

**GOVERNMENT ARTS AND SCIENCE COLLEGE
KOMARAPALAYAM.**



**DEPARTMENT OF CHEMISTRY
III SEMESTER**

**GENERAL CHEMISTRY – III
NEW SYLLABUS
(PERIYAR UNIVERSITY, SALEM)**

**UNIT – I
MATERIALS**

HANDLED BY

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Unit - I

Transition Element and Qualitative Analysis

Transition Element

Titanium : Ti

Occurrence :

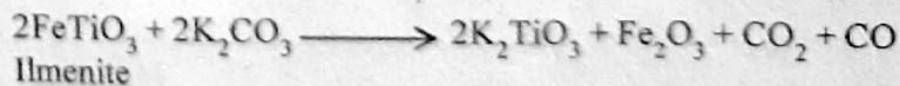
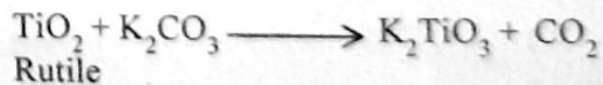
1. Oxide ores	a. Rutile	TiO ₂
	b. Brookite	TiO ₂
	c. Anatase	TiO ₂
2. Silicate ores	a. Sphene	CaTiSiO ₅
	b. Guarinite	CaTiSiO ₅
3. Titanate ores	a. Ilmenite.	FeTiO ₃
	b. Pervoskite	CaTiO ₃

Extraction

There are many methods for extracting titanium from its ores. The ores generally used are Rutile and Ilmenite.

1. Wohler's process :

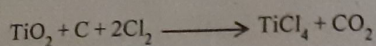
The finely powdered ore is fused with thrice the weight of K₂CO₃. The fused mass is cooled. The solid obtained is powdered and treated with dilute HF, potassium fluotitanate, K₂TiF₆ is got.



The potassium fluotitanate is boiled with water and cooled, Crystals of K₂TiF₆ separate.

The crystals of K₂TiF₆ are dissolved in boiling water and treated with NH₄OH when Ti(OH)₄ is precipitated. The precipitate obtained is washed, dried and ignited to get TiO₂. The oxide can not be directly used

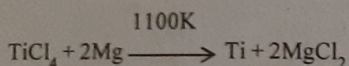
for the extraction of the metal. Therefore, it is first converted into TiCl_4 by heating a mixture of TiO_2 and carbon in a current of chlorine.



The metal Ti, extracted from TiCl_4 as described below.

i. Kroll process :

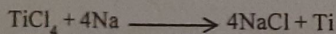
In this method TiCl_4 is reduced with magnesium in an inert argon atmosphere.



The product is washed in water to remove MgCl_2 . A spongy metal is got. It is melted in an electric arc under a high vacuum or in an atmosphere of inert gas (helium or argon) to get compact metal.

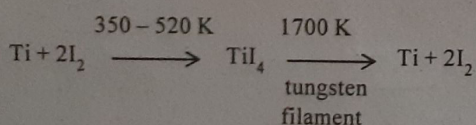
ii. Hunters method :

Titanium is obtained by heating titanium tetra chloride with metallic sodium in a steel bomb.



Refining :

It is purified by Van Arkel process. Titanium is heated with iodine when titanium tetraiodide is obtained. The tetraiodide is heated on a tungsten filament when it decomposes to give pure metal.



The metal is further purified by zone refining

Properties

Physical Properties

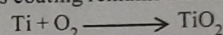
Metallic titanium has a silvery lustre and when polished resembles steel appearance. Amorphous form is a dark grey powder resembling iron

(reduced) in appearance. It is brittle at ordinary temperature but at low red heat it is readily malleable. The pure metal is very ductile. Its m.pt. and b. pt. are 1668°C and 3260°C . The fused metal is very hard and crystalline and scratches quartz.

Chemical Properties

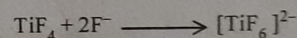
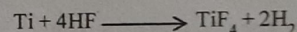
1. Action of air :

On exposure to air at ordinary temperature, titanium metal reacts with O_2 and N_2 of the air and forms a thin film (coating) of TiO_2 and TiN on the surface of the metal. This coating prevents the metal from corrosion. This coating remains stable in air upto 400°C .

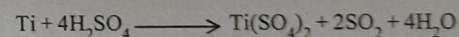
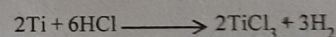


2. Action of conc. acids and alkalis :

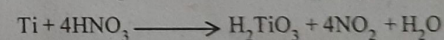
The metal remains passive towards the action of acids and alkalis. This behaviour is due to the formation of a protective film of TiO_2 on the surface of the metal. The metal dissolves in HF to give $[\text{TiF}_6]^{2-}$ ion.



The metal also dissolves in HCl and H_2SO_4 to give soluble salts.

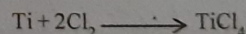


With HNO_3 , metalitic and (H_2TiO_3) is obtained.



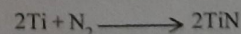
3. Action of halogens :

The metal readily combines with Cl_2 (at 350°C), Br_2 and I_2 to form the tetrahalides, TiX_4 .



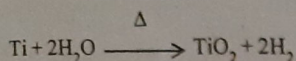
4. Combination with non - metals :

On being heated, the metal combines with H_2 , B, C and N_2 to produce TiH_2 , TiB , TiC and TiN . These are interstitial compounds and hard. These have refractory properties.

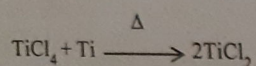


5. **Action on steam :**

Steam is decomposed by the metal

6. **Action on TiCl_4 :**

TiCl_4 is reduced to TiCl_2 when heated with Ti metal

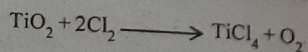
**Uses :**

1. Alloys of titanium are useful. Ferro titanium is used in steel industry. Titanium alloys are used for making filaments for vacuum tubes. This replaces costly platinum iridium alloy.
2. Used in photoelectric cells.
3. Titanium soaps impart special properties to paints and varnishes.
4. Titanium tetrachloride is used for smoke screens.
5. Titanium dioxide is useful in the manufacture of paints and pigments. Titanium compounds are also used for dyeing.
6. Titanous salts are used in volumetric analysis.
7. TiO_2 is used as a whitener in face powder, ceramics etc.

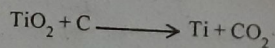
Important compounds1. **Oxides :**

Titanium dioxide, TiO_2 is the oxide of titanium. It is prepared from rutile. Finely powdered rutile is fused with Na_2CO_3 . The fused mass is dissolved in HF and the product is extracted with water to get K_2TiF_6 . It is treated with ammonium hydroxide to get TiO_2 precipitate.

Titanium dioxide is an amorphous white powder, yellow when hot. It reacts with chlorine to give titanium tetrachloride.



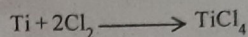
It is reduced by carbon to titanium at high temperatures.



It is very much useful as a pigment in paints varnishes. It is useful in glass industry, rubber industry and in cosmetics as a whitener.

2. **Halides**

Titanium tetrachloride, TiCl_4 is an important halide of titanium. It is prepared by passing chlorine over titanium heated to high temperature.



Titanium tetrachloride is a colourless fuming liquid. It is soluble in water. It is hydrolysed by steam to TiO_2 . It reacts with ammonia to give smoke screen.

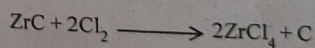
It is used for smoke screen. It is used as a starting material for the extraction of titanium.

Zirconium : Zr**Occurrence :**

1. Zircon : ZrSiO_4
2. Baddeleyite : ZrO_2

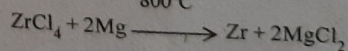
Extraction :

The ore is powdered and concentrated by gravity separation method. The concentrated ore is mixed with carbon and heated to a high temperature to form zirconium carbide. When ZrC is extracted with water and HCl pure ZrC is obtained. When it is heated with chlorine ZrCl_4 is formed.

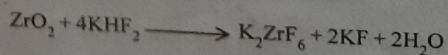


When zirconium tetra chloride is heated with magnesium at very high temperature of zirconium metal is obtained.

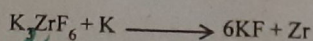
800°C

1. **From Baddeleyite, ZrO_2**

The ore is powdered and concentrated. The concentrated ore is fused with KHF_2 when fluozirconate is formed.



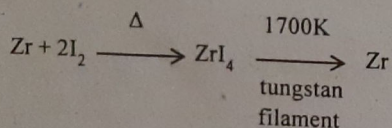
When it is boiled with water cooled and filtered K_2ZrF_6 crystals are formed. The dried K_2ZrF_6 when mixed with potassium and heated in a iron tube at low temperature gives zirconium metal



The metal is leached with dilute HCl then washed with ammonium chloride and finally washed with alcohol when Zr metal is obtained.

2. Preparation of pure metal (Van Arkel Method) :

Pure zirconium is obtained by heating impure zirconium with iodine when ZrI_4 is formed. When this compound is heated on tungsten filament, it decomposes to give pure metal.



Properties :

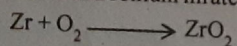
Physical Properties :

1. It is soft silver white metal m.p. is $1855^\circ C$.
2. It exists in crystalline and amorphous forms.

Chemical Properties :

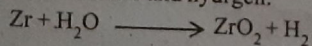
1. With air :

When zirconium is heated in air at high temperature to form zirconium dioxide and zirconium nitrate.

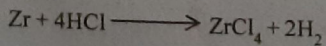


2. With water :

It does not react with cold water. But it decomposes steam to form zirconium dioxide and hydrogen.

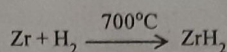


3. It reacts with dilute HCl to form $ZnCl_4$.



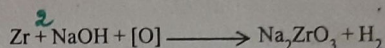
It dissolves in HF and aqua regia.

4. It reacts with hydrogen at $700^\circ C$ to form ZrH_2 .



5. With alkalis :

It reacts with alkalis only under high temperature to form the alkali zirconates.



6. Reaction with metals and non metals :

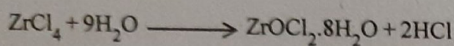
It reacts with Cu, Fe and Al to form alloys. At high temperature it reacts with halogens, sulphur, boron, silicon, carbon, phosphorus and nitrogen giving the corresponding compounds.

Uses of Zirconium :

1. Zirconium steel is a corrosion resistance alloy and it can also withstand wear and tear.
2. Zirconium chloride is used to prepare fire bricks which can withstand very high temperatures.
3. It is also used in nuclear reactors.
4. It is used as a catalyst in the synthesis of ammonia and hydrogenation reactions.
5. It is also used in radio transmitters and flash bulbs.
6. The glasses of Zirconium oxide are not affected by chemicals and has a very minimum expansion on heating.
7. It is also used to prepare precious stones and gems. It is obtained in various colours like bluish green, yellowish brown and red orange. Colourless zircon has 86% of the glittering property of a pure diamond.

Compounds :**Halides :**

ZrCl₄ is a white solid, prepared by chlorination of heated Zr or a mixture of ZrO₂ and charcoal. It fumes in moist air and it quickly undergoes hydrolysis by H₂O.



ZrCl₄ is monomeric and tetrahedral in the vapour but the solid consists of zigzag chains of ZrCl₆ octahedra.

It gives six - coordinate species by reaction with donors such as ethers, esters, POCl₃ and Cl⁻ ion.

ZrF₄ is a white crystalline solid which sublimes at 903°C and unlike other halides, is insoluble in donor solvents. It possesses 8 - coordinate structure with square antiprisms joined by sharing fluorines.

Zr⁴⁺ is relatively large, highly charged and spherical and with d⁰ configuration, it does not have stereochemical preferences. Hence Zr(IV) compounds show high coordination numbers and a variety of coordination polyhedra. Thus Li₂ZrF₆ and CuZrF₆·4H₂O contain octahedral ZrF₆²⁻ ion, Cu₂ZrF₈·12H₂O contains square antiprisms with ZrF₈ unit.

Oxides :

ZrO₂·nH₂O is formed as a white gelatinous precipitate by treatment of Zr(IV) solutions with alkali. This precipitate gives on strong heating a hard white insoluble ZrO₂. It has high m.p. 2700°C and is resistant to the attack of acids and alkalis. It possesses excellent mechanical properties - it is used for crucible and furnace cores.

ZrO₂ in its monoclinic (baddeleyite) form has a structure in which the metal atoms are 7 coordinate.

When ZrO₂ is dissolved in molten KOH and the excess solvent evaporated at 1050°C the crystalline compounds K₂ZrO₅ and K₂ZrO₃ are obtained. K₂ZrO₅ contains ZrO₆ octahedra sharing faces to form chains.

Analytical aspects :

Zr is readily detected in traces by its reaction with Alizarin S to produce a red lake or colour.

It is generally estimated as ZrO₂ after ignition of the brown precipitate with cupferron.

Vanadium : V**Occurrence**

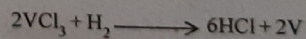
It is not found free in nature. This important ores are

1. Carnotite : K₂O, 2V₂O₃, V₂O₅·3H₂O
2. Patronite : V₂S₅
3. Vanadinite : 3Pb₃(VO₄)₂PbCl₂

Extraction**1. From carnotite**

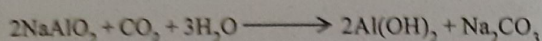
The ore is powdered and leached with concentrated nitric acid at 100°C. The solution is filtered and the insoluble impurities are removed. The solution is neutralised with NaOH and treated with barium chloride and H₂SO₄. Radium is precipitated as radium sulphate along with barium sulphate. The precipitate is filtered. The filtrate is treated with sodium carbonate solution. Now iron, calcium and aluminium are precipitated. It is filtered. The filtrate contains sodium uranyl carbonate and sodium vanadate. It is neutralised with HNO₃ and treated with NaOH. Uranium is precipitated as sodium uranate. It is filtered. The filtrate is treated with nitric acid and ferrous sulphate. Vanadium is precipitated as iron vanadate.

Iron vanadate is treated with chlorine, when vanadium tetrachloride is formed as a dark red liquid. This is freed from ferric chloride by distillation. Vanadium chloride is reduced by hydrogen at 600°C

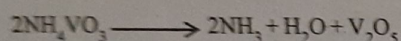
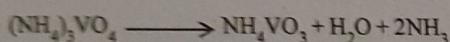
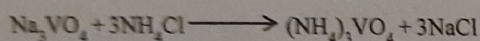
**2. From patronite**

The ore is concentrated and roasted at low temperature. Moisture and volatile impurities are removed. Then it is roasted with water, sodium

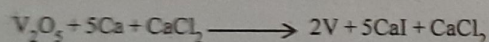
vanadate goes into solution. Sodium aluminate is present as impurity in the solution. It is removed as hydroxide by passing carbon dioxide through the solution.



The filtrate is treated with sodium hydroxide. Sodium metavanadate $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$ crystallises out leaving behind sodium silicate, molybdate and tungstate. The sodium meta vanadate solution is treated with ammonium chloride to get insoluble ammonium meta vanadate, NH_4VO_3 . The ammonium meta vanadate solid is heated to get vanadium pentoxide.



Vanadium pentoxide is reduced with a mixture of calcium and calcium chloride in a sealed tube. A little sodium or potassium is added to remove the last traces of air and moisture.



Properties of vanadium metal

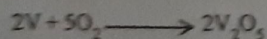
Physical properties :

Vanadium is a greyish white infusible metal while in the compact state it is silvery white. It is a hard, but light metal a good conductor of electricity but allows the current to flow in one direction. It is paramagnetic.

Chemical properties :

1. Reaction with air :

It is unreactive at room temperature. Thus on heating in air it gets oxidized to give red colour vanadium pentoxide.

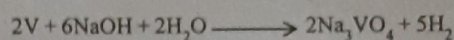


2. Reaction with acids :

Vanadium does not react with hydrochloric acid. Hot con. H_2SO_4 acid react with vanadium gives SO_2 , with hydrochloric acid gives hydrogen.

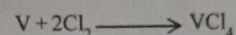
3. Reaction with Alkalis :

Vanadium does not react with alkalis, when it is fused with NaOH gives sodium vanadate and hydrogen released.



4. Reaction with halogens :

Vanadium heated with excess of dry chlorine, vanadium tetra chloride is formed. It is strong violet in colour.



5. Reaction with metals and non - metals :

Vanadium react with Cu, Fe, Ni and Al gives its metallic compounds. It precipitate the metals like Au, Ag and Pt from its salt solutions. It react with non metals like nitrogen, carbon, sulphur and silicon forming its compounds.

Uses :

1. Vanadium pentoxide is used as a catalyst in oxidation reactions.
2. Vanadium is useful in the metallurgy.
3. Vanadium carbide is used in the manufacture of incandescent lamps.
4. Vanadates are used in photography as developers and sensitizers.
5. Vanadium compounds are used as mordants in dyeing.
6. Vanadium compounds with their wide variety of colours have gained importance in paint and pigment fields.
7. Vanadium salts are poisonous when taken in large amounts. Vanadium salts are used as fungicides and insecticides.

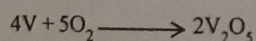
Important compounds

Vanadium exhibits +2, +3, +4 and +5 oxidation states in its compounds. They show different colours at different oxidation states. +2 state shows violet colour. +4 state shows blue or green colour. +5 state compounds are usually acidic and they are deep red in colour.

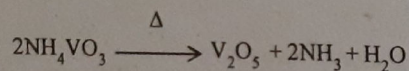
1. Oxides

Vanadium Pentoxide, V_2O_5

It is prepared by heating the metal or the lower oxide in air for a long time.



It is also obtained by heating ammonium meta vanadate.



It is a very stable compound. It occurs in the allotropic forms ;

1. a reddish yellow ochrous powder.
2. a pale yellow powder and
3. a dark brownish red needle crystals.

It is tasteless but poisonous. It is not volatile even at red heat. It is sparingly soluble in water. It is a very good conductor of electricity. With alkalis it forms a series of vanadates analogous to phosphates. e.g., ortho vanadate, Na_3VO_4 , meta vanadate, $NaVO_3$ and pyrovanadate, $Na_4V_2O_7$. V_2O_5 undergoes reversible dissociation at about 970 – 1400K. This may be responsible for the catalytic properties.

Vanadium pentoxide is used as a catalyst in the manufacture of sulphuric acid.

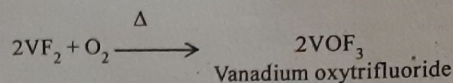
2. Halides

Fluorides :

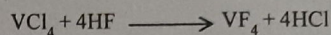
Three fluorides of vanadium are known. They are

- i. Vanadium trifluoride, $VF_3 \cdot 3H_2O$
- ii. Vanadium tetra fluoride, VF_4 and
- iii. Vanadium penta - fluoride, VF_5 .

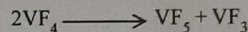
Vanadium trifluoride is obtained by dissolving vanadium trioxide in hydrofluoric acid. When heated in air, it gives vanadium oxytrifluoride.



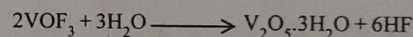
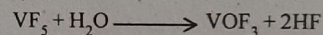
Vanadium tetrafluoride is obtained by the action of anhydrous hydrogen fluoride on vanadium tetrachloride at low temperature.



On heating, it disproportionates to trifluoride and pentafluoride.



Vanadium pentafluoride is obtained by heating vanadium tetrafluoride, VF_5 is extremely sensitive to moisture. It is hydrolysed to vanadium oxytrifluoride and then to the hydrated pentoxide.



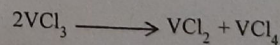
Chlorides :

Four chlorides of vanadium are known. They are

- i. Vanadium dichloride, VCl_2
- ii. Vanadium trichloride, VCl_3
- iii. Vanadium tetrachloride and
- iv. Vanadium oxytrichloride.

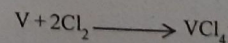
Vanadium pentachloride is not known.

Vanadium dichloride is obtained by heating vanadium trichloride in a current of nitrogen at 1075K

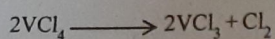


Vanadium trichloride is got by the action of HCl gas on vanadium.

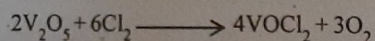
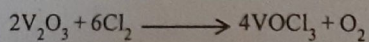
Vanadium tetrachloride is got by passing chlorine over heated vanadium



It is an unstable compound. It decomposes even at room temperature to give trichloride and chlorine.



Vanadium oxytrichloride is prepared by passing dry chlorine over heated V_2O_3 or V_2O_5 .



Molybdenum : Mo

Occurrence

Molybdenum never occurs free in nature. It occurs in the following ores.

1. Molybdenite : MoS_2
2. Wulfenite : PbMoO_4
3. Molybdite : $\text{FeO}_3 \cdot \text{MoO}_3 \cdot \text{H}_2\text{O}$
4. Hremannite : $\text{MoO}_2 \cdot 4\text{MoO}_2$

Extraction

Molybdenum is commonly extracted from molybdenite

1. Concentration of the ore :

The ore molybdenite is crushed into fine powder. The crushed ore is concentrated by froth flotation process.

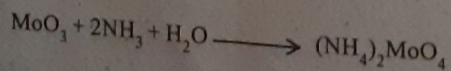
2. Roasting :

The crushed and concentrated ore of molybdenite is heated strongly in a current of air. Molybdenum trioxide MoO_3 is formed.

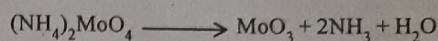


3. Purification of MoO_3 :

Impure molybdenum trioxide is dissolved in ammonia to get ammonium molybdate.

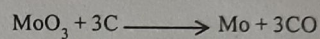
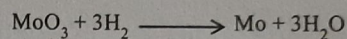


Ammonium molybdate is purified by recrystallisation. Crystals of ammonium molybdate are heated to decompose it to form pure molybdenum trioxide.

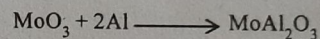


4. Metallurgy :

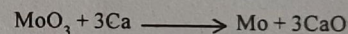
Metallic molybdenum can be obtained in several ways from MoO_3 . It may be reduced with hydrogen or carbon.



Alumino thermic reduction of MoO_3 gives almost 99% pure metal.



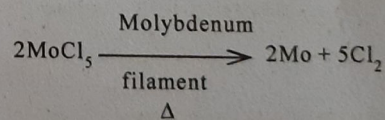
99% pure metal can be prepared by the reduction of the oxide with calcium shaving or zinc dust.



In all these methods Mo is obtained in the form of powder. The metal is obtained in compact form by pressing it at about 2600°C (near its m.pt.) This heating is done in an atmosphere of hydrogen.

Preparation of pure molybdenum metal

Thermal decomposition of molybdenum pentachloride on an electrically heated molybdenum filament gives pure metal.



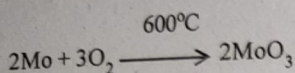
Properties :

Physical properties :

1. Pure molybdenum is a silver like white metal.
2. It is easily malleable and ductile.
3. Pure metal possesses metallic lusture.

Chemical properties :**1. Reaction in air :**

At room temperature molybdenum is stable, when heated at 600°C. It burns in air giving its oxide.

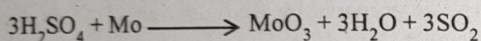
**2. Reaction with water :**

Pure metal is not affected by water. It decomposes steam at 700°C.

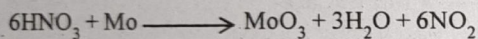
3. Reaction with acids :

Molybdenum does not react with hydrofluoric acids and hydrochloric acids.

It does not react with dil. H_2SO_4 . Hot. con. H_2SO_4 react with molybdenum evolving SO_2 gas.



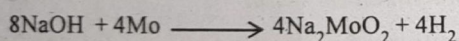
Hot dil. HNO_3 dissolves molybdenum to give nitrogen peroxide.



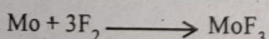
Molybdenum dissolves in aquaregia giving a blue coloured solution.

4. Reaction with Alkalis :

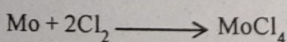
Molybdenum reacts with the molten alkali forming alkali molybdates.

**5. Reaction with halogens :**

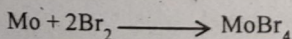
At room temperature molybdenum react with fluorine giving vaporable fluoride.



Molybdenum react with chlorine at low temperature to form MoCl_4 .



Bromine reacts at a high temperature.



It does not react with iodine even at 800°C.

6. Reaction with metals and non - metals :

It reacts with iron and nickel to form alloys, it also react with sulphur, phosphorus, boron and carbon to form the respective compounds.

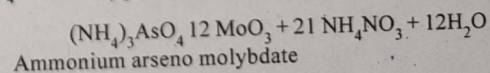
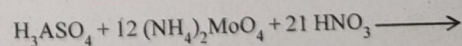
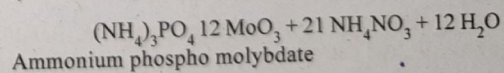
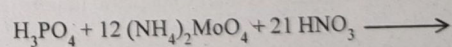
Uses :

1. It is used as an anticathode in X-rays tubes.
2. Molybdenum and tungsten form thermocouple for high temperature measurements.
3. Used in the manufacture of standard weights.
4. Used as a promoter in the Haber's process for the manufacture of ammonia.
5. Molybdenum steels are used for making high speed lathe tools and rifle barrel.
6. It is used as a substitute for platinum for electric resistance in resistance furnaces.
7. Sodium molybdate is used in ceramics for colouring pottery and porcelain, in the textile industry for dyeing silk and wool.
8. It is used as a mordant.

Important Compounds**1. Ammonium Molybdate, $(\text{NH}_4)_2\text{MoO}_4$**

Ammonium molybdate is obtained from molybdenite mineral. The mineral is first oxidised to trioxide. The trioxide is boiled with ammonium hydroxide solution to give ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$. This solution on evaporation gives crystals of para molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ are formed.

It is a yellow crystalline substance. It is soluble in water, It forms a yellow precipitate with phosphate and arsenate.



Uses :

It is used in the laboratory for the identification and determination of phosphate and arsenate.

2. Molybdenum blue

When an acidified solution of a molybdate or molybdic acid is treated with reducing agents like SO_2 , H_2S , HI , NH_2 , NH_2 or glucose, an intense blue colouration is obtained due to the formation of a mostly colloidal substance. This is called molybdenum blue.

It is a blue powder, very soluble in water. It resembles indigo in appearance. Molybdenum blue has varying composition from Mo_8O_{23} to Mo_9O_{26} . It is amorphous towards X - rays.

Tungsten : W**Occurrence**

Tungsten is also known as wolfram. It is not found native. In the combined state it occurs in the following ores.

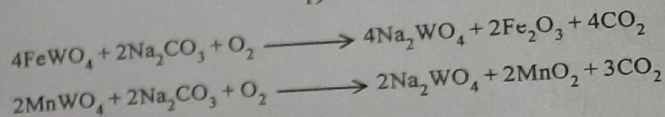
1. Wolframite : FeWO_4 and MnWO_4
2. Wolfram ochre or Tungstate : WO_3
3. Scheelite : CaWO_4
4. Hubnerite : MnWO_4

Extraction**1. Concentration :**

The wolframite ore is crushed to a fine powder. It is concentrated by electromagnetic separation since the ore contains magnetic impurities.

2. Roasting :

The crushed ore is roasted with sodium carbonate. Soluble sodium tungstate is formed. Iron and manganese get oxidised to their respective oxides.

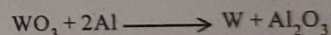
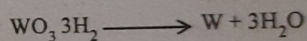
**3. Conversion to WO_3 :**

The roasted mass is then extracted with hot water. Sodium tungstate is soluble in water and hence it dissolves. Oxides of iron and manganese are removed by filtration. The filtrate containing sodium tungstate is treated with acid. Tungsten trioxide, WO_3 is precipitated. WO_3 is washed with water and then dried.

4. Reduction :

Tungsten may be obtained in metallic state by several methods.

WO_3 can be reduced with hydrogen, carbon, zinc, aluminium, magnesium and silicon.

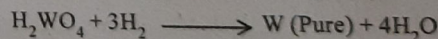


A pure variety of tungsten in powder form is obtained by heating tungsten oxide in quartz tubes in a carefully controlled furnace in a current of hydrogen.

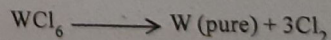
Preparation of pure tungsten :

Pure tungsten metal can be obtained

- i. by heating the tungstic acid, H_2WO_4 in a current of H_2 .



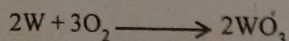
- ii. by thermal decomposition of WCl_6 vapour on a tungsten electric arc.

**Properties****Physical properties :**

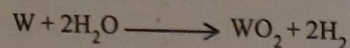
1. Pure tungsten resembles platinum possessing steel lustre.
2. The powder form is hard and brittle, but the crystalline form is malleable and ductile.
3. It can withstand high pressure and stress and strain.

Chemical properties :**1. Reaction with air :**

At high temperature it reacts with air forming its trioxides.

**2. Reaction with water :**

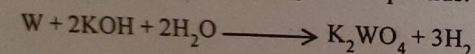
Red hot tungsten decomposes steam into hydrogen.

**3. Reaction with acids :**

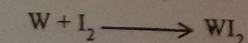
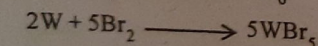
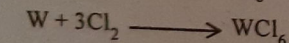
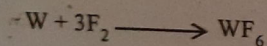
It does not easily react with even hot concentrated acids. It dissolves in aquaregia.

4. Reaction with alkalis :

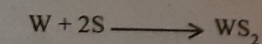
It reacts with alkalis forming its compounds.

**5. Reaction with halogens :**

Tungsten reacts with halogens at red hot conditions forming the halides.

**6. Reaction with non metals :**

It does not react with nitrogen. It reacts with sulphur and phosphorus in their vapour state.

**Uses :**

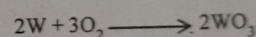
1. It is mainly used for preparing special steels and filaments of electric lamps, pen points and strings of musical instruments.
2. It is used as an anticathode in X - ray tubes.
3. It is used in making surgical instruments, gramophone needles, voltage regulators, contact points etc.

4. Sodium tungstate is used as a mordant in dyeing.
5. WO_3 is used as a yellow pigment while lead tungstate is used as a substitute for white lead.
6. Tungsten - molybdenum thermo - couples are used for high temperature work.
7. Lead - tungsten alloy finds use in making bullets and shots.
8. Oxides of tungsten are used in ceramics to impart different shades in glass and porcelain.
9. Tungsten has been tried as a catalyst for many reactions.

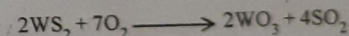
Important compounds**1. Tungsten Trioxide, WO_3**

It is prepared by any of the following methods.

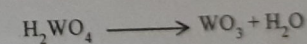
- i. By heating tungsten wire in oxygen at $530^\circ C$



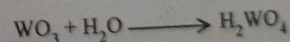
- ii. By roasting tungsten sulphide in a current of air.



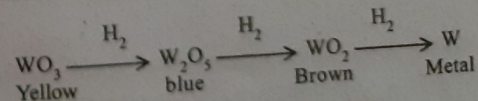
- iii. By igniting the tungstic acid.



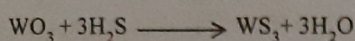
It is a bright yellow powder which changes orange when hot. It is insoluble in water but the hydrated form is soluble in water to give tungstic acid.



Hydrogen reduces the trioxide successively to blue oxide, a brown oxide and then the metal.



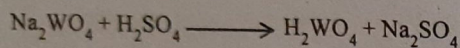
When heated with H_2S or CS_2 it forms sulphide.



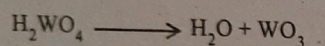
WO_3 is used as a mordant in dyeing. It is used in colouring glass ware and porcelain. It is also used as a pigment in oil and water colours.

2. Tungstic acid, H_2WO_4

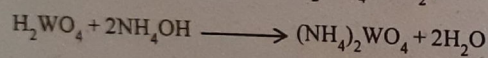
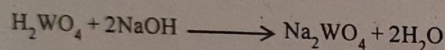
Tungstic acid is prepared by treating sodium tungstate or ammonium tungstate with hot H_2SO_4



Tungstic acid is soluble in hot water. On heating it gives the trioxide.



It forms tungstates with alkalis.



The composition of various tungstic acids are :

Meta tungstic acid : WO_3H_2O or H_2WO_4

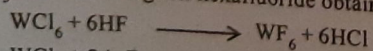
Para tungstic acid : $WO_3 \cdot 2H_2O$ or H_4WO_5

Ortho tungstic acid : $WO_3 \cdot 3H_2O$ or H_6WO_6

It is used in ceramic industries. It is also used in making pigments.

3. Tungsten Hexafluoride, WF_6

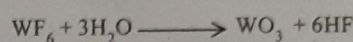
Tungsten hexachloride is distilled with anhydrous HF or AsF_3 or SbF_3 at $90^\circ C$. Tungsten hexafluoride obtained is cooled.



It is also obtained by the direct combination of fluorine and tungsten.



It is a colourless gas. It is the heaviest of all known gases. It is hydrolysed by water to give WO_3 .



It corrodes glass.

- It is quick. It takes only 45 minutes to treat one lot.

Platinum : Pt

Occurrence :

Platinum occurs native in nature in the form of alloys.

Important ores :

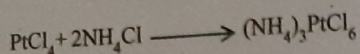
- Sperrylite : $PtAs_2$
- Cooperite : $Pt(AsS)_2$
- Braggite : $(Pt, Pd, Ni)S$

Extraction :

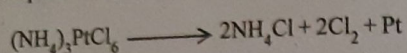
Platinum is extracted from the native ore. The ore is first finely crushed. It is washed in a powerful current of water. The residue contains the precious metals Ag, Pb, Os, Au, Rh, Pt, Ru and Ir as found in the original ore.

Gold is removed by amalgamation process. The rest of the ore is digested with aqua - regia. It dissolves all the precious platinum metals forming chlorides except osmium. Osmium is separated. The solution containing chlorides of the metals of the platinum family is evaporated to dryness and the residue is heated to $175^\circ C$. Palladium and rhodium tetrachlorides, are thus converted into the lower chlorides, $PdCl_2$ and $RhCl_3$. These two are insoluble in water while platinum tetrachloride and iridium tetrachloride are soluble. So this mixture is treated with water. Platinum tetrachloride and iridium tetrachloride pass into solution.

The solution is acidified and ammonium chloride is added a double salt of platinum $(NH_4)_3PtCl_6$ is formed. This gets precipitated. Iridium tetrachloride remains in solution.



The precipitate of ammonium chloroplatinate is ignited when it decomposes to give spongy platinum.



The spongy platinum is heated to redness and hammered to get the metal in the compact form.

Properties

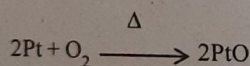
Physical Properties

Platinum is a lustrous bluish white metal. When pure, it is extremely ductile. It is highly malleable. Platinum wires and foils can be sealed into glass without cracking.

Chemical Properties :

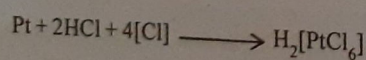
1. With oxygen :

At ordinary temperature platinum is resistant to oxidation. It combines with oxygen at high temperature and pressure to give the oxide PtO.



2. With acids :

Pure platinum is not attacked even by hot concentrated hydrochloric acid, nitric acid and sulphuric acid. If the metal is impure, it slightly reacts with sulphuric acid. It is dissolved by aqua - regia forming chloroplatinic acid, $\text{H}_2[\text{PtCl}_6]$.



3. With alkalis :

Platinum is commonly considered as an inert element. But it is attacked by fused alkalis.

4. With halogens :

It combines with fluorine and chlorine at red heat. With fluorine it gives platinum tetrafluoride, PtF_4 and with chlorine it gives platinum dichloride, PtCl_2 .

5. With other non - metals :

In finely divided state, It absorbs large quantities of hydrogen. Carbon phosphorus and arsenic attack platinum.

6. With metals :

It alloys with a number of metals like Sn, Pb, etc.

Uses :

1. Since platinum is almost inert, it is used in jewellery.
2. Since it is inert to chemicals, it is used for making crucibles, dishes etc.
3. It is used as electrodes in various electrolytic processes.
4. It is used as an important catalyst in the form of platinised asbestos.
5. Platinum salts are used in photography for the production of permanent prints.
6. Platinum is used for plating fancy and other presentation articles.
7. Platinum alloys serve as furnace windings in industrial electric furnaces. The alloys withstand a temperature of 1200°C .
8. Platinum wire is used for the oxidation of methyl alcohol to formaldehyde.
9. The alloy of platinum and iridium is used for standard weights and measures.
10. It is used to make dental plates and pins.

Compound of Platinum

Platinum chiefly forms two series of compounds - platinous and platinic corresponding to +2 and +4 oxidation states of platinum respectively.

Platinous compounds (Pt^{2+})

These compounds may be of the following types :

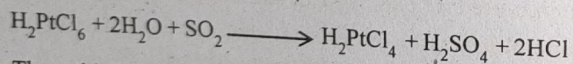
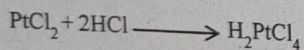
- i. Simple compounds e.g., PtCl_2 , PtI_2 .
- ii. Complex compounds. These are of the following types.
 - a. platinous amines e.g., $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
 - b. Tetrachloro complexes e.g., $\text{H}_2[\text{PtCl}_4]$, $\text{K}_2[\text{PtCl}_4]$,
 - c. Tetracyano complex, e.g., $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$

Most of the Pt(+2) complexes are four co-ordinated. They are diamagnetic with dsp^2 hybridisation and have square planar geometry. These are quite inert.

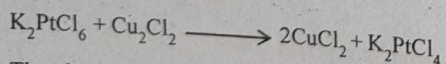
Here we shall discuss $\text{H}_2[\text{PtCl}_4]$ and $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ in which Pt is in +2 oxidation state.

1. **Hydrogen tetrachloro platinate (II) or tetra chloroplatinous acid, $\text{H}_2[\text{PtCl}_4]$:**

In this complex compound Pt is in +2 oxidation state. Here the co-ordination number of Pt is 4. It is obtained by dissolving PtCl_2 in HCl or by the reduction of H_2PtCl_6 with SO_2 .



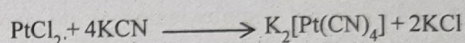
The acid does not crystallise but forms a dark brown amorphous solid on evaporation. Its salts are called chloroplatinites. Potassium chloroplatinite, K_2PtCl_4 may be better prepared by reducing chloroplatinate, K_2PtCl_6 by cuprous chloride.



The salt forms dark red crystals and is used in platinum printing in photography. The corresponding ammonium, silver or lead salts are also known.

2. **Potassium tetracyano platinate (II) or potassium platinocyanide, $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$**

It is also a complex compound of Pt in +2 oxidation state. It is obtained as yellow needles by mixing solutions of PtCl_2 and KCN in proper proportions and evaporating the solution to crystallisation.



Pt (+4) Compounds : Platinic compounds

These compounds may be of the following types :

- i. Simple compounds PtCl_4 .
- ii. Complex compounds. These may be
 - a. Platinic amines e.g., $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$
 - b. Hexachloro complexes e.g., $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$

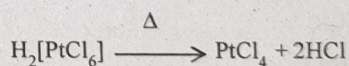
Now let us discuss some important compounds of platinum (+4).

3. **Platinum (IV) chloride or platinic chloride, PtCl_4**

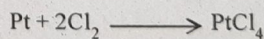
In this compound Pt is in +4 oxidation state.

Preparation of PtCl_4 :

- i. by heating $\text{H}_4[\text{PtCl}_6]$ at 370°C in a current of Cl_2 or at 165°C in H_2 .



- ii. by the action of Cl_2 on Pt - metal at $200 - 300^\circ\text{C}$.



Properties :

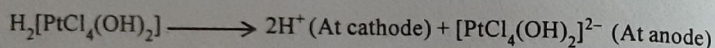
- i. It forms reddish - brown slightly hygroscopic crystalline mass.

ii. *Hydrolysis :*

It dissolves in water, giving yellowish - red solution which is strongly acidic. The acidic nature of the solution is due to the formation of a complex acid, $H_2[PtCl_4(OH)_2]$.



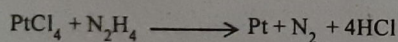
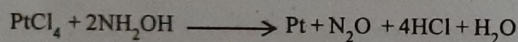
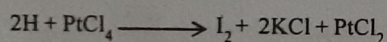
On electrolysis, this acid gives the complex anion on the anode showing platinum is discharged at the anode as a part of $[PtCl_4(OH)_2]^{2-}$ ion.



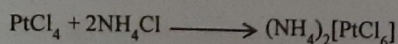
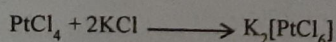
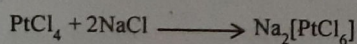
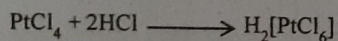
iii. *Oxidising Property :*

Reduction of $PtCl_4$:

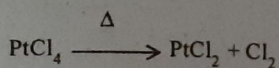
$PtCl_4$ oxidises KI to iodine and is itself reduced to $PtCl_2$. Thus $PtCl_4$ liberates I_2 from KI solution.



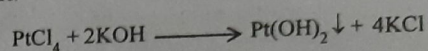
iv. Action of HCl and alkali metal halides. Complexes of $[PtX_6]^{2-}$ type. ($X = Cl, Br, I$) are obtained.



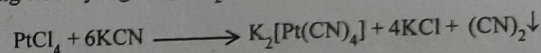
v. Action of heat. When heated at 853K, $PtCl_2$ is obtained.



vi. Action of KOH, $Pt(OH)_2$ gets precipitated when $PtCl_4$ reacts with KOH.



vii. Action of KCN. Potassium tetra cyano platinate (II), $K_2[Pt(CN)_4]$ along with cynogen, $(CN)_2$ are produced.



Uses :

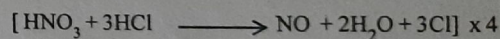
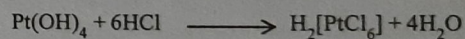
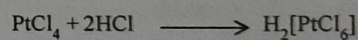
$PtCl_4$ is used for the preparation of $H_2[PtCl_6]$ and $K_2[PtCl_6]$. Both these compounds are very useful compounds.

4. Hydrogen hexachloro platinate (IV) or hexachloro platonic acid, $H_2[PtCl_6]$

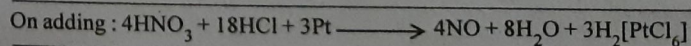
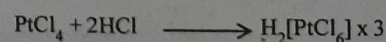
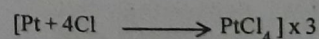
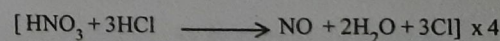
Preparation :

It is prepared

i. by the action HCl on $PtCl_4$ or $Pt(OH)_4$



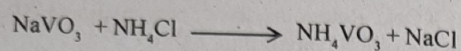
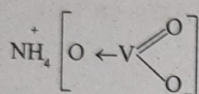
ii. by the action of aqua regio ($HNO_3 + 3HCl$) on pure platinum metal.



The solution is evaporated with HCl till HNO_3 is completely removed from the reaction mixture. On cooling, the red - brown crystals of $H_2PtCl_6 \cdot 6H_2O$ are left behind.

Ammonium Meta Vanadate, NH_4VO_3

Sodium meta vanadate react with ammonium chloride to give ammonium meta vanadate.

**Structure****Tungsten bronzes, M_xWO_3**

These are the non-stoichiometric compounds having a general formula, M_xWO_3 ($\text{M} = \text{Li}, \text{Na}, \text{K}$ etc. and $x < 1$). These are also called metal tungstate bronzes. They are obtained by reducing alkali metal or alkaline earth metal tungstates by H_2 , metallic Na or metallic W or -electrically.

Properties

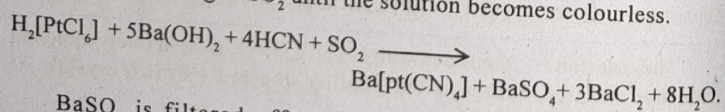
- i. These are insoluble in water, chemically inert.
- ii. They have metallic lustre and are conductors of electricity.
- iii. These are highly coloured. Their colour depends on the value of x as shown below:

$x =$	0.93	0.64	0.46	0.32
Colour =	Gold yellow	Orange	Red-violet	Blue-violet

Uses : Tungsten bronzes are used as pigments.

Barium platinocyanide $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$

It is prepared by warming $\text{H}_2[\text{PtCl}_6]$ solution with baryta. water. $\text{Ba}(\text{OH})_2$ and passing in SO_2 until the solution becomes colourless.



BaSO_4 is filtered off and the filtrate is crystallised to get $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$. It is a lemon-yellow powder which is soluble in It is used for fluorescent screens in X-ray work.

PRINCIPLES OF QUALITATIVE ANALYSIS**Semi micro techniques****Principles :**

Qualitative analysis is concerned with finding out or identifying the constituents in a unknown substance. Qualitative analysis can be carried out on various scales. In **macro analysis** the quantity of the substance used is 0.5 – 1 g. and the volume of solution taken for the analysis is about 20 ml. In **semi - micro analysis**, the quantity of the substance used is about 0.05 g and the volume of the solution used in a about 1 ml. For **micro analysis** the quantity of the substance and the volume of the solution used are about on hundredth of that used in a macro analysis. There is not sharp line of demarcation between semi - macro and micro analysis. The former is called centigram analysis and the latter milligram analysis.

It should be noted that only the scale of the operation has been reduced ; the concentrations of the ions remain unchanged. There are advantages in adopting the semi - micro technique.

Advantages of semi-micro techniques :

1. Reduced consumption of chemicals.
2. The greater speed of the analysis, due to working with smaller quantities of materials and saving of time in carrying out the various standard operations like filtration, washing, evaporation, saturation with H_2S etc.
3. Increased sharpness of separation.
4. The amount of H_2S used is considerably reduced.
5. Much space is saved both on the reagent shelves and in the lockers provided to keep the apparatus.
6. The desirability of securing a training in the manipulation of small amounts of materials.

Apparatus : In semi - micro analysis since the quantity of the substance taken is only small we need special small apparatus called semi - micro apparatus. The reactions involved are exactly the same as in macro method.

Examples :

1. **Test tubes and centrifuge tubes :**

Small pyrex test tubes (usually 75 x 10mm, 4 ml. Sometimes 100 x 12 mm, 8 ml) are used for reactions which do not require boiling. When a precipitate is to be separated by centrifuging, a test tube with a tapered bottom, known as a centrifuge tube is used. For rapid concentration of a solution, the semi - micro boiling tube (60 x 25 mm. Pyrex) is used.

2. **Droppers or dropper pipettes :**

Droppers are of two types. They are

1. Reagent dropper
2. Capillary dropper

They can be conveniently made in laboratories with pyrex glass tubes of 7 mm bore. They are used to draw off supernatant liquid after centrifuging and for transferring liquids from one vessel to another .

3. **Reagent bottles :**

Strong acids, bromine and other corrosive liquids can be kept in T.K. type dropping bottles. All other non corrosive reagents can be kept in 100 ml bottles provided with one holed stoppers through which the dropper pipette is introduced.

4. **The centrifuge :**

The separation of a precipitate from a supernatant liquid is carried out using a centrifuge. The tube and its contents, and a similar tube containing an equal volume of water are placed in diagonally opposite buckets of the centrifuge and the cover is placed in position. Upon rotational for a short time and after allowing buckets to come to rest and removing the cover, it will be found that the precipitate has separated at the bottom of the tube. The operation (centrifugation) replaces filtration.

The supernatant liquid can be removed by means of a capillary dropper. The clear liquid is called the centrifugate. The advantages of centrifugation are ;

- i. Speed
- ii. Precipitates from corrosive liquids which cannot be filtered through filter paper can be made to separate.
- iii. Even small amount of precipitate can be made to settle and
- iv. The washing of the precipitate can be carried out rapidly and efficiently.

5. **Heating block :**

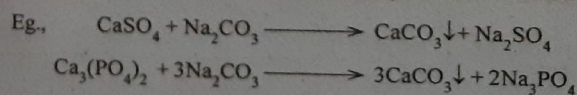
It is inconvenient to heat the semi - micro tubes over a free flame. For this, an aluminium heating block can be used. On the top face several holes of sufficient depth and diameter are drilled to accommodate the semi - micro test tubes, boiling tubes, beakers or crucibles. A cylinder of tin plate is slipped over the block to serve as flame guard.

6. **Semi - micro burners :**

A semi micro burner is used for heating. Burners made of cast metal are commercially available.

Principle involved in sodium carbonate extract preparation

About 5mg of the substance and 15 mg of A. R. sodium carbonate are taken in a semi micro beaker. 5ml of distilled water is added and boiled for 15 minutes on the heating block, adding distilled water at intervals to make up for the loss of evaporation. The precipitate is removed by centrifugation and the clear centrifugate known as sodium carbonate extract contains the anions as the sodium salts, together with the excess of sodium carbonate. As a result of the reaction the cations are eliminated as insoluble carbonates, basic carbonates, hydroxides or oxides.

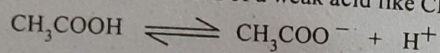


Common Ion Effect :

Definition : The suppression of dissociation of a weak acid or a weak base by adding a solution of strong electrolyte having an ion common with the weak acid or the weak base is called common ion effect.

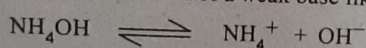
Illustrations with example :

1. Let us consider the dissociation of a weak acid like CH_3COOH .



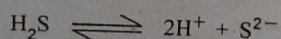
Let us, take the strong electrolytes, HCl and CH_3COONa ; HCl has H^+ in it. CH_3COONa has CH_3COO^- in it. i.e., these electrolytes have a common ion in each of them, as the equilibrium, existing in a solution of acetic acid. So if a solution of HCl or CH_3COONa is added to acetic acid solution the dissociation of acetic acid will be suppressed. i.e., the equilibrium will move towards left.

2. Let us consider the dissociation of a weak base like NH_4OH



The dissociation of NH_4OH will be suppressed if we add a solution of NH_4Cl or NaOH .

3. In the case of H_2S , which dissociates as follows,



If acid is added, the dissociation is suppressed. This will reduce the concentration of S^{2-} in the solution.

Application in qualitative analysis :

1. Common ion effect is used in qualitative analysis to decrease the concentration of S^{2-} from H_2S by adding HCl in the second group analysis for basic radicals.
2. Similarly the concentration of hydroxide ions from NH_4OH is lowered by adding NH_4Cl in third group analysis of the basic radicals.
3. In the purification of table salt hydrogen chloride gas is passed through a saturated solution of sodium chloride. The common ion is chloride ion.
4. In preparation of soap, soap is precipitated by addition of sodium chloride. The common ion in this case is sodium ion.

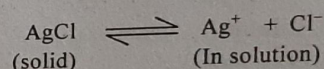
Solubility Product**Solubility :**

Definition : The maximum amount of a solute dissolved in a fixed quantity of solvent (say 100g) is called solubility.

Solubility product :

Definition : The solubility product of a sparingly soluble salt is the product of the concentrations of ions in the saturated solution.

Explanation : When a slightly soluble ionic solid such as silver chloride is placed in water. Ag^+ ions and Cl^- ions from the solid phase pass into solution till the solution becomes saturated. Now there exists an equilibrium between the ions present in the saturated solution and the solid phase. Thus



Applying the law of chemical equilibrium, the value of equilibrium constant.

$$K = \frac{a_{\text{Ag}^+} a_{\text{Cl}^-}}{a_{\text{AgCl}}}$$

Since the activity of a solid is taken as unity the above expression may be written as

$$K_{\text{AgCl}} = a_{\text{Ag}^+} a_{\text{Cl}^-} \text{ (or) } K_{\text{sp}} = a_{\text{Ag}^+} a_{\text{Cl}^-}$$

K_{sp} is called the solubility product. It is a constant at a given temperature.

Solubility Product and solubility :

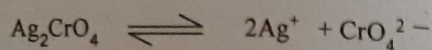
Suppose, solubility of a sparingly soluble salt like silver chloride is S moles per litre. It may be assumed that the dissolved salt is completely dissociated and the concentrations of both silver and chloride ions are S moles per litre. Now, the solubility product of silver chloride will be

$$K_{\text{sp}} = a_{\text{Ag}^+} a_{\text{Cl}^-} = S^2$$

Hence, solubility of silver chloride is related to solubility product as follows:

$$S = \sqrt{K_{\text{sp}}}$$

For Ag_2CrO_4 dissociating as

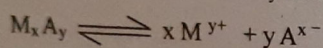


$$K_{\text{SP}} = (2a)_{\text{Ag}^+}^2 a_{\text{CrO}_4^{2-}} = (2S)^2 S = 4S^3$$

$$\text{and } S = \sqrt[3]{\frac{K_{\text{SP}}}{4}}$$

The same relationship is applicable to $\text{Ag}_2\text{C}_2\text{O}_4$ also

For a sparingly soluble salt such as M_xA_y dissociating as



$$K_{\text{SP}} = (x a_{\text{M}^{y+}})^x (y a_{\text{A}^{x-}})^y$$

Determination of solubility product :

Substances like BaSO_4 , AgCl , PbSO_4 , AgI , PbI_2 , Ag_2CrO_4 are examples for sparingly soluble salts. Since they are sparingly (slightly) soluble their solutions may be considered as solutions at infinite dilution. The equivalent conductance measured for this solution may be taken as equivalent conductance at infinite dilution.

A saturated solution of the sparingly soluble salt in water is prepared and its equivalent conductance measured. Now

$$v = kV$$

Where k is the specific conductance and V is the volume in containing 1 gram equivalent of the electrolyte. Knowing v and k the volume containing one gram equivalent V is calculated. From V the amount of the solute present in one litre can be calculated. This gives the solubility of the substance.

From the solubility (s) of the sparingly soluble substance the solubility product (K_{SP}) may be calculated. Suppose we consider AgCl as the sparingly soluble salt it ionises as,



and the equilibrium constant

$$K = \frac{a_{\text{Ag}^+} a_{\text{Cl}^-}}{a_{\text{AgCl}}}$$

Since the salt is sparingly soluble a_{AgCl} may be taken as 1

$$\text{Then, } K_{\text{SP}} = c_{\text{Ag}^+} c_{\text{Cl}^-}$$

Since the solution is dilute the concentration of the ions may be considered instead of activity.

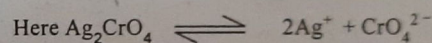
$$\text{Then } K_{\text{SP}} = c_{\text{Ag}^+} c_{\text{Cl}^-} = s \cdot s = s^2$$

Problems :

1. The solubility of silver chromate in water is 8×10^{-5} mole/litre at 25°C . Calculate its solubility product at the temperature.

Solution : Solubility of $\text{Ag}_2\text{CrO}_4 = s = 8 \times 10^{-5}$ mole / litre.

$$\text{Solubility product} = K_{\text{SP}} = ?$$



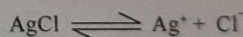
$$K_{\text{SP}} = (2\text{Ag}^+)^2 (\text{CrO}_4^{2-}) = (2s)^2 S$$

$$4s^3 = 4(8 \times 10^{-5})^3 = 2.0484 \times 10^{-12}$$

$$\text{The solubility product } \text{Ag}_2\text{CrO}_4 = 2.0484 \times 10^{-12}$$

2. The solubility product of silver chloride is 1.54×10^{-10} at 25°C calculate the solubility of silver chloride in g per liter.

Solution : Silver chloride dissociates as



$$K_{\text{SP}} = s \cdot s = s^2$$

$$s = \sqrt{K_{\text{SP}}} = \sqrt{1.54 \times 10^{-10}} = 1.24 \times 10^{-5}$$

This is g. eq. / lit

$$s = 1.24 \times 10^{-5} \times 143.25 = 1.78 \times 10^{-3} \text{ g/litres}$$

$$\text{Solubility of AgCl in g/lit} = 1.78 \times 10^{-3}$$

3. The solubility of silver chloride at 20°C is 0.00116 g / lit. Calculate the solubility product.

Solution : Solubility = 0.00116 g / lit converting it into moles / lit

$$= \frac{0.00116}{143.45} = 1.115 \times 10^{-5}$$

$$X K_{SP} = s^2 = (1.115 \times 10^{-5})^2 = 1.244 \times 10^{-10}$$

$$X \text{ Solubility product of AgCl} = 1.244 \times 10^{-10}$$

4. The solubility product of silver chromate is 9×10^{-12} at 20°C . Calculate the solubility in gm / litre.

Solution : We know for Ag_2CrO_4 the relationship between s and K_{SP}

$$K_{SP} = 4s^3$$

$$4s^3 = K_{SP}$$

$$s^3 = K_{SP} / 4$$

$$X S = \sqrt[3]{K_{SP} / 4} = \sqrt[3]{9 \times 10^{-12} / 4}$$

$$= \sqrt[3]{2.25 \times 10^{-12}} = 1.310 \times 10^{-4} \text{ mol / lit}$$

Covering in to g / lit

$$= 1.310 \times 10^{-4} \times 331.74 = 4.346 \times 10^{-2} \text{ g / lit}$$

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 = 4.346 \times 10^{-2} \text{ g / lit}$$

Principles of Solubility product and its applications:

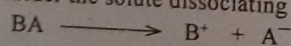
Principle :

When the ionic product of a solute in a solution exceeds its solubility product then it is precipitated.

Explanation :

A solution of a solute contains the dissociated ions of the solute. The product of the concentration of the ions is known as the ionic product of the solute. If this value is more than the solubility of that solute, then, the solute will be precipitated.

For example, consider the solute dissociating as



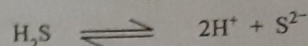
Let its solubility product be K_{SP} . Let its ionic product be X .

If in a particular solution of BA, X is greater than its K_{SP} then it will be precipitated.

Application in Qualitative Analysis :

Precipitation of sulphides of groups II and IV :

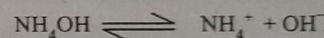
In qualitative analysis, the sulphides of group II are precipitated in presence of dilute HCl while those of group IV are precipitated only in the presence of NH_4OH . It may be explained as follows : Hydrogen sulphide is a weak acid. It ionises to a lesser extent only.



The ionisation is further suppressed by the addition of dilute HCl (common ion effect), Therefore the concentration of S^{2-} becomes still smaller. But even this low concentration is larger, than the solubility product of sulphides of copper, cadmium, bismuth, arsenic, antimony and tin. Thus these cations are precipitated as sulphides in the II group.

The solubility products of sulphides of Ni, Co, Mn and Zn are comparatively higher. The S^{2-} ion concentration in the presence of dilute HCl is insufficient for precipitation. So they are not precipitated in Group II. In the presence of NH_4OH , the hydroxyl ions combine with H^+ ions H_2S to give unionised water. So more of H_2S ionises and thus the concentration of S^{2-} ions in solution increases. Hence it becomes so high that the, solubility product of NiS etc., is exceeded and so they are precipitated.

Precipitation of hydroxides of Group III : Ammonium hydroxide is a weak base and ionises in solution to a very small extent.



In presence of highly ionised NH_4Cl due to an increase in the number of NH_4^+ ions the ionisation of NH_4OH is further suppressed. Thus the concentration of OH^- ions is very low. Under these conditions the solubility products of the hydroxides of Al, Fe and Cr alone are exceeded and those are precipitated. The hydroxides of Zn, Mn, Ni, Mg and Co are not precipitated from their salt solutions. It is because these hydroxides possess a comparatively higher value of solubility products.

Complexation Reactions in Qualitative Analysis and Spot Tests :

Complexation i.e., complex formation reactions are used widely in qualitative analysis of substances. E.g.,

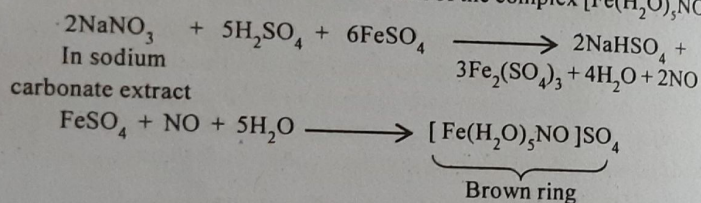
1. Identification of chloride, bromide and iodide :

All the three ions give precipitates with Ag^+ AgCl dissolves in dilute ammonium hydroxide. AgBr is partially soluble while AgI is insoluble in dilute ammonium hydroxides. This is because AgCl gives the complex $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ with even dilute ammonium hydroxide. So it dissolves. AgBr gives the complex $[\text{Ag}(\text{NH}_3)_2]\text{Br}$ only with concentrated ammonium hydroxide. So AgBr is only partially soluble in dilute ammonium hydroxide.

AgI does not form a complex under these conditions. So it remains insoluble.

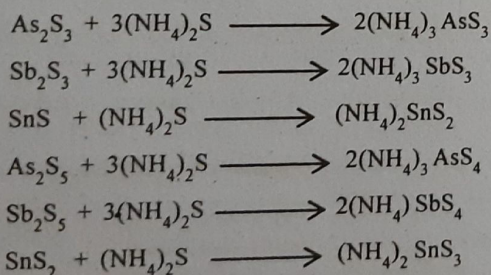
2. Confirmation of nitrate : Brown Ring Test :

The sodium carbonate extract of the substance to be tested for nitrate is taken. It is neutralised with dilute sulphuric acid, boiled and cooled. A freshly prepared solution of ferrous sulphate is added and concentrated sulphuric acid is added in drops along the side of the test tube. A brown ring appears. This is due to the formation of the complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$.



3. Separation of group II A and II B radicals :

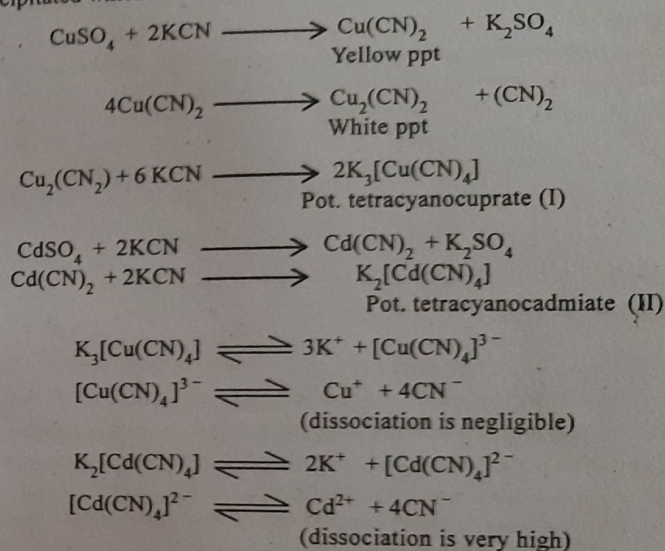
In the second group analysis for basic radicals yellow ammonium sulphide is employed to separate radicals belonging to group II A (also called copper group containing Hg, Pb, Bi, Cu and Cd) and group II B (also called tin group containing As, Sb and Sn). Tin group sulphides dissolve in yellow ammonium sulphide forming complexes while copper group sulphides remain undissolved as they do not form complexes with yellow ammonium sulphide.



4. Separation of copper and cadmium ions :

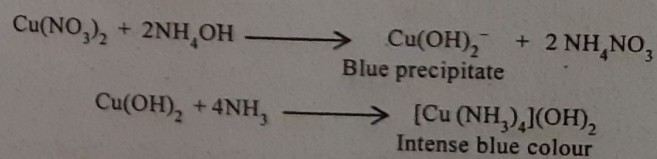
When KCN is added in excess to a solution containing copper and cadmium ions both copper and cadmium form complexes. The copper complex is more stable than the cadmium complex. So, When H_2S is passed

in the aqueous solution of these two complexes cadmium alone gets precipitated which is filtered. Thus the two can be separated.

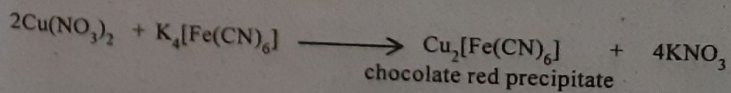


5. Identification of copper :

a) When ammonium hydroxide is added in drops to excess, first a blue precipitate is formed which dissolves in excess ammonium hydroxides forming intense blue solution, due to the formation of the complex tetra ammine copper II hydroxide.



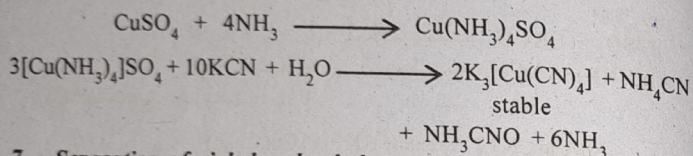
b) When potassium ferrocyanide is added to a solution of copper salt in presence of acetic acid a chocolate red precipitate of copper ferrocyanide is formed.



6. Identification of cadmium in presence of copper :

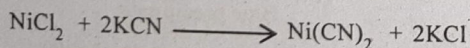
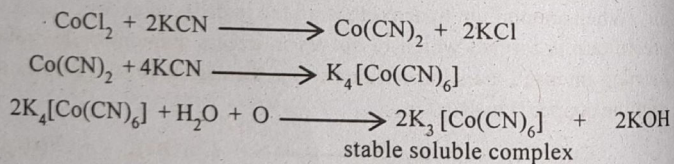
To the solution of the mixture of cadmium and copper excess ammonia is added followed by dilute potassium cyanide solution until the blue colour is discharged. The solution is diluted and H_2S is passed formation of a yellow precipitate shows the presence of cadmium.

Both Cu^{++} and Cd^{++} form cyano complexes. The copper complex is more stable than cadmium complex. So when H_2S is passed only Cd^{2+} is precipitated as CdS while Cu^{++} remains in solution.



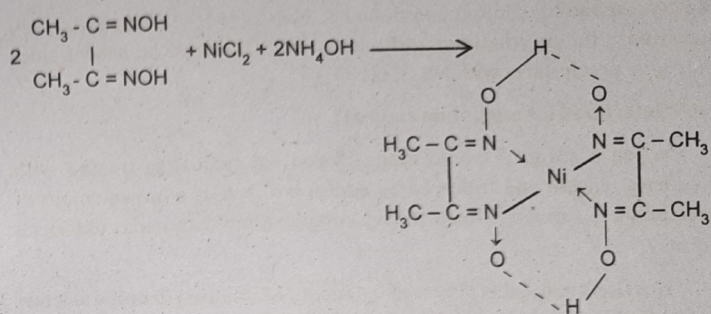
7. Separation of nickel and cobalt :

When KCN is added in excess to a solution containing nickel and cobalt ions, cobalt ion forms a complex salt potassium cobalto cyanide, $K_4[Co(CN)_6]$. This complex salt is further oxidised by air in presence of acids to form a stable complex, potassium cobalticyanide, $K_3[Co(CN)_6]$. Now the mixture is boiled with NaOH and bromine water. $Ni(CN)_2$ alone is converted into insoluble black nickel oxide while the cobalt complex remains in solution. Thus they can be separated.



8. Identification of nickel :

When a solution of dimethyl glyoxime is added to an ammoniacal solution of a nickel salt a scarlet rose red precipitate is formed, which is a complex called bisdimethyl glyoximato nickel (II)

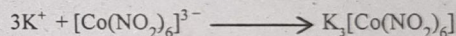


Bisdimethyl Glyoximato Nickel (II) (DMG)

9. Detection of potassium ions :

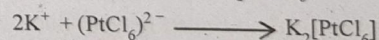
K^+ ions in solution can be detected using the following reactions :

i. Sodium hexanitrito cobaltate (III) solution : $Na_2[Co(NO_2)_6]$



A yellow precipitate of potassium hexanitrito cobaltate (III) is obtained. The precipitate is insoluble in dilute acetic acid. When larger amounts of sodium are present or if the reagent is added in excess, a mixed salt, $K_2Na[Co(NO_2)_6]$ is formed. The precipitate forms immediately in concentrated solutions and slowly in dilute solutions. Ammonium salts give a similar precipitate and must be absent. Iodides and other reducing agents interfere and should be removed before applying the test.

ii. Hexachloroplatinic (IV) acid : $H_2[PtCl_6]$



A yellow precipitate of potassium hexachloroplatinate (IV) is obtained. The precipitate is slightly soluble in water but insoluble in 75 percent alcohol.

iii. Sodium hexanitrito cobaltate (III) - Silver Nitrate reaction :

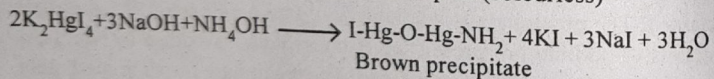
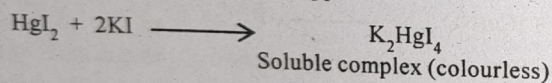
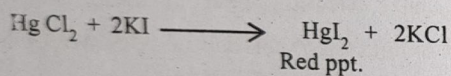
This is a modification of reaction (i) and is applicable to halogen free solutions. Potassium salts on reactions with $Na_3[Co(NO_2)_6]$ and $AgNO_3$ solution give the compound $K_2Ag[Co(NO_2)_6]$. This is less soluble than

the corresponding sodium compound $K_2Na[Co(NO_2)_6]$. The test is more sensitive. Lithium, thallium and ammonium salts must be absent since they give precipitates with $Na_3[Co(NO_2)_6]$.

10. Detection of Ammonium radical :

When a solution containing ammonium radical is treated with Nessler's reagent and followed by addition of NaOH a brown colour or precipitate is formed. This test uses complexation reaction as described below :

Nessler's reagent is prepared by adding KI solution in drops to a few drops of $HgCl_2$ till the bright red precipitate of HgI_2 dissolves, giving a clear solution. The solution contains the complex $K_2[Hg, I_4]$. This in presence of NaOH, gives a brown colour or precipitate with ammonium radical.



Spot Test Reagents

1. Aluminon Reagent

(0.1% aqueous solution of the ammonium salt of a urine tricarboxylic acid).

The test is applied to the precipitate of aluminium hydroxide. Since certain other elements interfere. Dissolve the aluminium hydroxide precipitate in drops of N HCl, add 2 drops of the reagent, shake, allow to stand for 5 minutes and add excess of ammoniacal ammonium carbonate solution to decolourise any excess dyestuff and lakes due to traces of chromium hydroxide and silica.

A bright red precipitate (or colouration) is got.

2. Cupferon Reagent :

(1 gm of α - benzoinoxime in 20 cc of rectified spirit).

To a drop of the weakly acid test solution add a drop of the reagent and one drop of ammonia.

A green colour is developed.

3. DMG (Di methyl glyoxime) :

(1% in the spirits) - Ferric chloride

This reagent is used to identify the Tin from given solution. To a drop of the test solution add one drop of HCl, 2 drops of 0.1F FeCl₃, 5 drops of 5% tartaric acid, and then 3 drops of dimethyl glyoxime reagent followed by one cc of aq. NH_3 .

A red colour is developed.

Tartaric acid is added to prevent the formation of ferrichrynoxide.

DMG (1% alcoholic solution of dimethyl glyoxime).

to a drop of the test solution add one drop of the reagent and drops of aq. NH_3 .

A red spot is obtained.

4. Thiourea Reagent :

Thiourea used as 5% aqueous solution in detection of Bismuth.

To a drop of the test solution in nitric acid add a drop of the reagent.

An intensive colour is developed.

5. Magneson (Para nitro benzene - azo - resorcinol), 0.01 g in 100 cc in N NaOH.

To a drop of the test solution add a drop of the reagent and a drop of N NaOH.

A blue precipitate is formed.

6. Alizarin :

This reagent is applied to confirm the aluminium.

To a drop of the acid test solution as in (i) on a glass slide add a drop of the reagent. Expose to ammonia vapour and dry at 100° . when the violet colour due to ammonium alizarinate disappears.

A red colour is obtained.

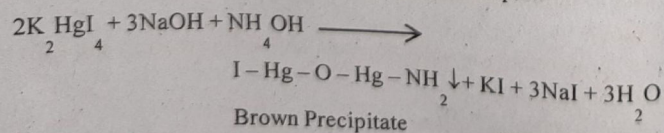
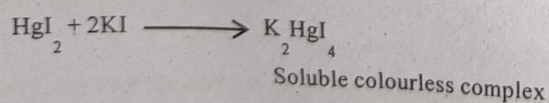
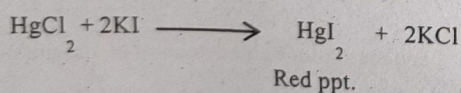
7. Nessler's reagent :

(Detection of ammonium radical)

When a solution containing ammonium radical is treated with Nessler's reagent and followed by addition of NaOH a brown colour or precipitate is formed. This test uses complexation reaction as follows.

Nessler's reagent is prepared by adding KI solution in drops to a few drops of HgCl_2 fill the bright red precipitate of HgI_2 dissolves, giving a clear solution. The solution contains.

The complex $\text{K}_2[\text{HgI}_4]$. This in presence of NaOH, gives a brown colour or precipitate with ammonical radical.



Separation of cations into groups

Based on the principle of common ion effect and solubility product, the cations are classified into the following six groups in qualitative inorganic analysis. Each group has a specific group reagents which precipitates the metals belonging to that group alone in the form of their insoluble compounds. The group reagents are added in an order. When a precipitate is formed in any group, it is filtered off and identified by its specific reactions. The different analytical group with group reagents are given below.

Number and name of the group	Group metals	Group reagent	Nature of the precipitate
Group I	Ag^+ , Hg^+ and Pb^{2+}	Dilute HCl	Chlorides of Ag, Hg(ous) and Pb.
Group II	Hg^{2+} , Pb^{2+} , Bi^{3+} , Cu^{2+} , Cd^{2+} , As^{3+} , Sb^{2+} , Sn^{2+} and Sn^{4+}	H_2S in presence of dil. HCl.	Sulphides of Hg(ic), Pb, Bi, Cu, Cd, As, Sb and Sn.
Group III	Al^{3+} , Cr^{3+} , Fe^{2+} , Fe^{3+} , (Mn^{2+})	NH_4Cl and NH_4OH	Hydroxides of Al, Cr, Fe and (Mn).
Group IV	Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+}	H_2S in presence of NH_4Cl and NH_4OH	Sulphides of Co, Ni, Mn and Zn
Group V	Ca^{2+} , Sr^{2+} and Ba^{2+}	NH_4Cl , NH_4OH and excess of $(\text{NH}_4)_2\text{CO}_3$	Carbonates of Ca, Sr and Ba
Group VI	Mg^{2+} , Na^+ , K^+ and NH_4^+	No common reagent	No similar Precipitate