

Chapter 2

Analytical Separation of Cations

Analysis for anions (acid radical) and for cations (basic radical), the two parts of inorganic qualitative: analysis, are carried out separately. Either part may be attacked first.

Cations are positively charged fragments or ions of salt or compound. They are frequently referred to as the metals or basic radicals.

In studying an unknown, a visual examination should come first. If the unknown is a solution, what color is it ? Color is important because some inorganic ions reveal their identities through color alone.

If the unknown is a solid, the color is also important, but it does not necessarily indicate the colors of the individual ions. Thus,

Pb^{2+} and I^- are both colorless, but they combine to give the bright yellow PbI_2 .

Identification of cations cannot be performed by tests on the original substances (or salts), therefore we have to some schemes for the systematic separation of cations.

Flowcharts are used to represent the steps in qualitative analysis, particularly for the analysis of cations, which is more systematic than the analysis of anions. A flowchart is a schematic outline that begins with the ions in question, indicated the reagents and the conditions for each step, and gives the formulas for the chemical products that result.

In considering qualitative analysis and in carrying out the procedures in the laboratory, keeping track of the analytical steps is essential. We recommend that you refer to the flowcharts frequently.

Flowcharts can be written in various ways, in which precipitates or undissolved solids are carried to the left and ions in solution are carried to the right.

Cations

Common cations (basic radical) may be divided, for purposes of qualitative analysis, into a number of groups; the members of any group are precipitated by a particular group reagent. Thus by the addition of a slight excess of dilute hydrochloric acid to a solution containing all the common cations, a precipitate is obtained consisting of the chlorides of silver; lead and mercurous, similarly by the use of the appropriate group reagents, the remaining cations are separated into different groups.

Generally, analytical separation of cations depends on the varying solubilities of their **chlorides, sulphides, hydroxides and carbonates**. The various groups are summarized in the following table.

Group	Group reagent	ions	Formula of precipitate
Group 1 (silver group)	cold, dilute-hydrochloric acid	Hg ₂ ²⁺ , Pb ²⁺ , Ag ⁺	Hg ₂ Cl ₂ , PbCl ₂ , AgCl
Group II (Copper and arsenic group)	H ₂ S in presence of dilute HCl	Hg ²⁺ , Pb ²⁺ , Bi ³⁺ , Cu ²⁺ , Cd ²⁺ , Sn ²⁺ , Sb ³⁺ , As ³⁺	HgS, PbS, Bi ₂ S ₃ , CuS, CdS, SnS, Sb ₂ S ₃ , As ₂ S ₃
Group III (Iron group)	Aq. NH ₃ in presence of aq. And NH ₄ Cl	Al ³⁺ , Cr ³⁺ , Fe ³⁺ , Mn ³⁺	Al(OH) ₃ , Cr(OH) ₃ , Fe(OH) ₃ , Mn(OH) ₃ ,
Group IV (Zinc Group)	H ₂ S in presence of aq. And NH ₄ Cl	Ni ²⁺ , Co ²⁺ , Mn ²⁺ , Zn ²⁺ .	NiS, CoS, MnS, ZnS
Group V (Calcium Group)	(NH ₄) ₂ CO ₃ in presence of aq. And NH ₄ Cl	Ba ²⁺ , Ca ²⁺ , Sr ²⁺	BaCO ₃ , SrCO ₃ , CaCO ₃
Group VI (Alkali Group)	No particular reagent	Mg ²⁺ , K ⁺ , Na ⁺ , NH ₄ ⁺	Different ppted form

The steps in cations analysis fall into the following general sequence:

1- Separation of the cations into a series of groups

The cations of each successive group are precipitated as compounds with anions supplied by the group reagent. The precipitate (residue) containing the cations of one group are separated (usually by centrifugation). Then the group reagent for the next group is added to the remaining solution (centrifugate).

2- Separation of the cations in each group from each other

A series of reactions is carried out that eventually leads to the separation of each cation in a group from all of the others in that group. The reactions are carefully chosen to take advantage of similarities and differences in chemical properties.

3- Identification of individual cations

The presence of cation is confirmed by one or more reactions characteristic of that cation.

For ideal separation of cations

- a) The groups should not be too large (3 or 5 members).
- b) The precipitation of each group should be complete.

- c) The precipitates should be sufficiently insoluble, (filter rapidly and wash well).
- d) The precipitates should have no tendency to adsorb other ions (or cations) from the medium i.e. no interference.

The insoluble precipitate is formed by the addition of the “group reagent”. This group reagent is specific for each group of cations. The active part of these reagents is the anionic part.

A typical analytical scheme for the separation of the cations into groups is summarized in the table.

Scheme for separation of cations						
HCl or a soluble chloride, preferably NH ₄ Cl, added to unknown; filtered						
precipitate: contains chlorides of lead (Pb), silver (Ag), and mercurous mercury (Hg) PbCl ₂ (white) AgCl (white) Hg ₂ Cl ₂ (white) Group I	solution: H ₂ S passed into the acid solution; filtered					
	precipitate: treated with NH ₄ OH; ammonium poly- sulfide (NH ₄) ₂ S _x ; and (NH ₄) ₂ S; filtered		solution: neutralized with NH ₄ OH and NH ₄ Cl; filtered			
	precipitate: contains cupric, lead, cadmium, bismuth, and mer- curic sulfides Group IIa	solution: contains arsenic, antimony, and tin cations Group IIb	precipitate: contains aluminum (Al), chro- mium (Cr), and ferric (Fe) hydroxides Al(OH) ₃ (white) Cr(OH) ₃ (gray- green) Fe(OH) ₃ (brown) Group IIIa	solution: H ₂ S passed into alkaline solution; filtered		
				precipitate: contains cobalt (Co), nickel (Ni), manganese (Mn), and zinc (Zn) sulfides CoS (black) NiS (black) MnS (buff) ZnS (white) Group IIIb	precipitate: barium, strontium, and calcium carbon- ates (all white) Group IV	solution: evaporated and NH ₄ OH and (NH ₄) ₂ CO ₃ added; filtered solution: contains magnesium, sodium, and potas- sium ions Group V

Cation Group I (Silver Group)

Mercurous Hg_2^{2+}
Lead Pb^{2+}
Silver Ag^+

Cations Group I bring together three metal ions that form chlorides which are insoluble in acidic solution. The group reagent is cold, dilute-hydrochloric acid, and this group is sometimes known as the hydrochloric acid group, the chloride group, or the silver group. The chlorides of all the other cations in our cation analysis scheme are soluble in acidic solution.

Condition of precipitation

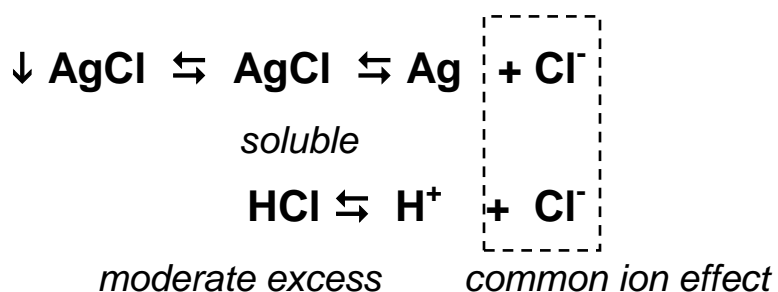
- (1) Cold hydrochloride acid is used to prevent the solubility of PbCl_2 in hot solution.
- (2) 6M cold hydrochloric acid

Use of a moderate excess of hydrochloric acid to precipitate the group serves two purposes:

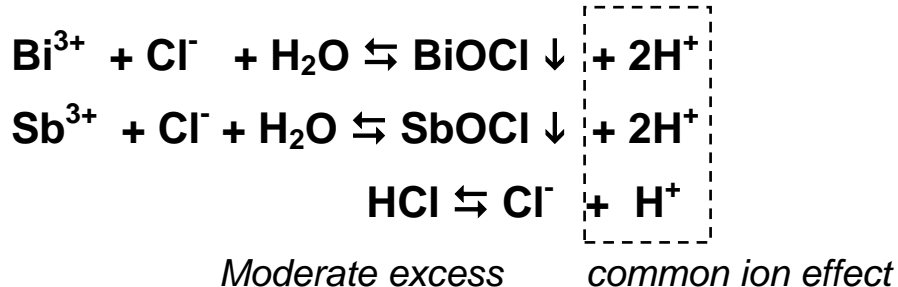
- (1) The excess chloride ion "encourages the precipitation of group I (Le Chatelier's principle) the common ion effect of

the Cl^- . i.e.: (decrease the solubility of the chloride precipitates of group I)

Example:



(2) Also, if the unknown contains Bi^{3+} or Sb^{3+} (from the subsequent group) the hydrogen ion prevents the precipitation of them as oxychlorides.



i.e. Solubility of $\text{BiOCl} \downarrow$ or $\text{SbOCl} \downarrow$ if these cations are present with group I-cations (Bi^{3+} , Sb^{3+}) by the common ion effect of the H^+ .

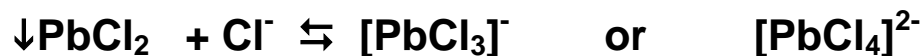
Too large excess of the acid is avoided:

- (1) Dissolves the silver and lead chlorides by complex formation. Mercury (I) chloride does not dissolve because the chloro complexes of mercury (I) are very unstable.

Example:

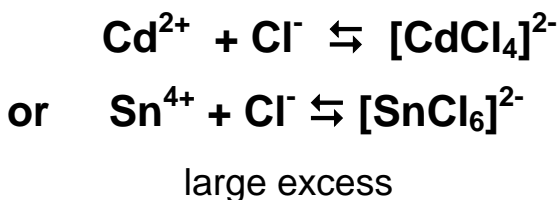


*Large excess Silver dichloride
 soluble complex*



*Large excess Lead trichloride Lead tetrachloride
 Soluble complexes*

- (2) Also, if the unknown contains Cd^{2+} and Sn^{4+} (from the subsequent groups), the high chloride concentration forms stable soluble complexes with them and inhibits the precipitation of CdS and SnS_2 by $\text{H}_2\text{S}/\text{H}^+$.



Separation of Cation Group I

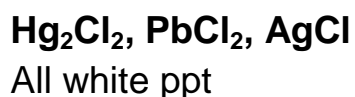


Procedure 1

Cold 6 M HCl

Residue

Centrifuge



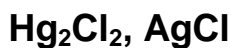
(if only cation of group I present discard, otherwise save for cation of group II)

Procedure 2

H_2O , Boil

Residue

Centrifuge

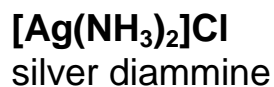
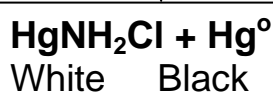


Procedure 4

Conc. NH_4OH

Residue

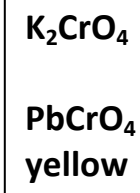
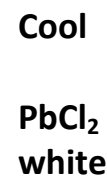
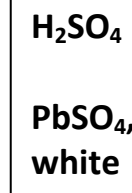
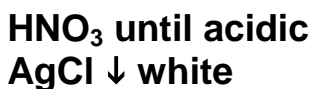
Centrifuge



Procedure 3

Divided into 3 portion

Dissolve in aqua regia, evaporate
1. SnCl_2
2. KI



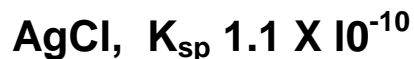
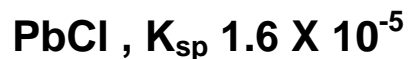
$\therefore \text{Hg}_2^{2+}$ present

Ag^+ present

Pb^{2+} present

Procedure 1:

The solubility products of the precipitates of group I cations are:



Solubility product constants indicate that lead (II) chloride is much more soluble than the chlorides of mercury (I) or silver (I). Because the solubility in water of PbCl_2 increases from about 0.036 mol/L at 20°C to about 0.12 mol/L at 100°C, cold solutions are used in this procedure to maximize precipitation of the lead(II) ion. Addition of excess hydrochloric acid initially reduces the solubility of each chloride by the common ion effect, but a large excess then increases the solubilities of AgCl and PbCl_2 as a consequence of the formation of chloro complex ions. In any cases, a sufficiently large concentration of Pb^{2+} ion remains in solution to form PbS ppt. with cation group II.

Procedure 2:

Boiling the precipitate with water increases the rate of dissolution of lead (II) chloride and maximizes its removal.

Procedure 3:

It crystals of lead (II) chloride separate as the solution cools, it is necessary to reheat until they dissolve so that enough Pb^{2+} is in solution to give a clear test. The tests are conducted on the hot solution. Lead (II) chromate is a more distinctive precipitate and less soluble than lead (II) sulfate. Chromate precipitations thus the better confirmatory test for the lead (II) ion.

Procedure 4:

Formation of a grey to black residue with conc. NH_4OH is the confirmatory test for the Hg_2^{2+} ion. The easily complexed Ag^+ ion remains in solution. Therefore, aqueous ammonia serves to confirm both the presence and the absence of the Hg_2^{2+} ion to and to separate silver (I) from mercury (I).

Procedure 5:

To the ammoniacal silver (I), slow addition of nitric acid results in precipitation of white silver chloride, which then redissolves upon shaking because of the presence of excess ammonia. Consequently, nitric acid must be added until the solution is definitely acidic before the presence or absence of the Ag^+ ion can be confirmed.

Silver (I) ion (Ag⁺)

- In solution, the Ag⁺ ion is colorless, but many solid silver (I) compounds that form with colorless anions are colored (e.g., AgBr, cream; AgI, Ag₃PO₄, yellow; Ag₂S, Ag₂O, black.)
- The most water-soluble silver (I) compound is the nitrate.
- its coordination number is 2

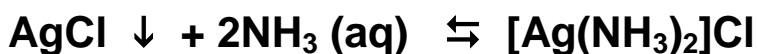
Reactions Important in the Separation and identification of Ag⁺

1. Group Precipitation.



white

2. Dissolution by Complex Ion Formation:



silver diammine

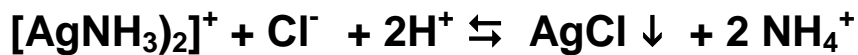


silver dicyanide



silver dichloride

3. Confirmatory Test



This is a neutralization reaction.



yellow

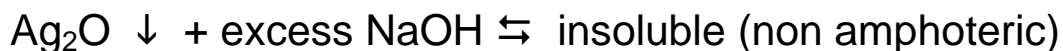
This is a precipitation reaction

4. Reaction with NaOH

Produces black precipitate insoluble in excess NaOH.



black

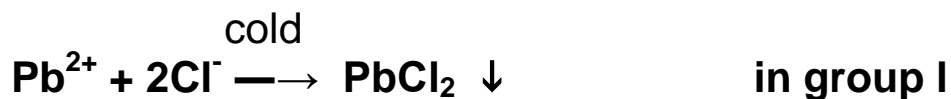


Lead(II) ion (Pb^{2+})

- its coordination number is 3 or 4
- its oxide is amphoteric (dissolves in both acid and alkali)

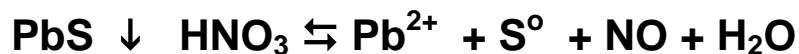
Reactions Important in the Separation and identification of Lead (Pb^{2+})

1. group Precipitation

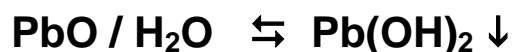


2. Dissolution

a) By oxidation of sulphide



b) Reaction with sodium hydroxide





c) Reaction with ammonium hydroxide

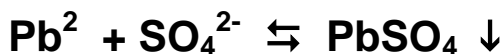
Produces white basic salts (ppt) which is insoluble in excess NH_4OH (differentiate between Pb^{2+} , Ag^+ , Cu^{2+} , Ca^{2+}).



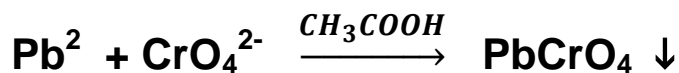
Lead hydroxychloride

white basic salt

5. Confirmatory Tests



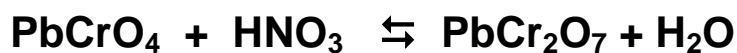
White



yellow

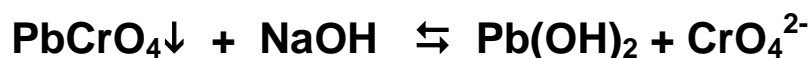
The reaction of Pb^{2+} with chromate gives yellow precipitate in weakly acidic medium (dil. acetic acid).

As if we use strong acidic medium (mineral acids) as dil. HNO_3 it will dissolve the yellow precipitate of PbCrO_4 and transform it to soluble dichromate salt.



lead dichromate (soluble)

Also if we use strong alkaline medium, the yellow precipitate of PbCrO_4 will dissolve (amphoteric character)



Plumbite



Yellow lead iodide



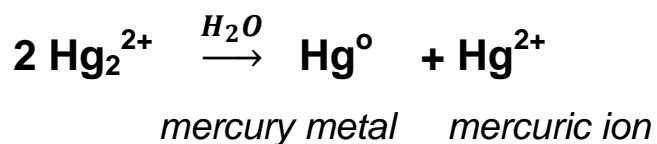
*soluble complex
lead tetraiodide*

Mercurous (I) ion, Hg_2^{2+}

Mercuric (II) ion, Hg^{2+}

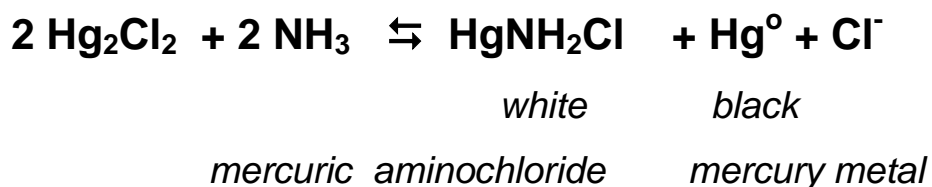
The mercurous ion is precipitated as chloride in the silver group; the mercuric ion is precipitated as sulphide in the copper-arsenic group. Each mercury atom has two (6s). The loss of two electrons by a mercury atom produces the mercuric ion (Hg^{2+}). The loss of one electron by a mercury atom gives a mercurous ion (Hg_2^{2+}) which is unique among ions in that it has a single (6s) electron in its outermost orbit. Two of these ions combine to form the ion ($^+\text{Hg}:\text{Hg}^+$) or simply Hg_2^{2+} , in which the two mercury atoms are bonded together by a pair of shared electrons (a covalent metal — metal bond).

The Hg_2^{2+} ion is found in a number of solid compounds. In aqueous solutions, its existence is limited to the pH region below about 3 to 4. At higher pH values, a disproportionation reaction with water or hydroxide ion takes place?



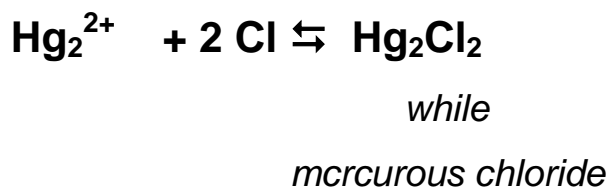
This also may called self oxidation-reduction reaction. Therefore precipitation reactions involving mercurous ion are complicated by disproportionation reactions yielding elemental mercury and mercuric compounds,

Example :

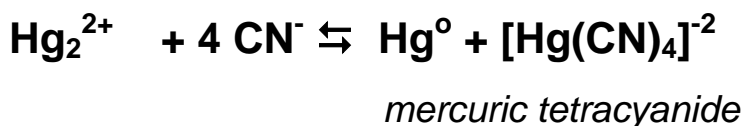


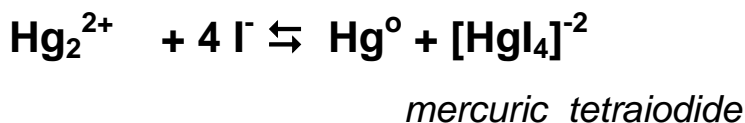
Reactions Important in the Separation and Identification of Mercurous (Hg_2^{2+})

1. Group Precipitation

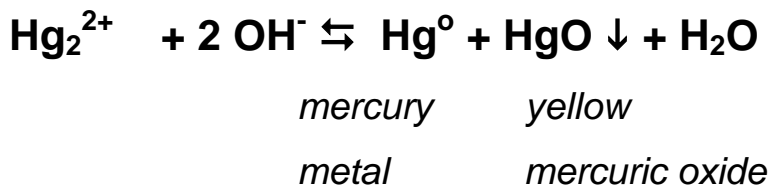


2. Complex formation

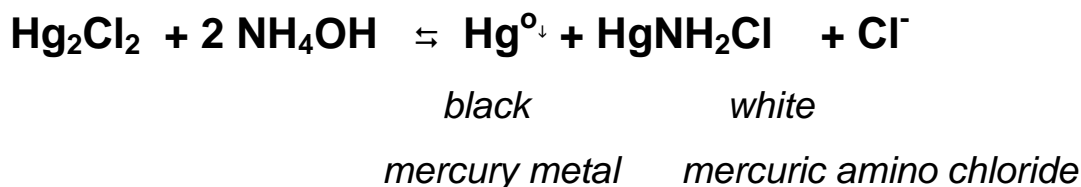




3. Reaction With NaOH (non amphoteric)



4. Confirmatory Test



- Dissolution of mercuric amino chloride and mercury metal in aqua regia (1 :3) of Conc. HNO₃ and Conc. HCl

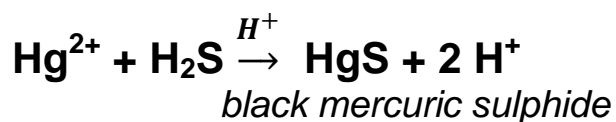


Then test for HgCl₂

Reactions Important in the Separation and Identification of Mercuric (Hg^{2+})

Mercury (II) sulfide (group II) is the least soluble sulfide. It is not soluble in either dilute nitric acid or hydrochloric acid. But dissolves in hot aqua regia with the formation of a chloro complex.

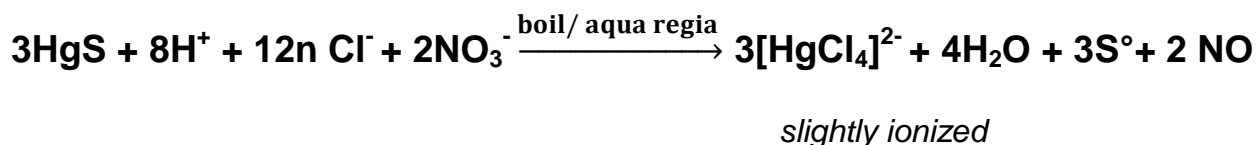
1. Group Precipitation



2. Dissolution by:

I. Aqua regia (1: 3) cone. HNO_3 : cone. HCl

Oxidation of S^{2-} and complex ion formation with mercuric



N.B.

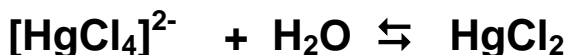
(a) We have to boil HgS with aqua regia nearly to dryness:

- To get rid of chlorine (Cl₂) (resulting from decomposition of excess aqua; regia) by heating otherwise it will oxidize SnCl₂ and so prevents the reduction of HgCl₂



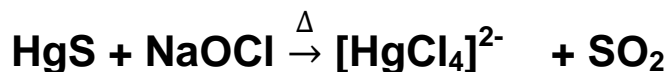
- if evaporation is continued to complete dryness mercury will be completely lost by volatilization.

(b) After boiling nearly to dryness, cool, dilute with water so decompose the HgCl₄²⁻ complex (weakly ionized)



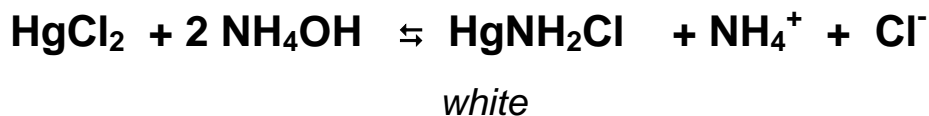
then test with SnCl₂, NH₄OH or KI

II. Hypochlorite reagent

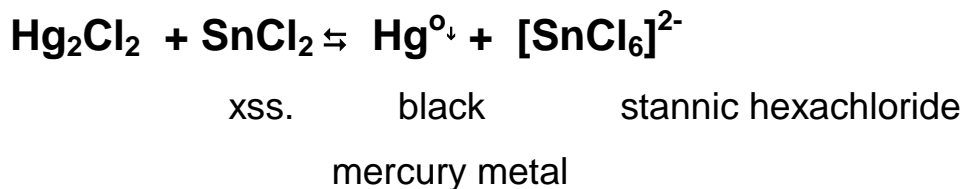
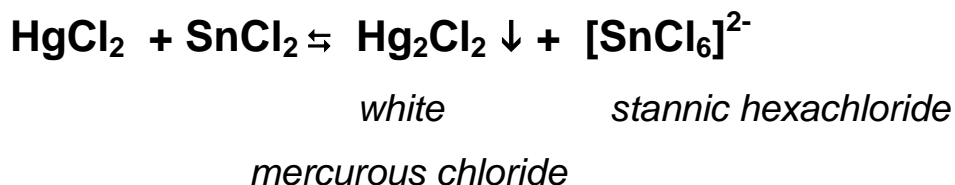


3. Confirmatory tests:

a) With ammonium hydroxide (NH₄OH)

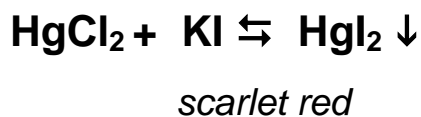


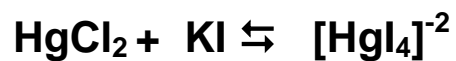
b) With stannous chloride reagent SnCl₂



it is an oxidation-reduction reaction.

c) With potassium iodide





xss

mercuric tetraiodide

soluble complex

- Differentiate between mercuric and mercurous.?

- How can you separate and identify mixture of $\text{Hg}_2^{2+}/\text{Hg}^{2+}$?