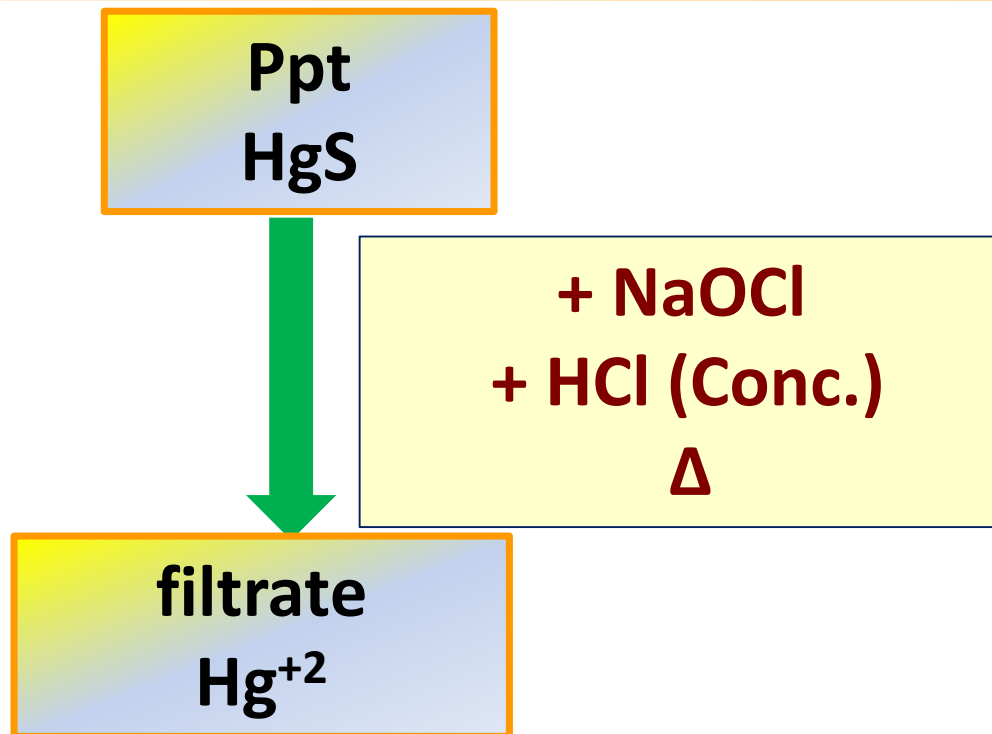
H₂S group: Copper subgroup



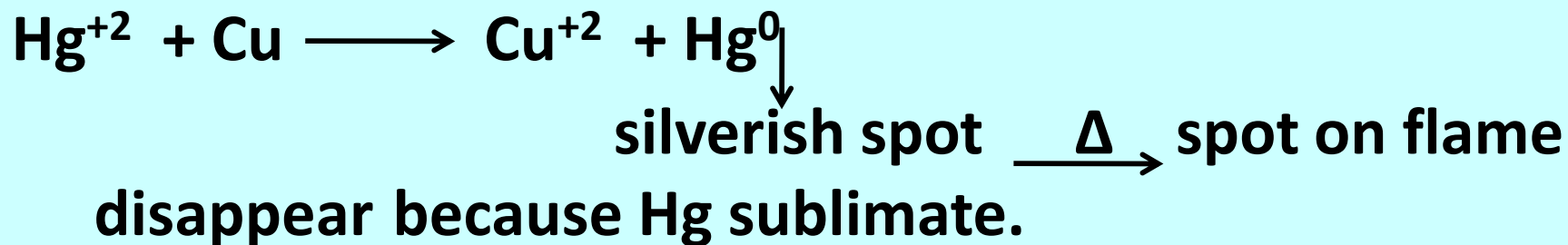
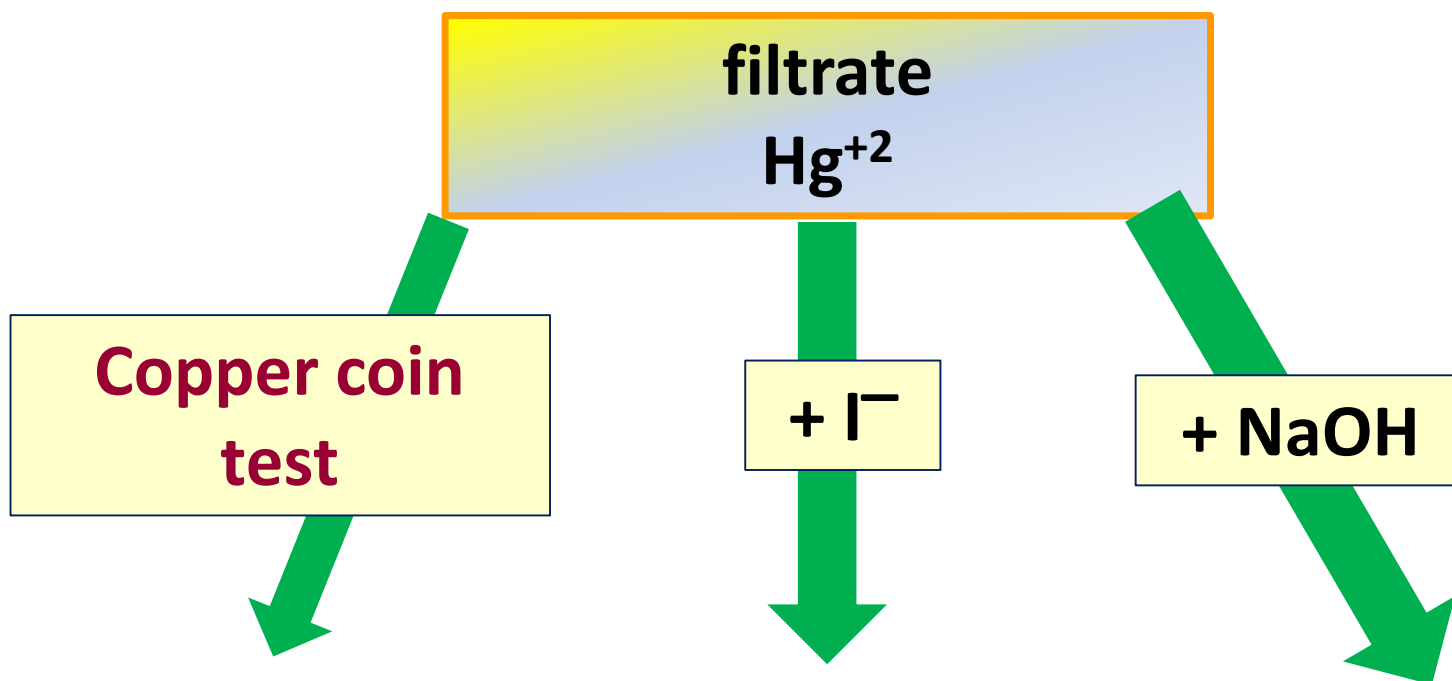
H₂S group: Copper subgroup



H₂S group: Copper subgroup

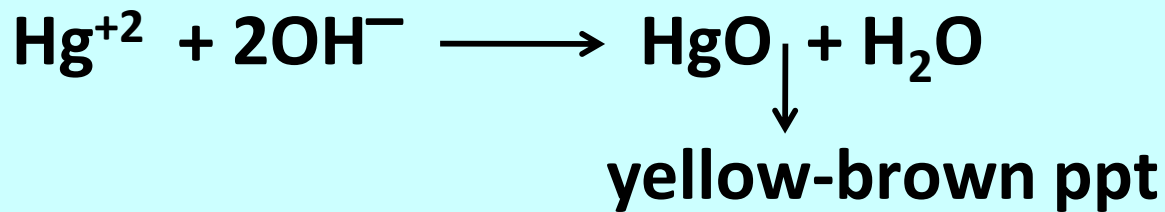
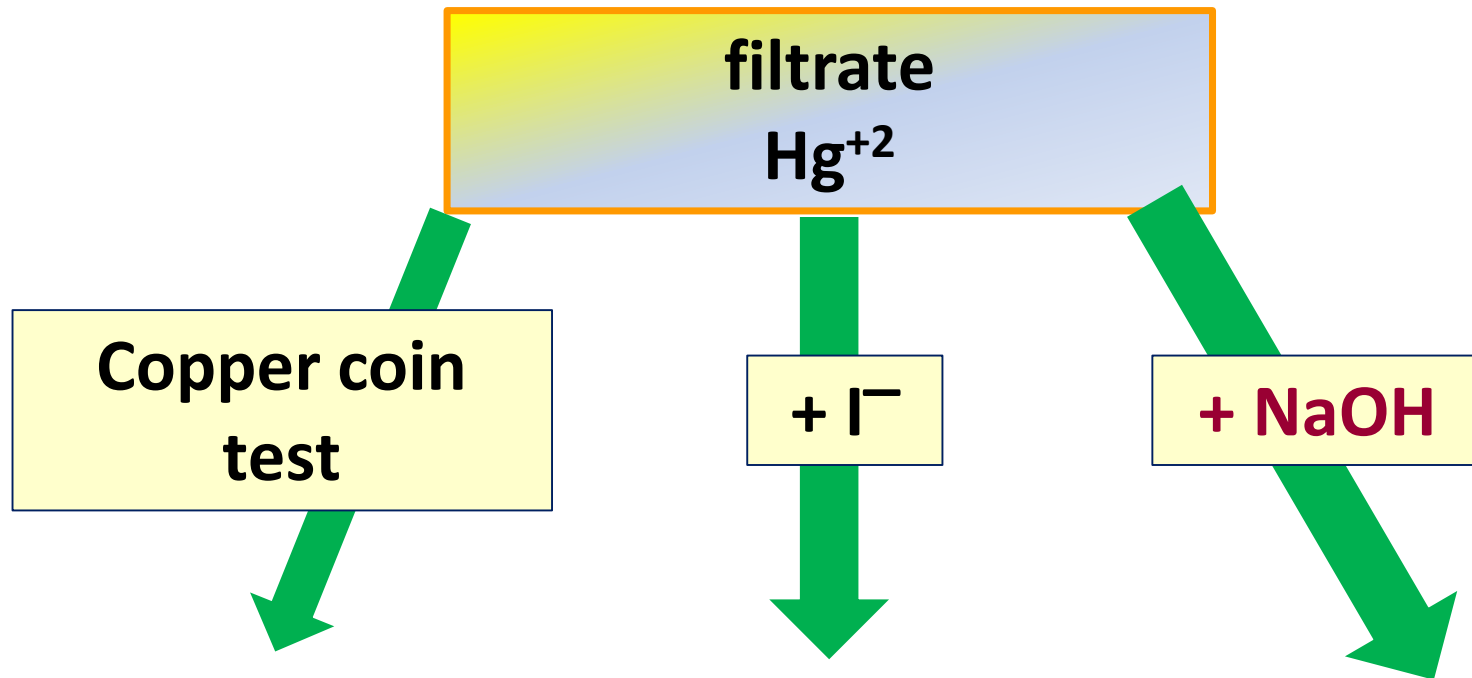


H₂S group: Copper subgroup



Hg₂⁺² is a malfunction

H₂S group: Copper subgroup

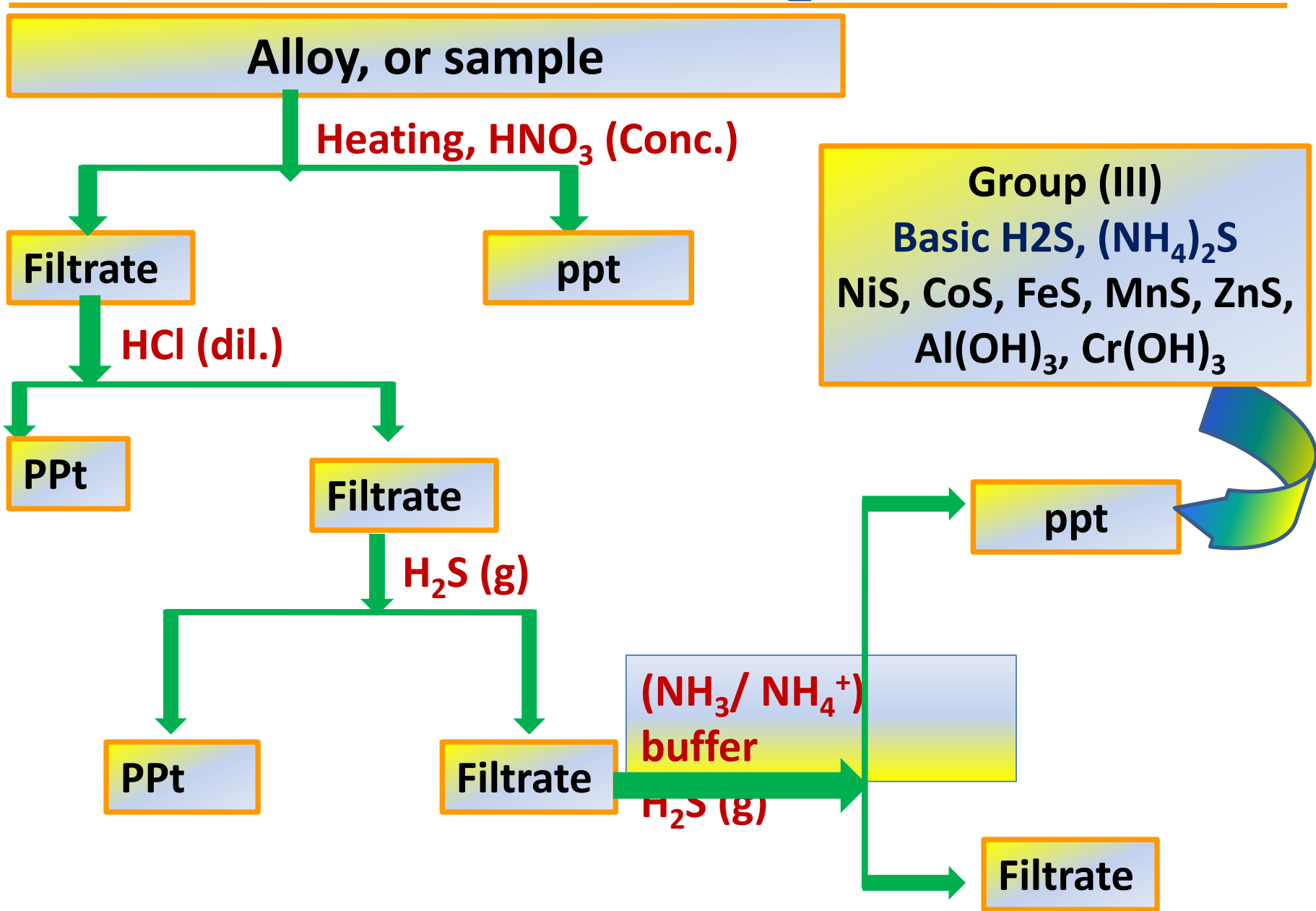


Qualitative inorganic analysis

part (II)

Cations

Group (III): Basic H₂S group



Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Group (III)

Basic H_2S , $(\text{NH}_4)_2\text{S}$

NiS ,	CoS ,	FeS ,	MnS ,	ZnS ,	$\text{Al}(\text{OH})_3$,	$\text{Cr}(\text{OH})_3$
Black,	black,	black,	red,	white,	white,	green

Group (III)

Cations form insoluble sulfide or hydroxide salts

K_{sp} of sulfide salts is high, that they were soluble in acidic media

Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Group (III)
Basic H_2S , $(\text{NH}_4)_2\text{S}$
 NiS , CoS , FeS , MnS , ZnS , $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$

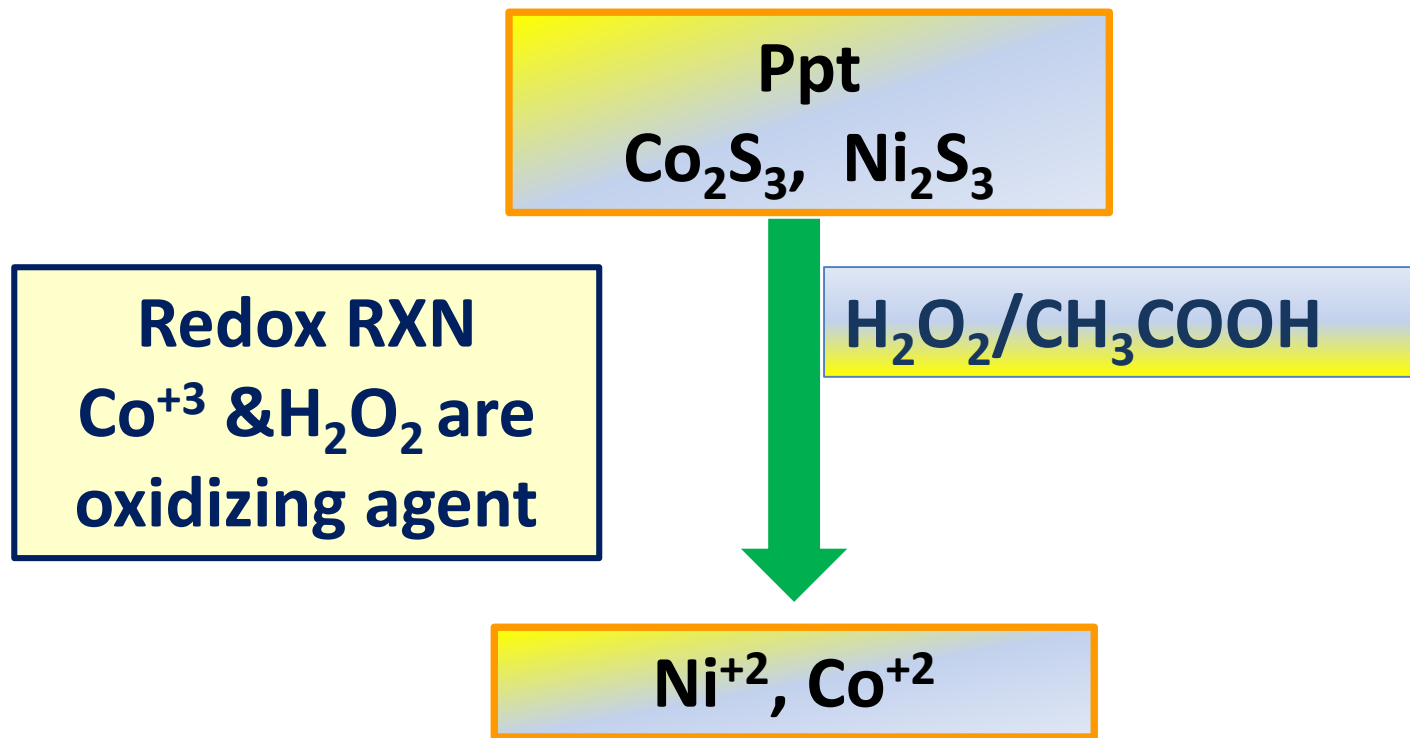
Digestion of ppt for 30 min.
Add HCl (dil.)
Centrifugation

Ppt
 Co_2S_3 , Ni_2S_3

Filtrate
 Mn^{+2} , Zn^{+2} , Fe^{+3} , Al^{+3} , Cr^{+3}

Sulfide salts of this group are soluble in acidic media.
 Co_2S_3 , Ni_2S_3 are insoluble in acids [HCl (dil.)]

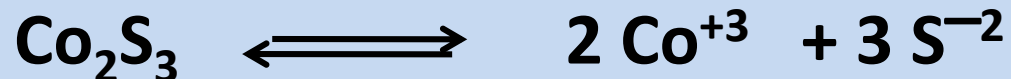
Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group



Notice: Co_2S_3 , Ni_2S_3 have cation in oxidation state +3
The products are in oxidation state +2

Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

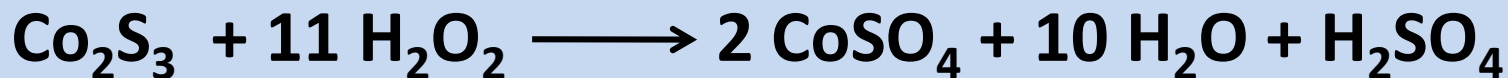
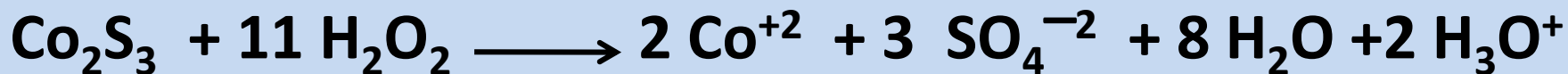
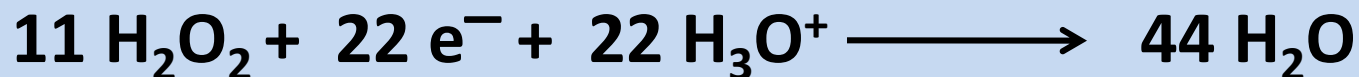
Equations and Explanation



Oxd. Half RXN:

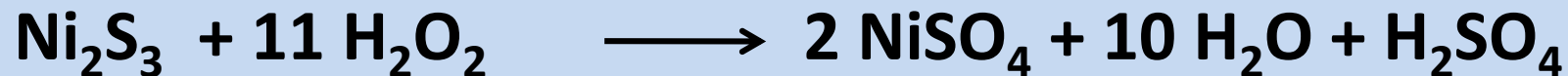


Red. Half RXN:



Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Equations and Explanation



Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Ni^{+2} , Co^{+2}

Separate filtrate in 2 test tubes

Add NH_4SCN , ether
detect Co^{+2}

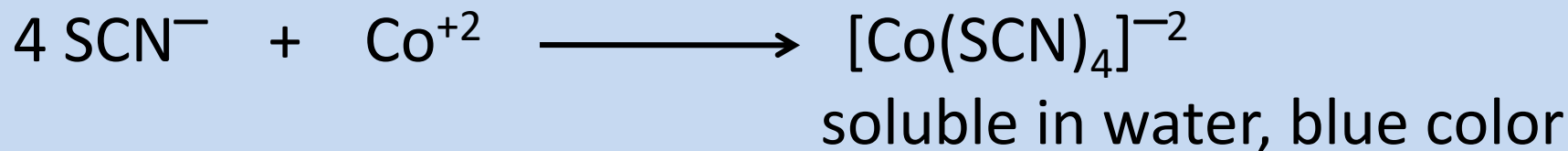
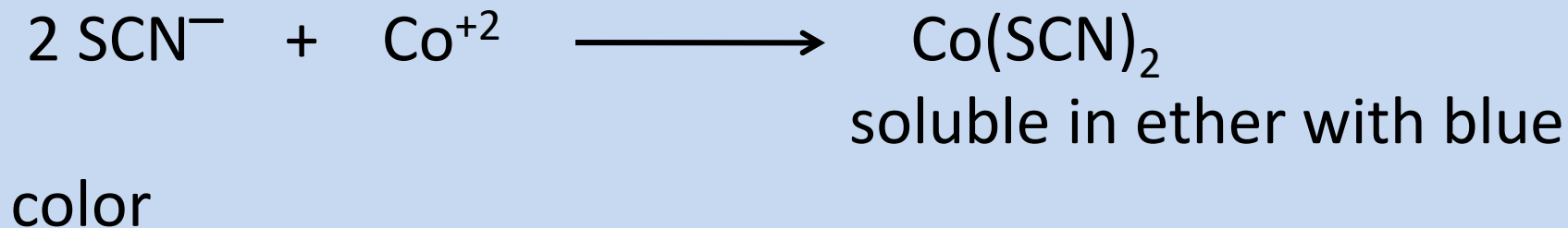
Add Dimethylglyoxime
(DMG) detect Ni^{+2}

Aqueous and ether
phases are blue

Red ppt
[$\text{Ni}(\text{DMG})_2$]

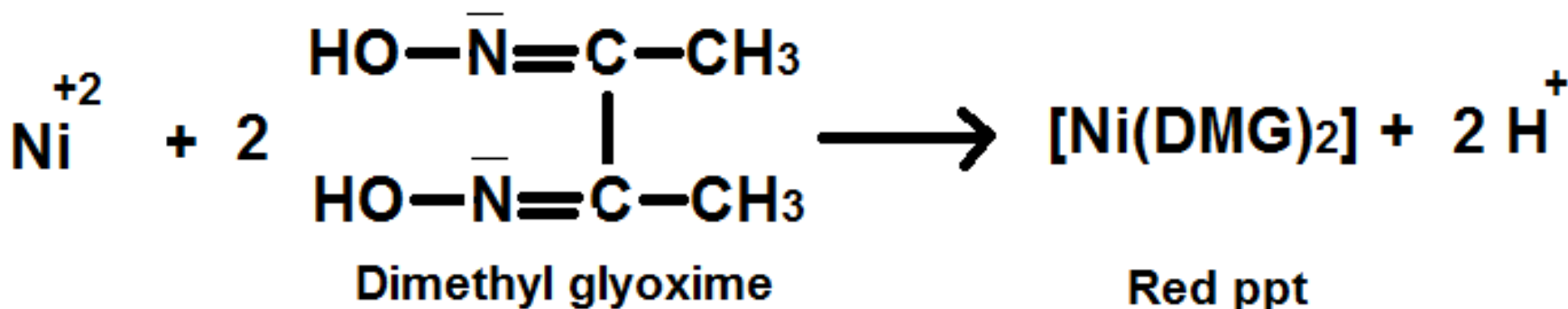
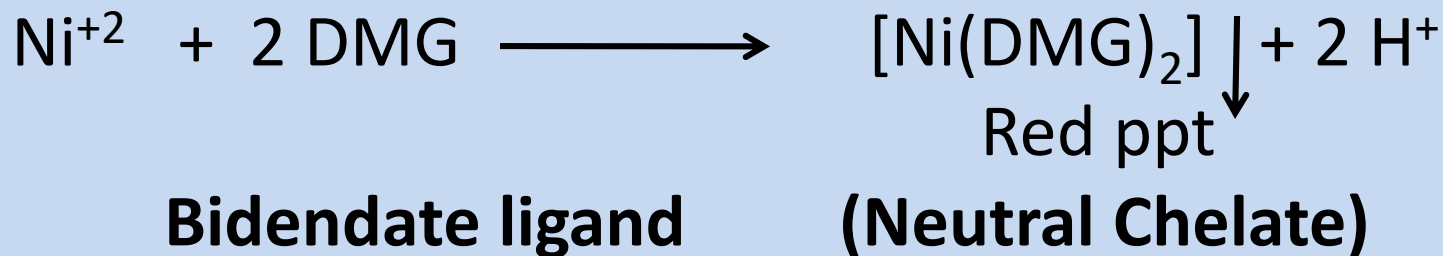
Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Equations and Explanation

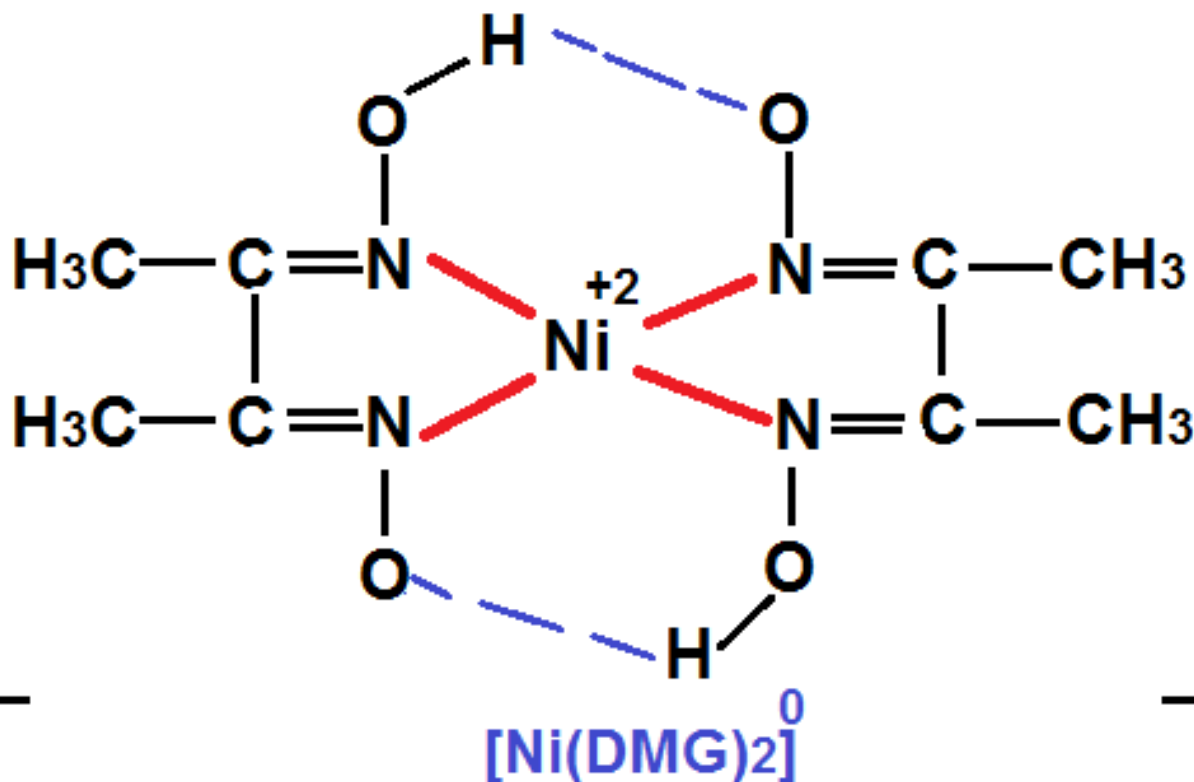


Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Equations and Explanation

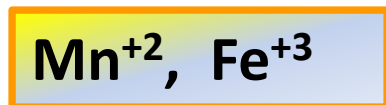
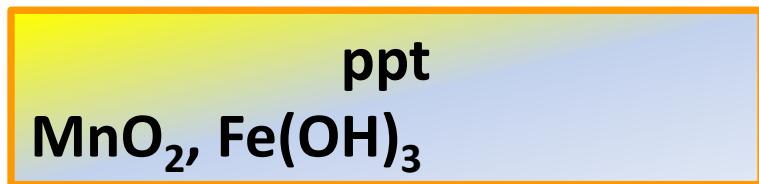
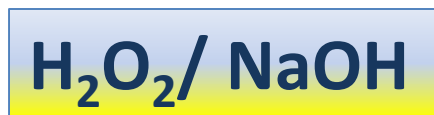


Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

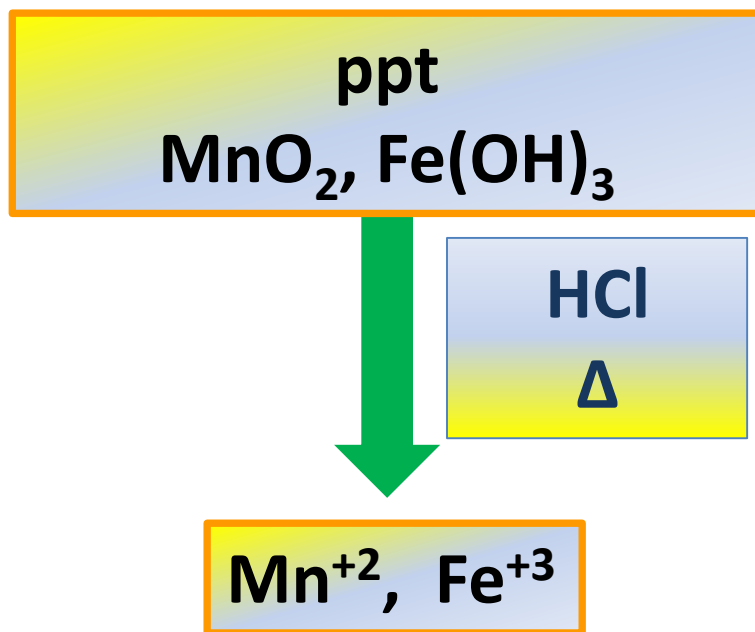


— — — — Coordination bond
- - - - H- Bond

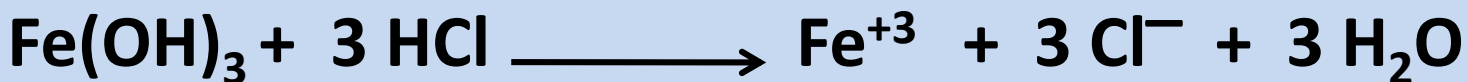
Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group



Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group



Equations and Explanation



Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Mn^{+2} , Fe^{+3}

Separate filtrate in 2 test tubes

Detect Fe^{+3}

Add NH_4SCN , ether

↓
Ether phase is red

Add $\text{K}_4[\text{Fe}(\text{CN})_6]$

↓
Prussian blue ppt

Detect Mn^{+2}

Add $\text{PbO}_2 + \text{HNO}_3$

↓
Violet color of solution
 MnO_4^-

Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

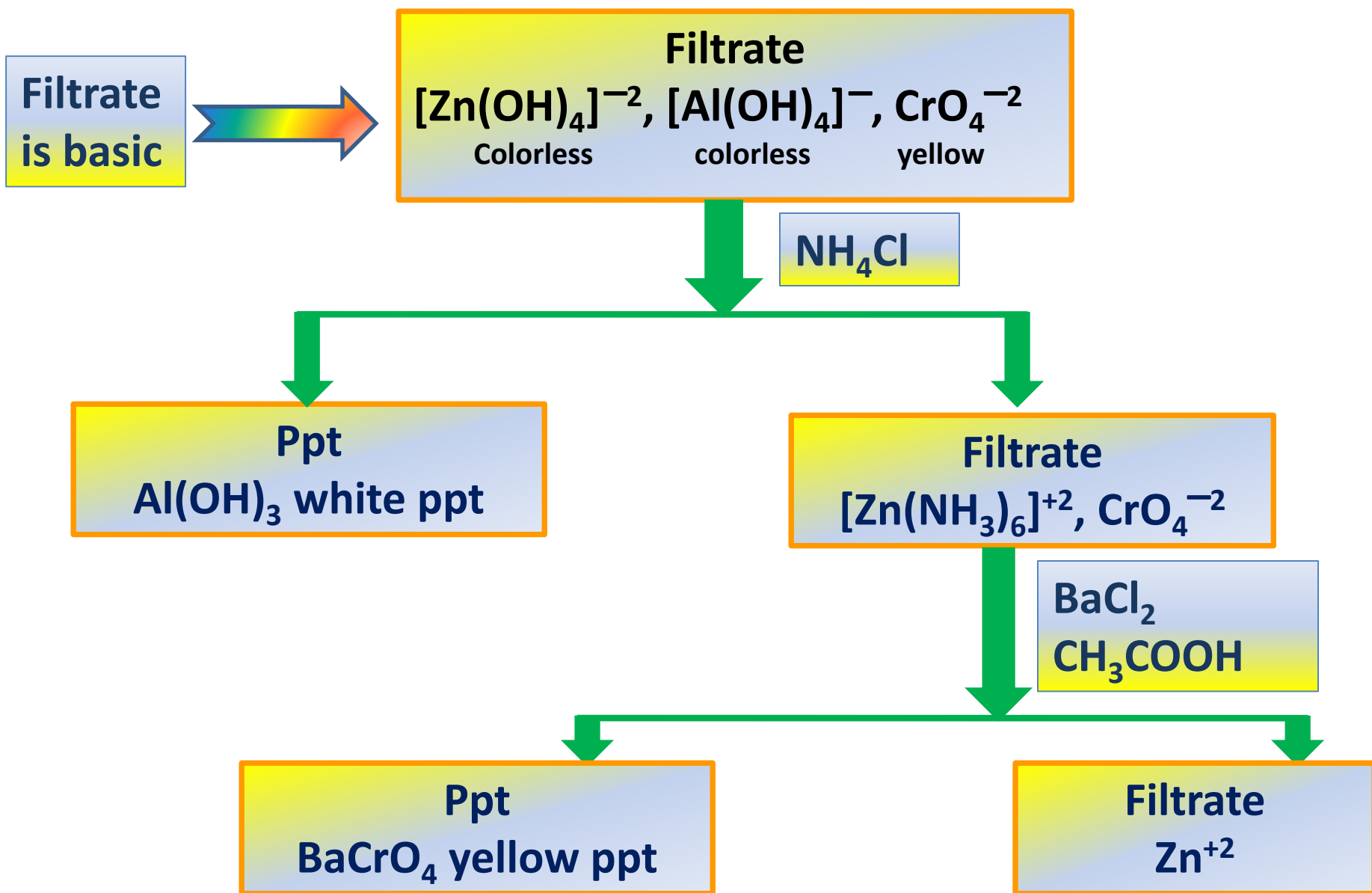


Which is oxidizing agent, and reducing agent???

In this RXN HNO_3 was not the oxidizing agent. It is just acidic media.

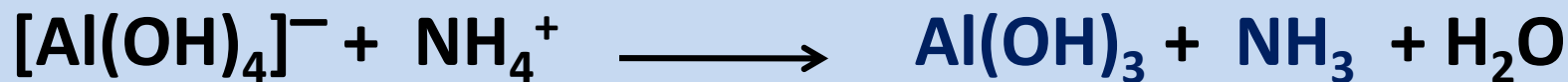
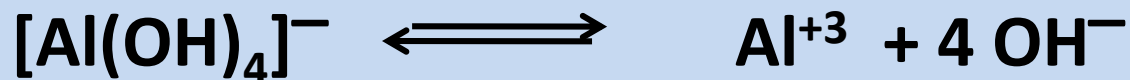
MnO_4^- has violet color and it decolorizes when e.g. S^{-2} (reducing agent) is added, since it converts to colorless in acidic pH (Mn^{+2}).

Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group



Group (III): Basic H_2S , $(\text{NH}_4)_2\text{S}$ group

Equations and Explanation



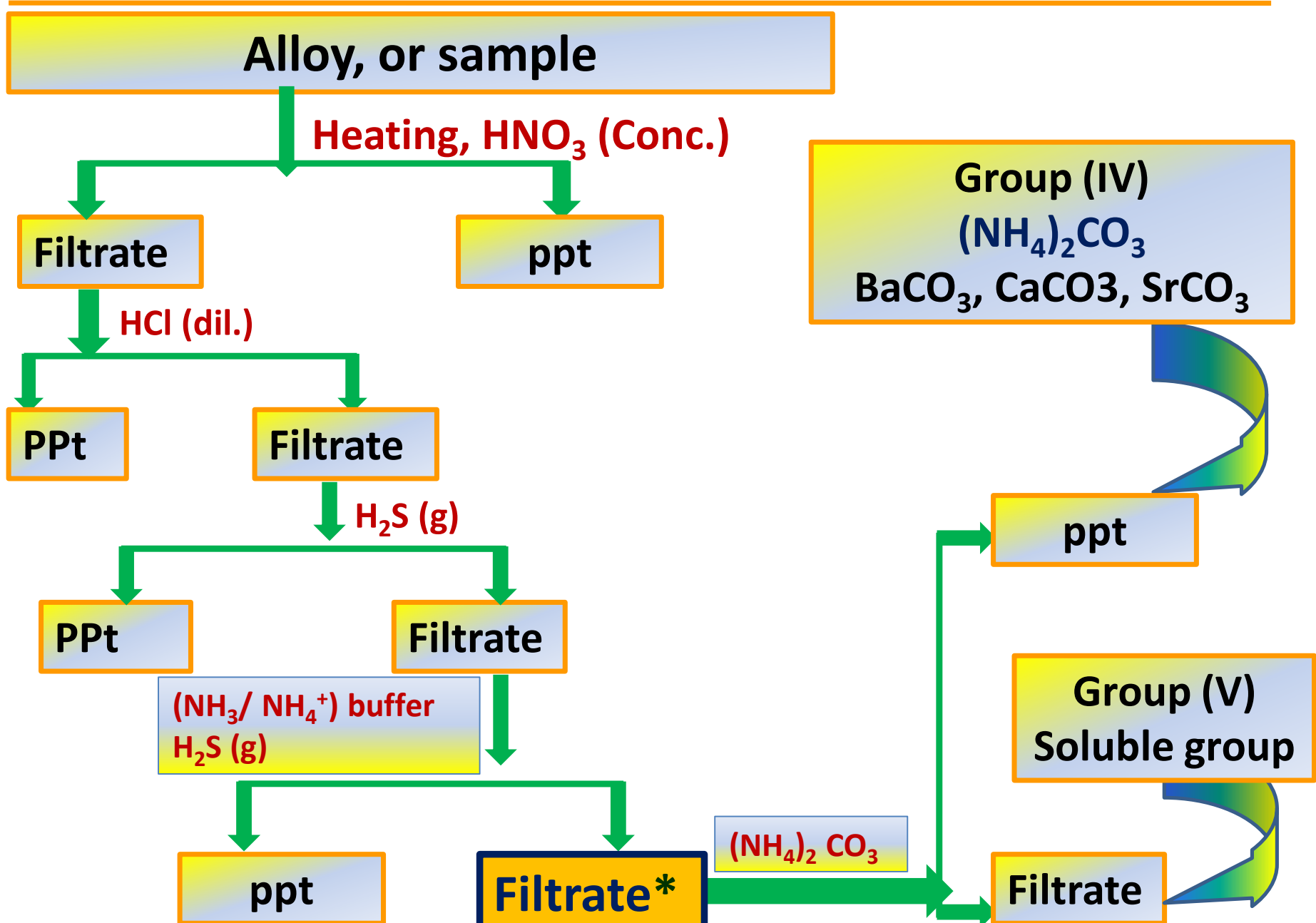
Qualitative inorganic analysis

part (II)

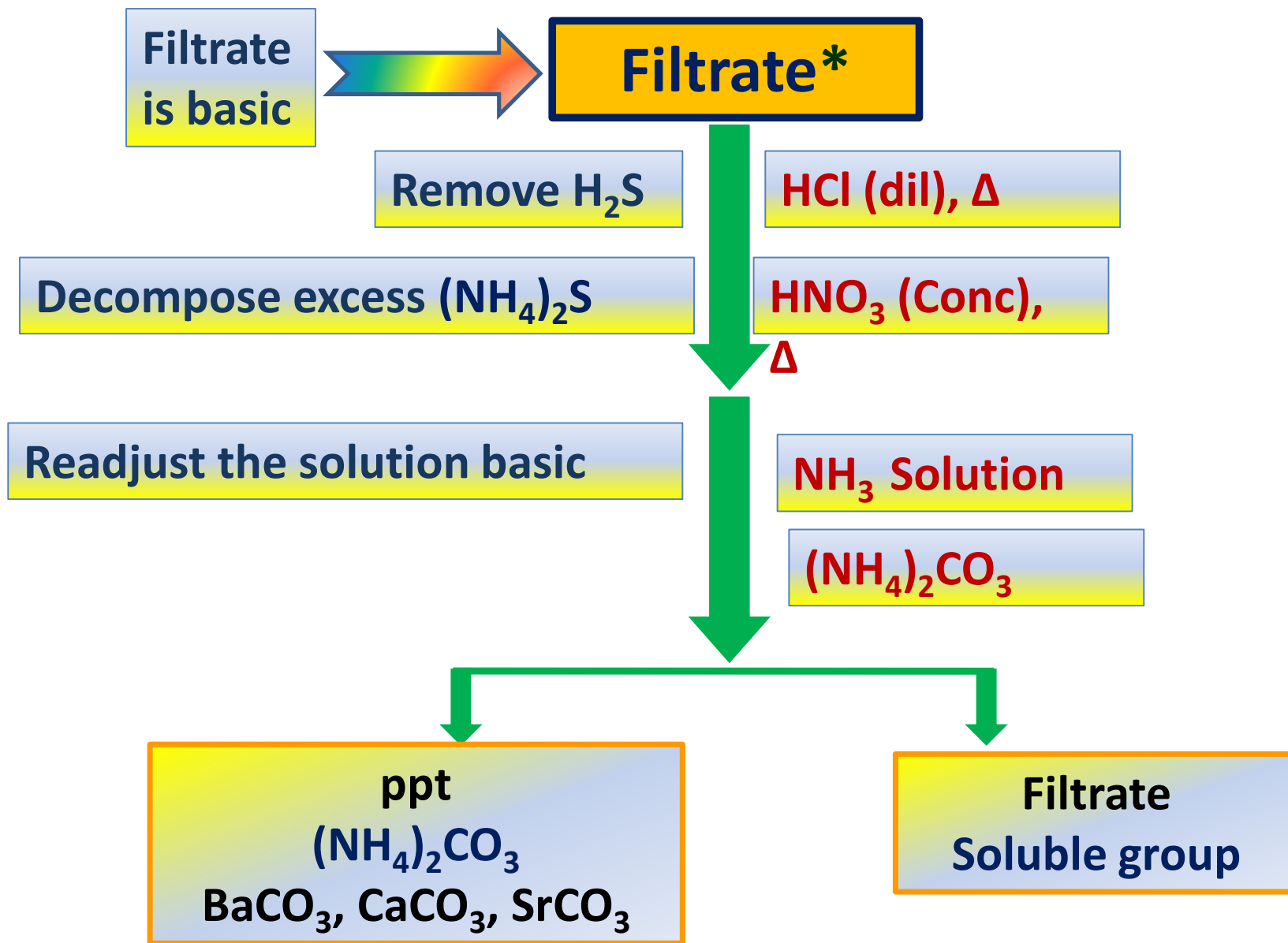
Cations

Dr. Mai Ramadan

Group (III): Basic H₂S group

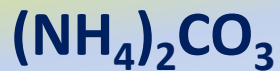


Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group



Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group

Group (IV)



Group (IV)

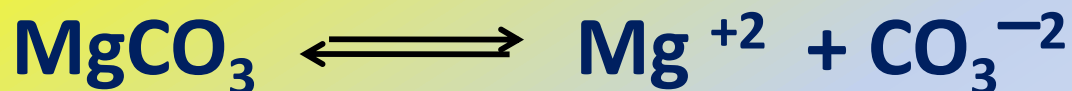
Cations form insoluble carbonate salts

Note:

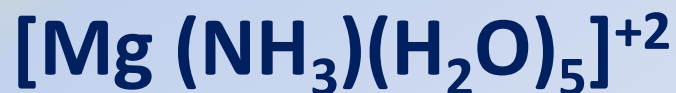
Mg⁺² is not precipitated in this stage as MgCO_3 or $\text{Mg}(\text{OH})_2$, due to the presence of NH_4^+ -salts.

Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group

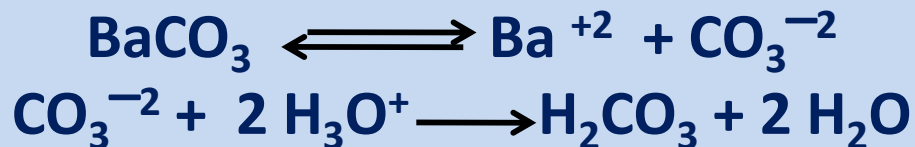
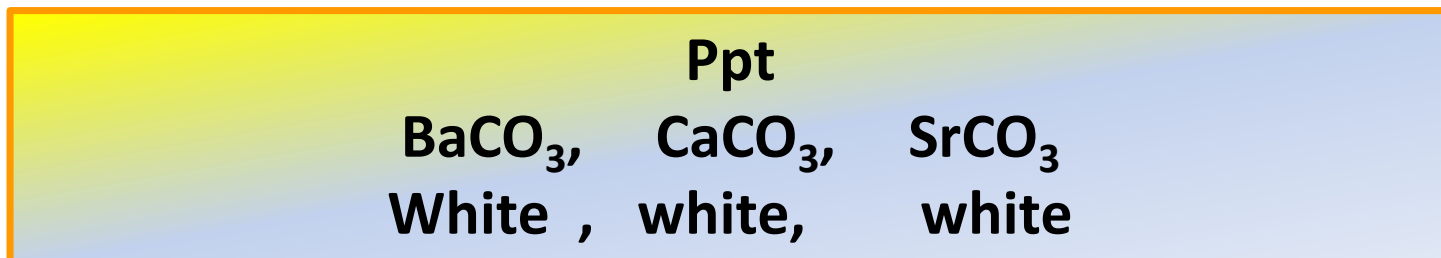
MgCO_3 has a high k_{sp}



Mg^{+2} forms soluble complex with NH_3



Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group



Buffer (pH 4-5)



Ppt



Filtrate

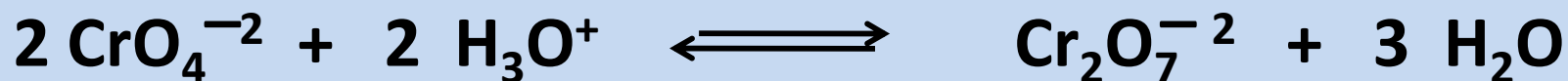


Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group

Equations and Explanation

Buffer system (pH 4-5) is important

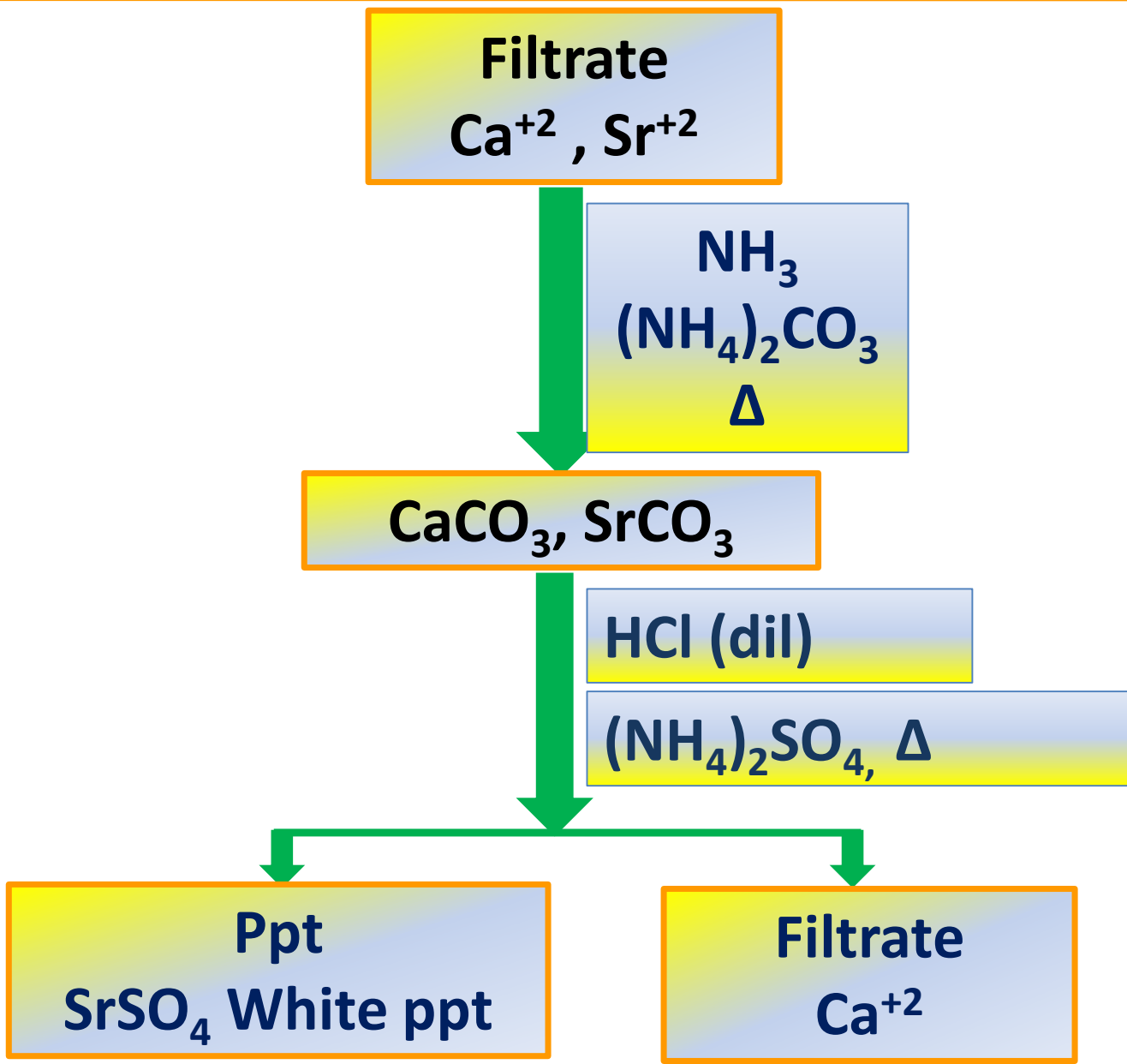
pH < 4



pH > 5

Ca^{+2} , Sr^{+2} are precipitated.

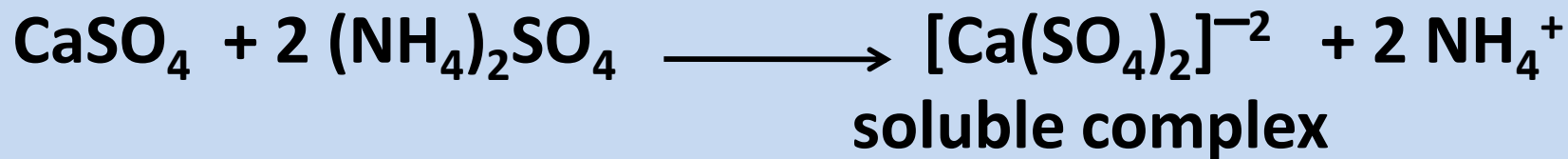
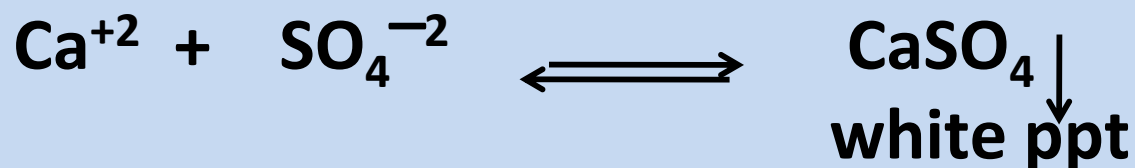
Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group



Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group

Ca^{+2} is not precipitated as sulfate salt in this condition, by adding $(\text{NH}_4)_2\text{SO}_4$.

Equations and Explanation

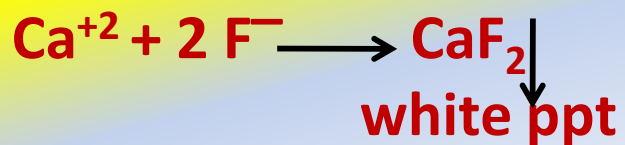
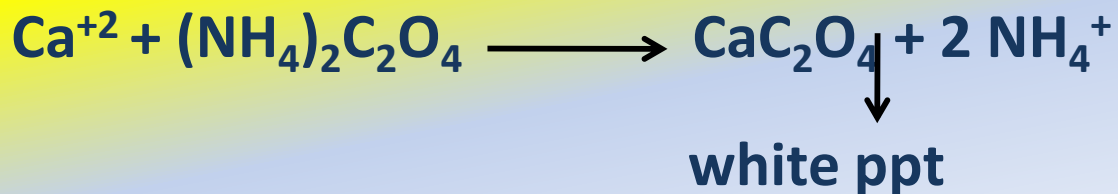


Group (IV): $(\text{NH}_4)_2\text{CO}_3$ group

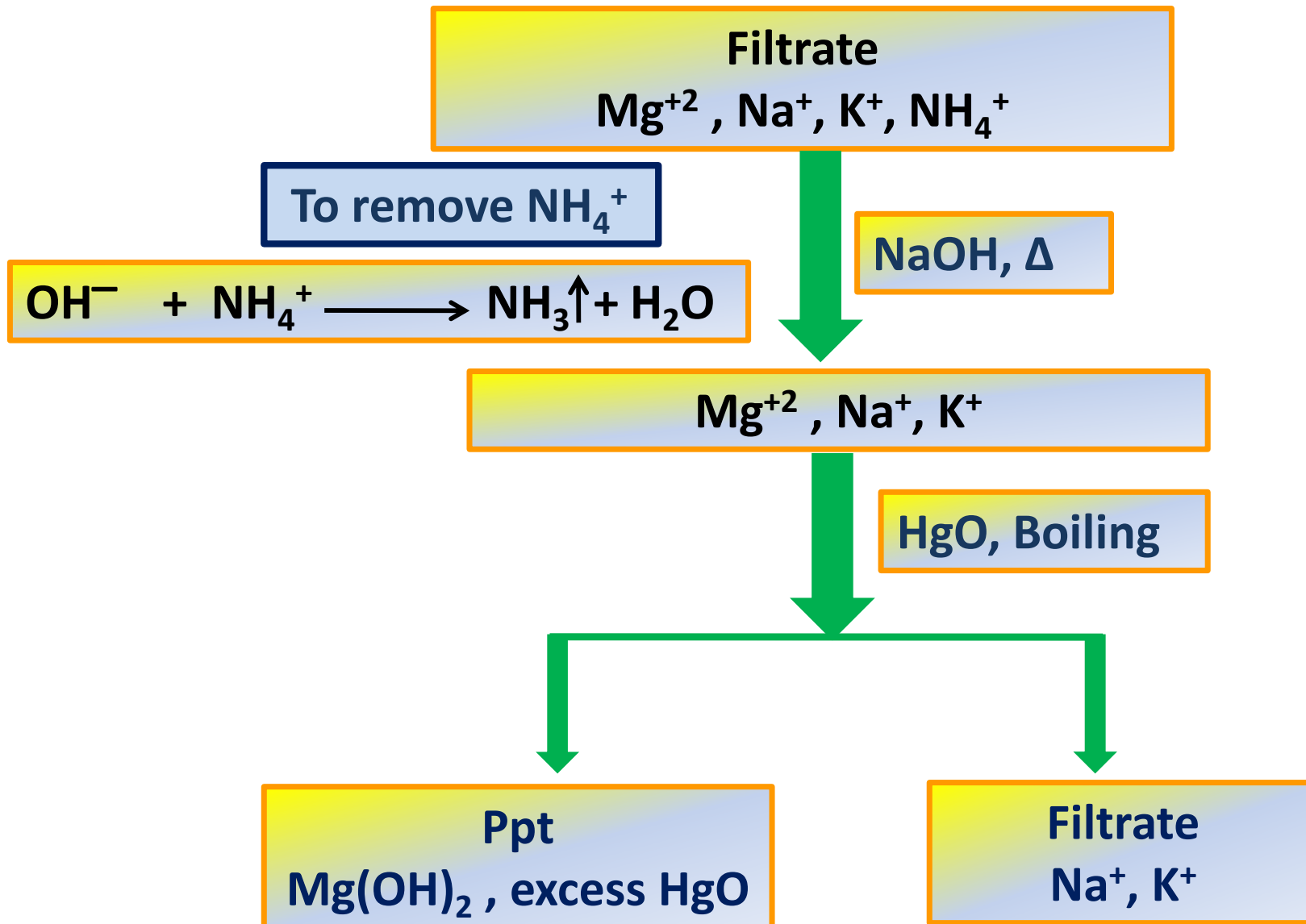
Filtrate
 Ca^{+2}

Add NH_3
then $(\text{NH}_4)_2\text{C}_2\text{O}_4$

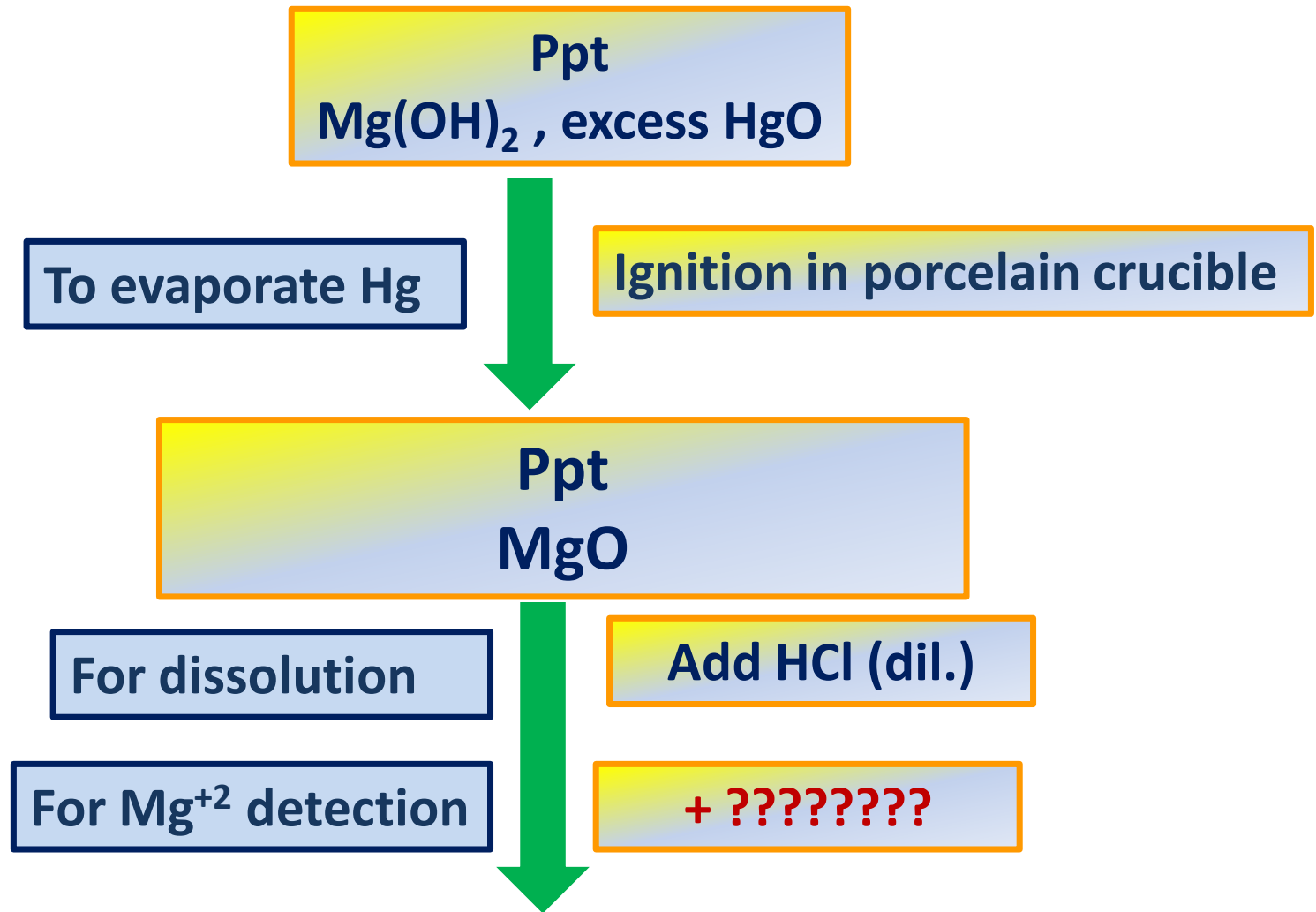
F^-



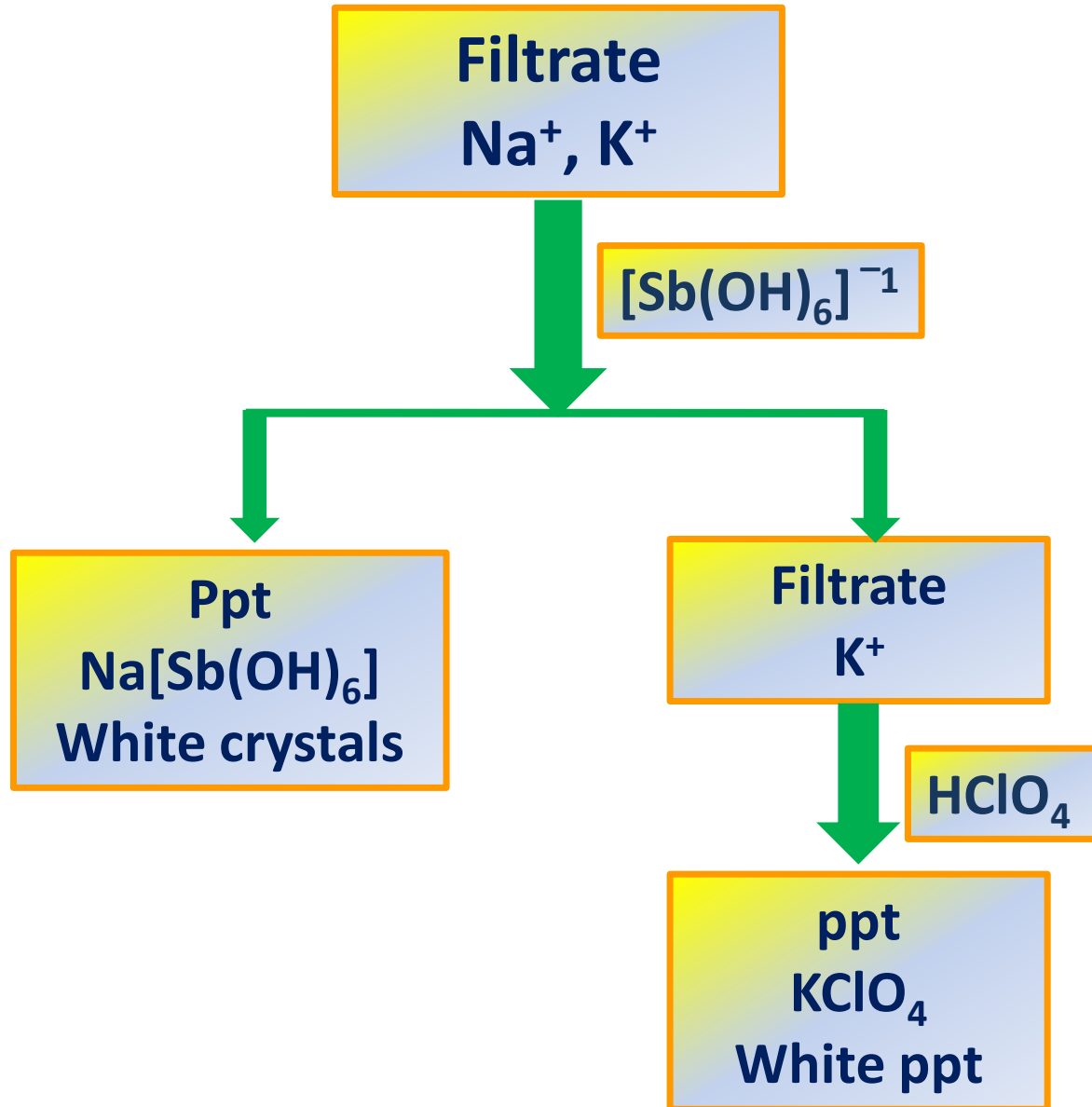
Group (V): Soluble group



Group (V): Soluble group



Group (V): Soluble group



Exercise

Describe only schematic how could the following ions be separated:

Ag^+ , Pb^{+2} , Cu^{+2} , Bi^{+3} , As^{+3} , Sn^{+2} , Fe^{+2} , Ni^{+2} , Ca^{+2} , Na^+ , K^+ .

Exercise

A chemist has the following results for analysis of a salt:

A- Pulverize the sample with KHSO_4 a vinegar odor was characterized.

B- Upon adding HCl (dil) to sample solution a white ppt was formed which was soluble upon heating

C- Upon passage of H_2S to acidified solution of sample a black ppt was formed, which was soluble in HNO_3 (conc.)

D- Upon addition of KI solution to sample a yellow crystals was formed.

1. What is the salt?

2. Explain your judgment with equations?

3. Give a malfunction for test (A)? Then explain how to be removed (One solution)?