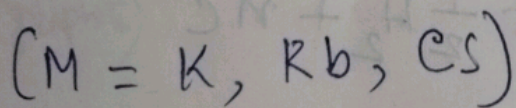
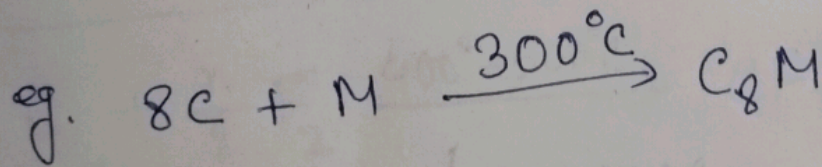


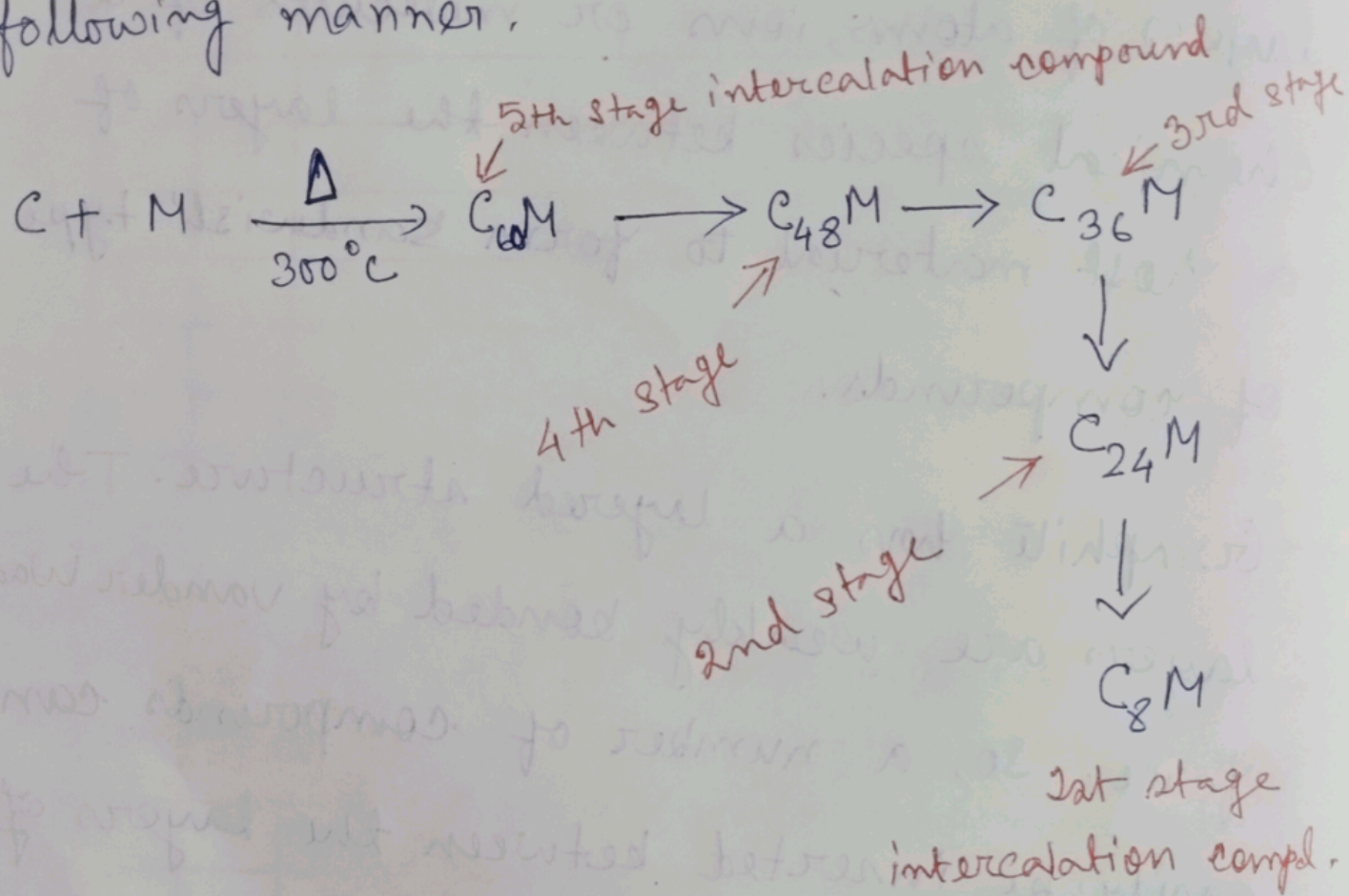
Intercalation compounds of graphite

Intercalation compounds means insertion of layers of atoms, ions or molecules of a chemical species between the layers of a host material to form 'sandwich' type of compounds.

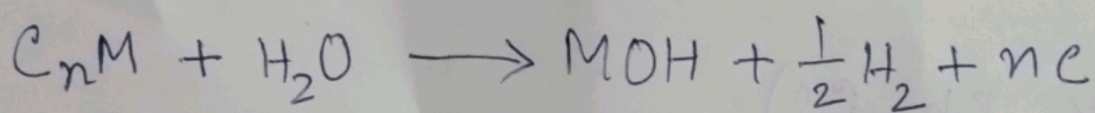
Graphite has a layered structure. The layers are weakly bonded by vander Waals' force. So, a number of compounds can easily be inserted between the layers of graphite. Therefore, graphite readily form intercalation compound.



These intercalation compounds of graphite with alkali metals form gradually in following manner.



These compounds are highly reactive. They react with H_2O to produce metal hydroxide and hydrogen gas.



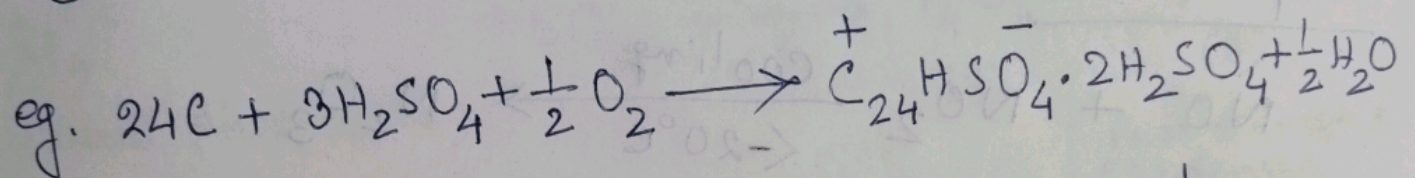
Intercalation compounds of oxoacids and metal halides

Graphite + concentrated oxoacids

↓ oxidizing condition

Intercalation compounds of oxoacids

(Also called lamellar graphite salts)

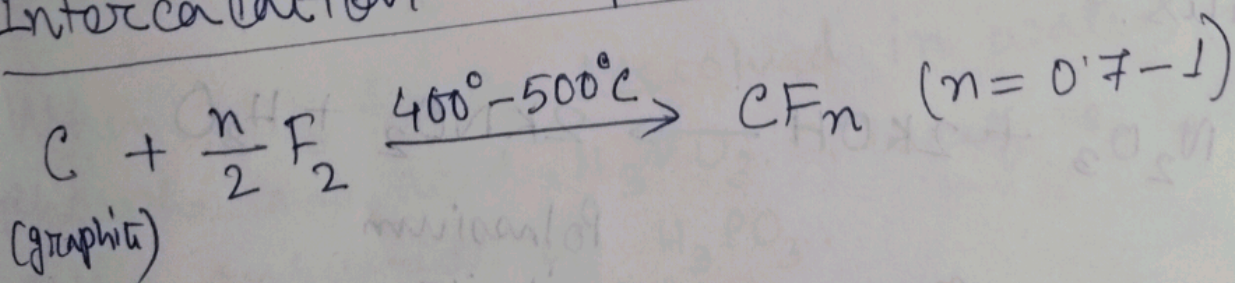


1st stage compd.
(Blue)

NB: Electrical conductivity of intercalated graphite salts are higher than graphite.

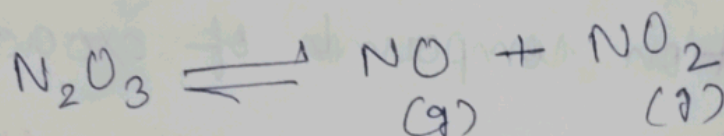
Flowing with ~~B~~

Intercalation compounds of graphite

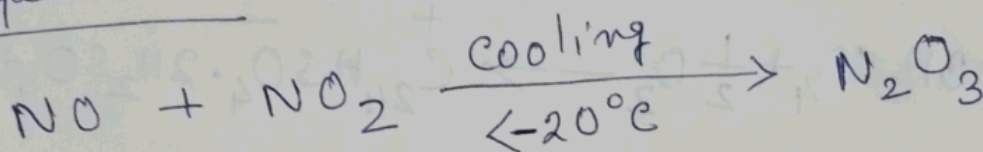


Oxides of nitrogen, phosphorus and chlorine

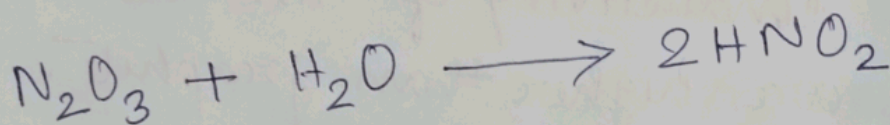
Nitrogen trioxide: N_2O_3 ^{at low tempⁿ}
It exists only in solid state. In liquid state, and vapour it dissociates into NO and NO_2 .



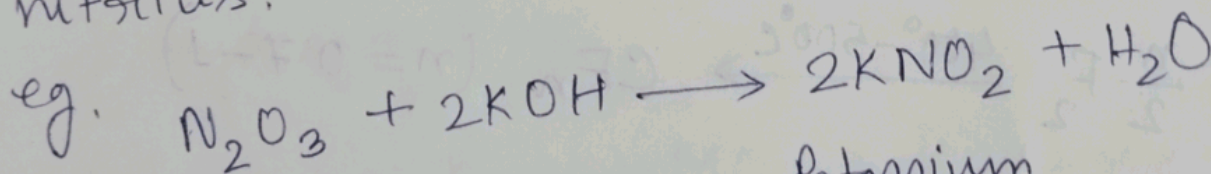
Preparation:-



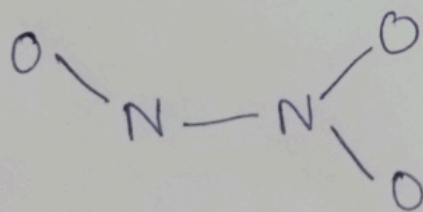
N_2O_3 is also called ~~anhydride~~ ^{anhydride} of nitrous acid as with water, it gives nitrous acid.



When dissolved in alkali, N_2O_3 produces nitrites.



Potassium
nitrite



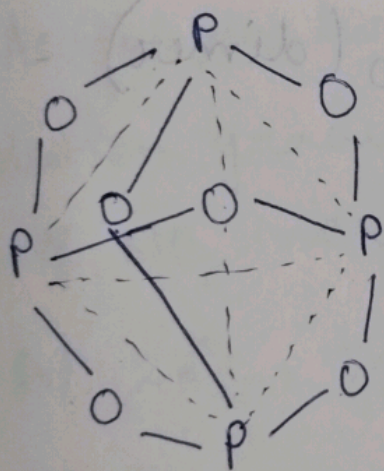
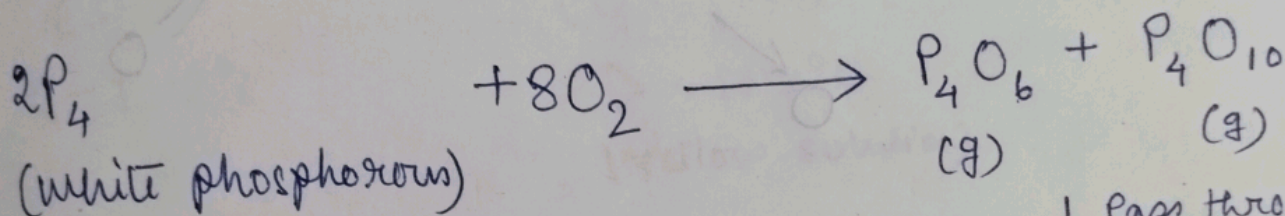
← Str. of N_2O_3
(Planar)

Phosphorous trioxide; (P_2O_3)

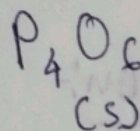
It exists as a dimer (P_4O_6).

Preparation:-

By combustion of white phosphorous in a limited supply of air.

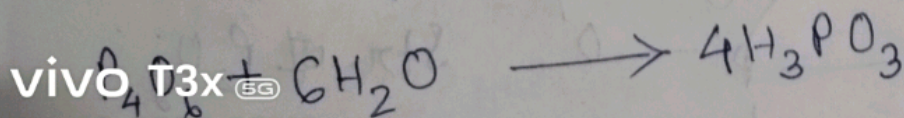


Pass through a
Condenser
($50-60^\circ C$)



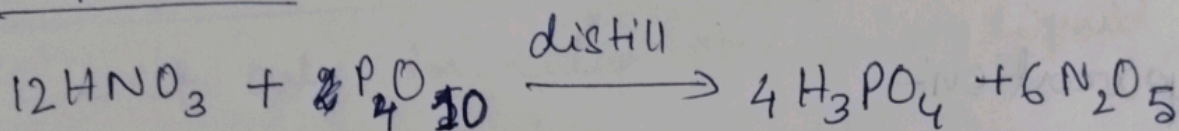
Str. of P_4O_6 (tetrahedral)

When P_4O_6 is dissolved in water, it gives phosphorous acid, H_3PO_3 . Therefore, P_4O_6 is called anhydride of H_3PO_3 .

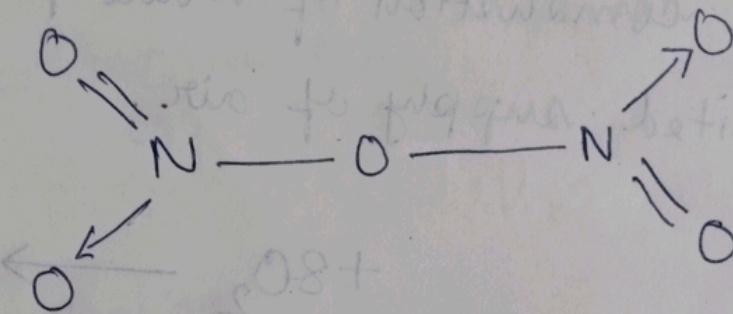


Nitrogen pentoxide (N_2O_5)

Preparation:- From nitric acid and phosphorous pentoxide

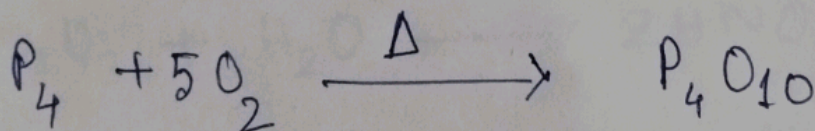


Structure:-

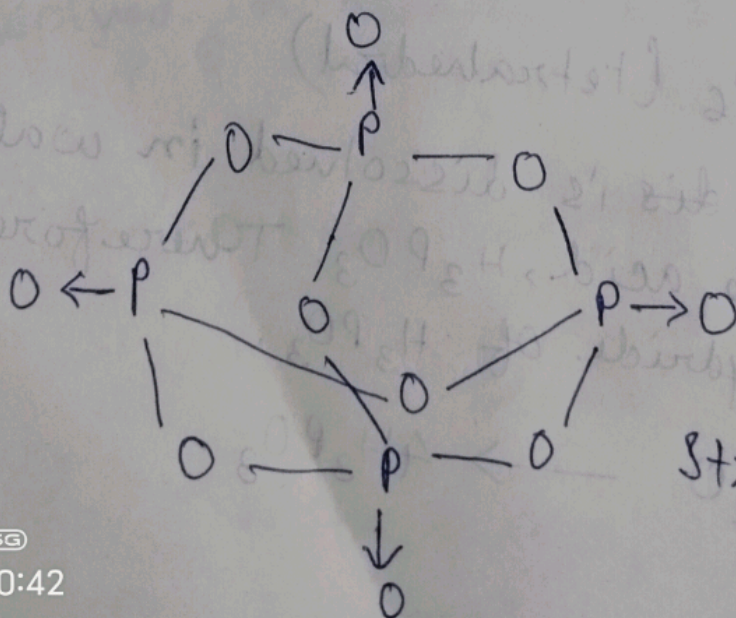


Phosphorous pentoxide:- P_4O_{10} (dimer)

Preparation:-

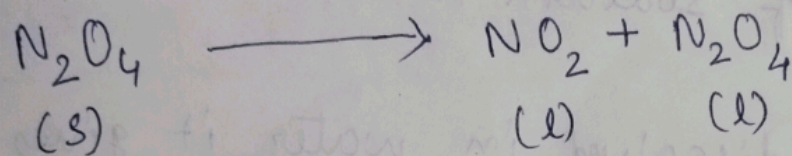
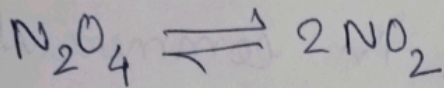


Phosphorous)



Nitrogen dioxide, NO_2 (^{also} exist as dimer, N_2O_4)

NO_2 and N_2O_4 exists as in a temp^r dependent equilibrium.



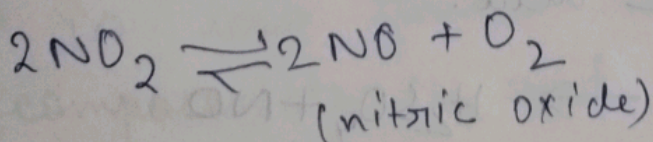
$< -11.2^\circ\text{C}$

$> -11.2^\circ\text{C}$

(yellow solution)

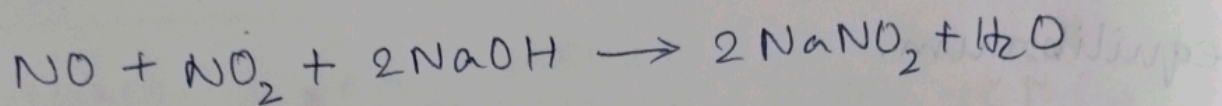
As temperature rises, the yellow colour of the solution gradually changes to orange and % of NO_2 increases.

- At 22°C , the liquid boils giving brown vapour.
- At 100°C , composition is 90% NO_2 + 10% N_2O_4
- Above 140°C , only NO_2 exist.
- Beyond this temp^r, NO_2 get dissociate.



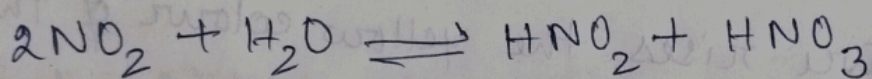
(colourless)

- If, the gas is treated with pure alkali at 300°C , it produces pure nitrite.



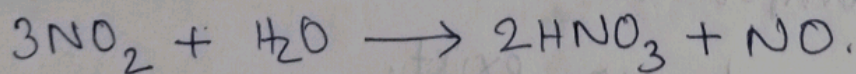
This fact is utilized in commercial preparation of sodium nitrite.

- When NO_2 is dissolved in water, it gives mixture of nitrous acid and nitric acid.

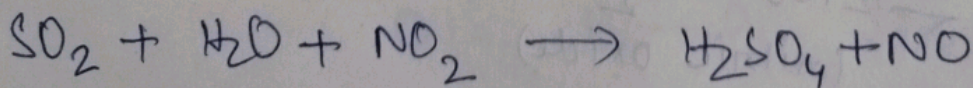


Hence, NO_2 is called mixed anhydride of these two acids.

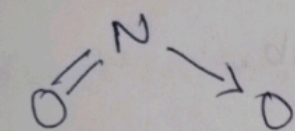
- The hot aqueous solution of NO_2 gives NO.



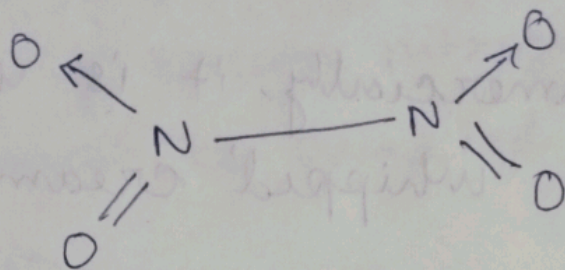
- In aqueous solution, it oxidizes sulphur dioxide to sulphuric acid.



Structure:



monomer

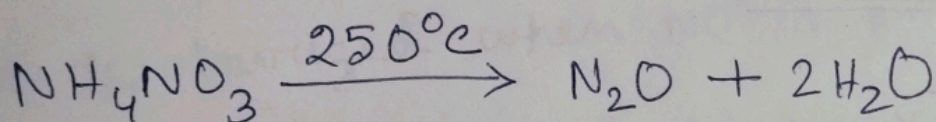


Dimer

Nitrous oxide (N_2O)

Preparation:-

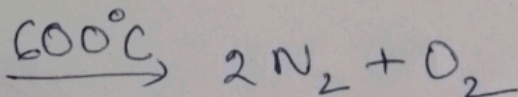
From ammonium nitrate:



- Nitrous oxide produces hysterical laughter, hence it is known as "laughing gas".
- In small amount, it acts as an anesthetic.

Chemical properties:

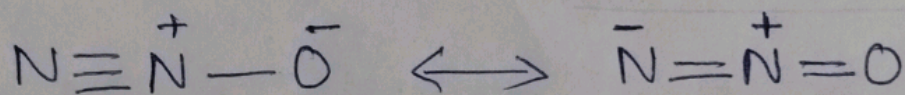
It is less reactive. At high tempⁿ, it decomposes to N_2 and O_2 .



Uses:-

- Commercially, it is used as propellant gas in 'whipped' cream bomb.
- It is used as anesthetic.

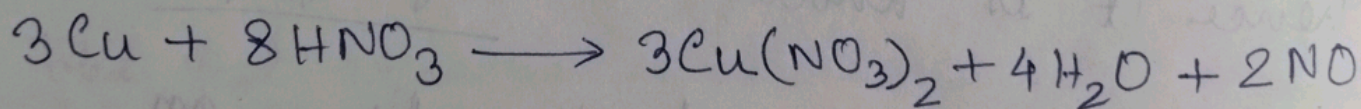
Structure:- Linear.



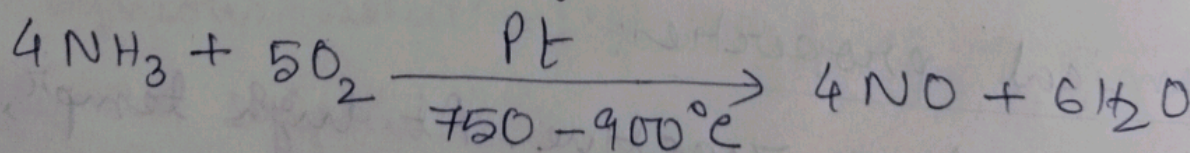
Nitric oxide, NO

Preparation:-

By the action of cold, dilute nitric acid on copper turnings.



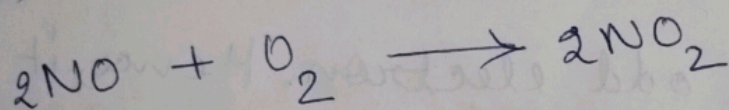
On commercial scale, NO is produced by catalytic oxidation of ammonia.



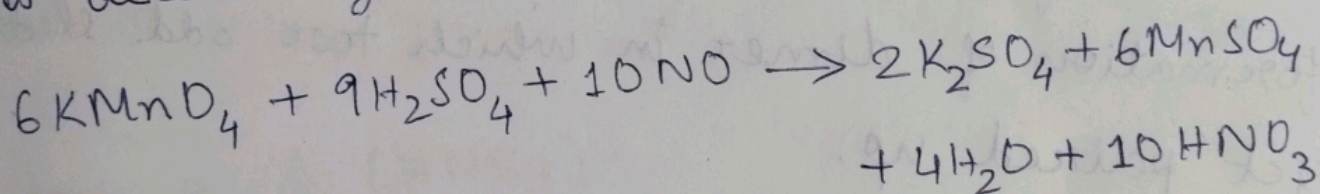
- NO is a colourless gas, which readily combine with O_2 giving brown nitrogen dioxide. Hence, NO must be handled out of contact with air.

Chemical properties:-

(1) Reaction with O_2 :

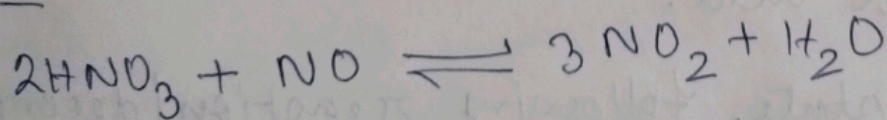


(2) ~~It~~ is Acidified potassium permanganate is decolorized when NO is passed into it.



The reaction with $KMnO_4$ is quantitative and is therefore used for estimation of NO.

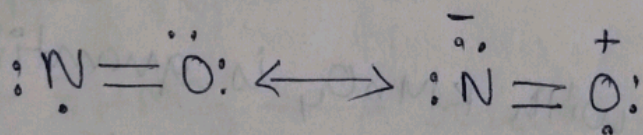
(3) NO is oxidized to NO_2 with conc. HNO_3 .



(4) NO is absorbed in FeSO_4 solution giving a dark brown complex, $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$. This compound is responsible for the formation of brown ring in the ring test for nitrates.

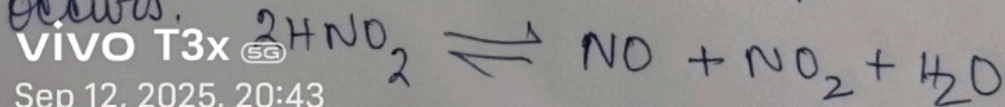
Magnetic property:-

'NO' molecule has 11 valence electrons. So, it ~~contains~~ contains one odd electron. Hence, it is paramagnetic in gaseous state. But, it is diamagnetic in solid state due to the formation of dimer in which two odd electrons get paired up.

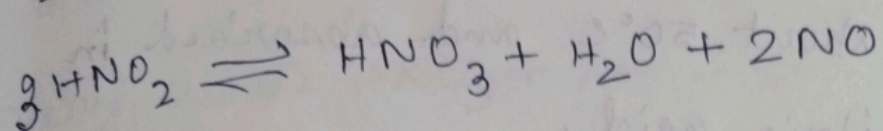


Nitrous acid, HNO_2

- It is very unstable.
- It is a weak acid.
- In vapour state, following reaction (decomposition) occurs.

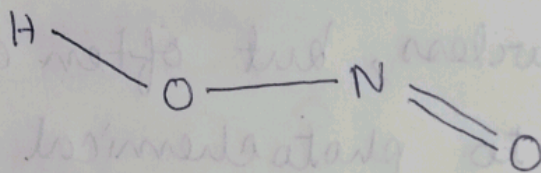


• In aqueous solution, it undergoes autooxidation.



• HNO_2 behaves both as oxidizing and reducing agent. It reduces strong oxidizing agents like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2O_2 etc. It oxidizes strong reducing agents like HI , H_2SO_3 etc.

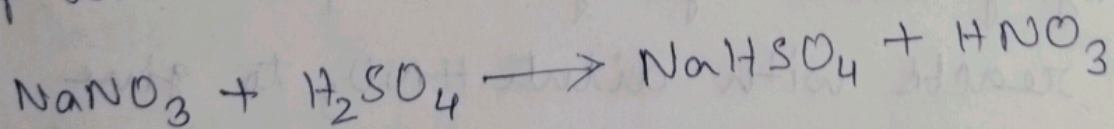
Structure: In gaseous state, HNO_2 has trans configuration.



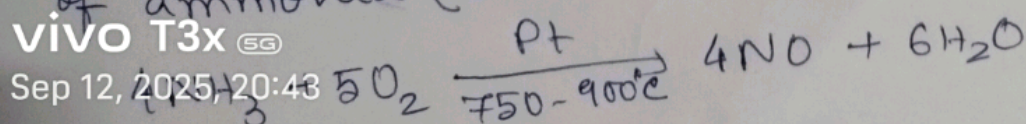
Nitric acid (HNO_3)

Preparation:

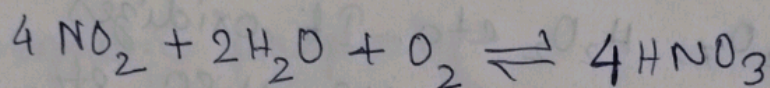
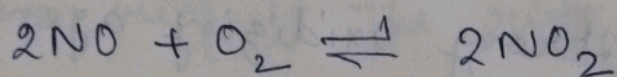
(1) Laboratory method: By heating a mixture of sodium nitrate and conc. H_2SO_4 .



(2) Commercial method: By catalytic oxidation of ammonia (Ostwald's method)

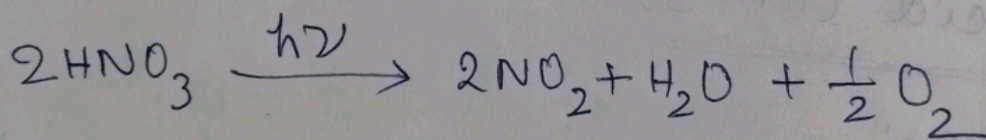


The NO is oxidized by air to NO_2 which is cooled to about 50°C and absorbed in air to give nitric acid.



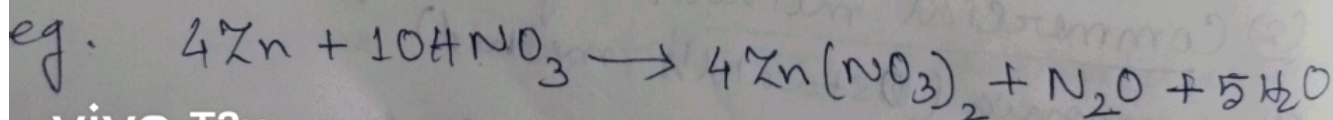
Properties:-

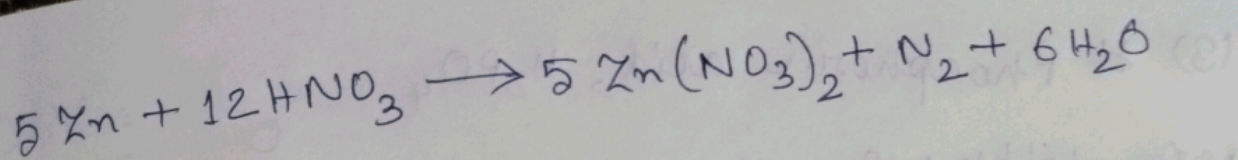
- Concentrated HNO_3 solution is usually colourless, but often develops a yellow colour due to photochemical decomposition to nitrogen dioxide.



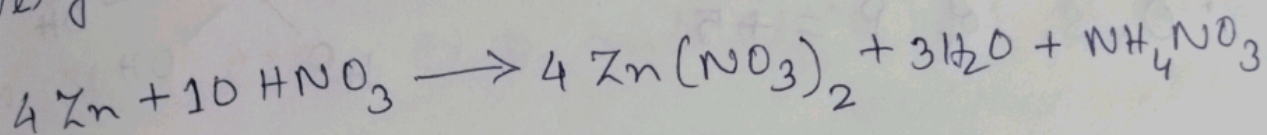
Action on metals:-

Metals lying below hydrogen in spectrochemical series reacts with dilute HNO_3 to give metal nitrates.





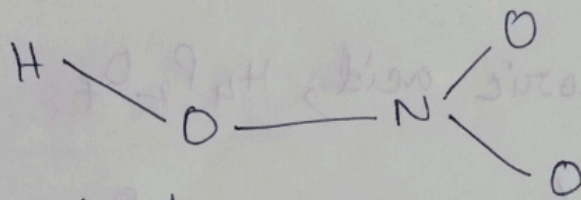
Very dilute $\text{HNO}_3 + \text{Zn} \rightarrow$



Structure:-

Gaseous HNO_3

is a planar molecule.

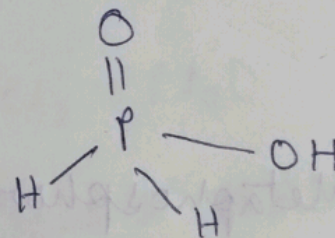


Some oxoacids of phosphorus:-

(1) Phosphinic acid, H_3PO_2

- Basicity: 1

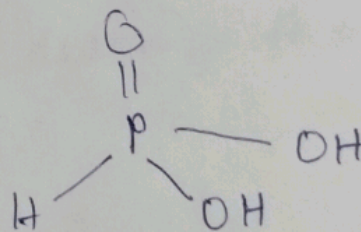
- Oxidation state of $\text{P} = +1$



(2) Phosphonic acid, H_3PO_3

- Basicity: 2

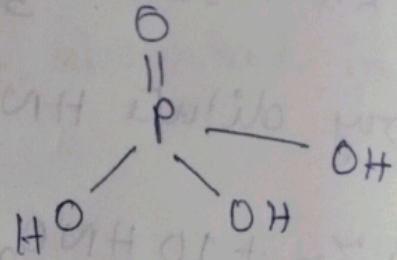
- O.S. of $\text{P} = +3$



(3) Phosphoric acid, H_3PO_4

• Basicity: 3

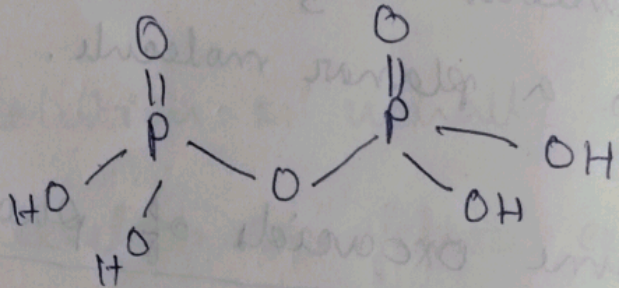
• O.S. of P = +5



(4) Diphosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$

• Basicity: 4

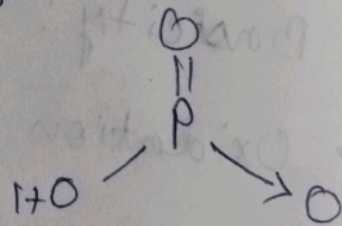
O.S. of P = +5



(5) Metaphosphoric acid, HPO_3

• Basicity: 1

• O.S. of P = +5



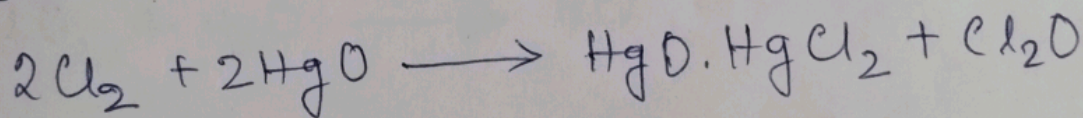
Oxides of Chlorine

Chlorine forms a number of oxides such as Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 . All of them are unstable.

Dichlorine oxide, Cl_2O :-

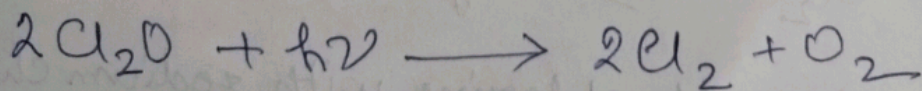
Preparation:-

By passing chlorine over freshly precipitated mercuric oxide.

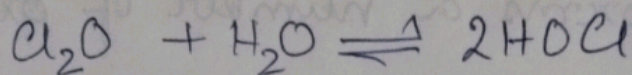


It is an orange liquid below 2°C . Above 2°C , it is yellowish brown gas. At higher tempⁿ, the gas explodes.

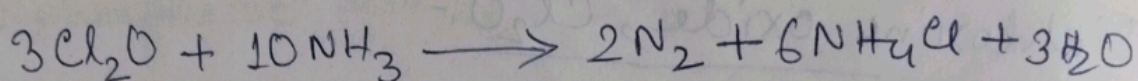
• It undergoes photochemical decomposition to give oxygen and chlorine.



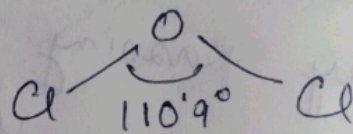
It dissolves in water to form hypochlorous acid.



Its gaseous mixture with NH_3 explodes violently.



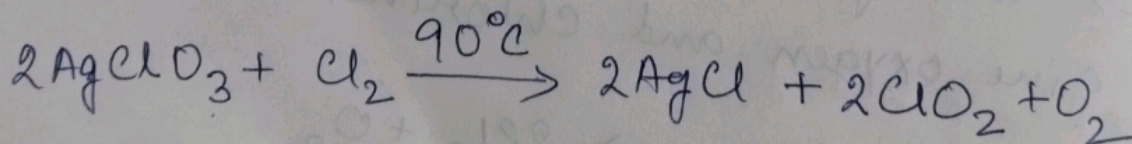
Structure: Angular shape.



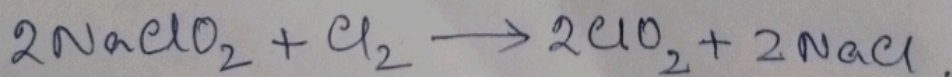
Chlorine dioxide, ClO_2

⊕ Preparation:-

① By treating silver chloride with dry chlorine at 90°C .



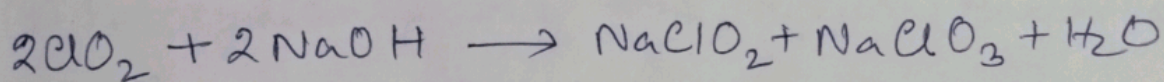
② By the action of chlorine with sodium chlorite.



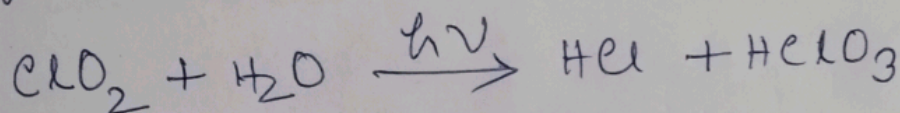
• It is a paramagnetic, yellowish brown gas.
Boiling point: 11°C .

Reactions:-

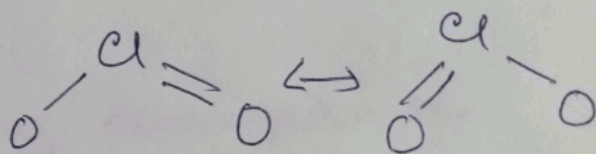
(1) With alkali:



(2) Aqueous solution of ClO_2 undergoes photochemical decomposition to give a mixture of chloric acid and hydrochloric acid.



Structure: Angular.



Oxoacids of Chlorine:-

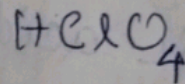
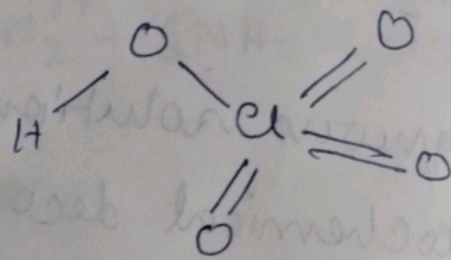
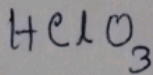
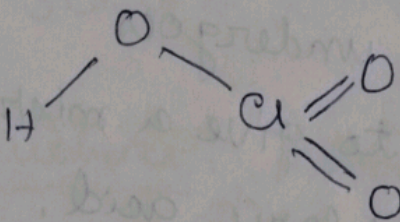
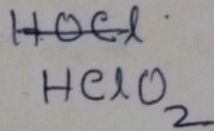
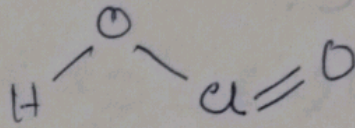
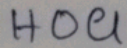
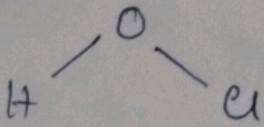
$\text{HOCl} \rightarrow$ Hypochlorous acid $\rightarrow$ +1

$\text{HOClO}_2 \rightarrow$ Chlorous acid $\rightarrow$ +3

$\text{HClO}_3 \rightarrow$ Chloric acid $\rightarrow$ +5

$\text{HClO}_4 \rightarrow$ Perchloric acid $\rightarrow$ +7

Structure

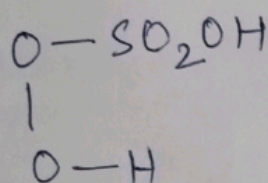


Peroxoacids of sulfur

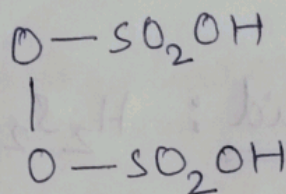
Two peroxosulphuric acids are known.

(1) Peroxysulphuric acid, H_2SO_5 (Caro's acid)

(2) Peroxydisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid)



Caro's acid



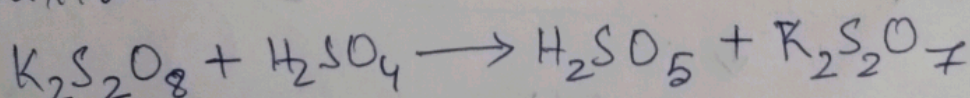
Marshall's acid

(1) Caro's acid H_2SO_5

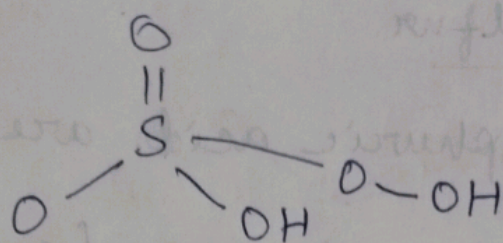
Preparation: (1) By the low conversion of peroxydisulphuric acid in aqueous solution.



(2) By grinding potassium peroxydisulphate crystals with conc. H_2SO_4 in a freezing mixture.



Structure:



Peroxy sulphuric acid

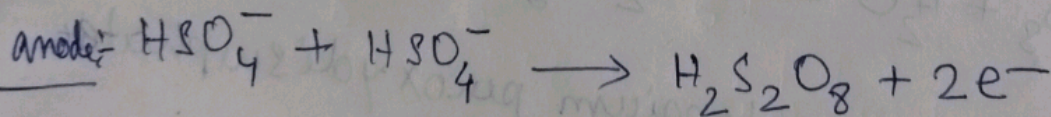
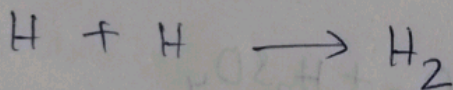
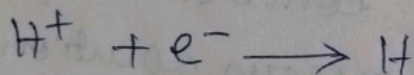
Basicity: It is considered as monobasic acid.

Marshall's acid: $\text{H}_2\text{S}_2\text{O}_8$

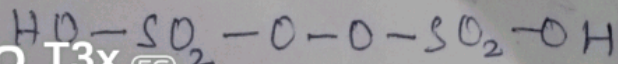
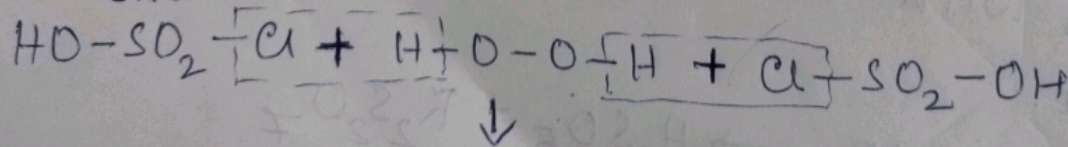
Preparation:

① By anodic oxidation of sulphuric acid:

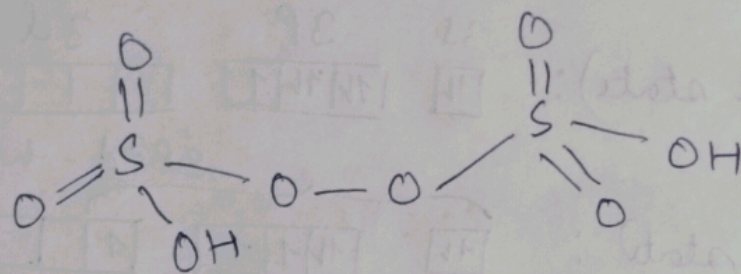
Cathode:



② By ~~the~~ sulphonation of hydrogen peroxide by chlorosulphonic acid.



Structure:

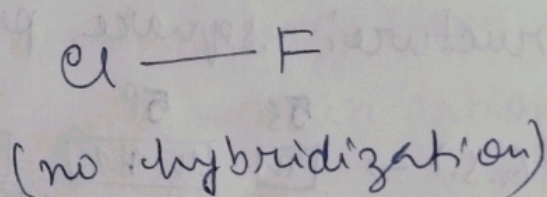
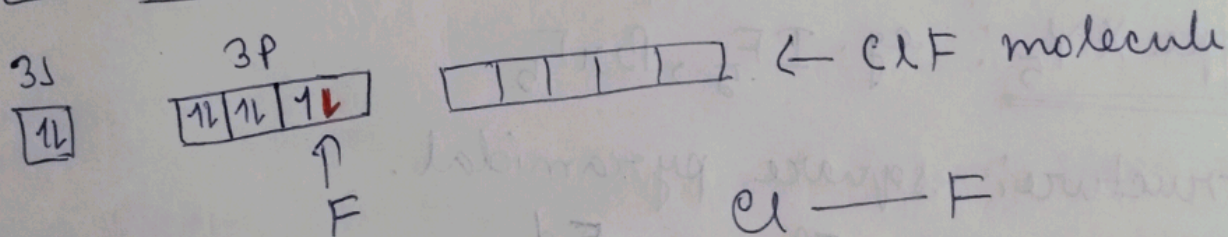
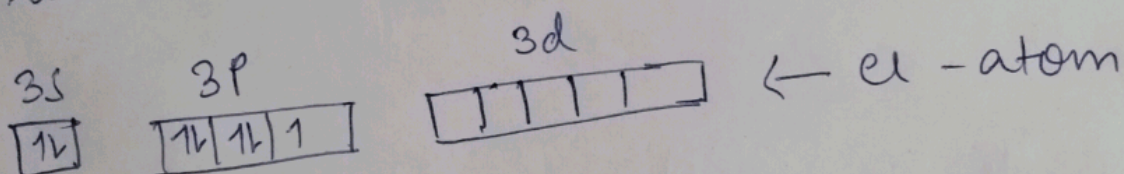


Peroxydisulphuric acid

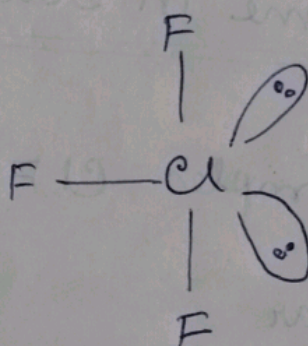
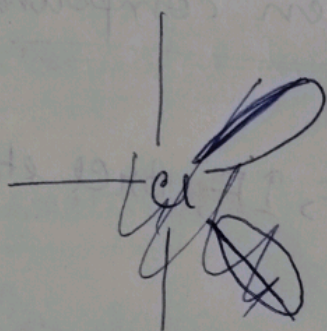
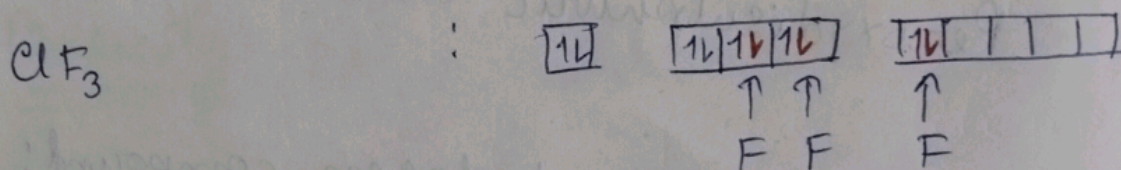
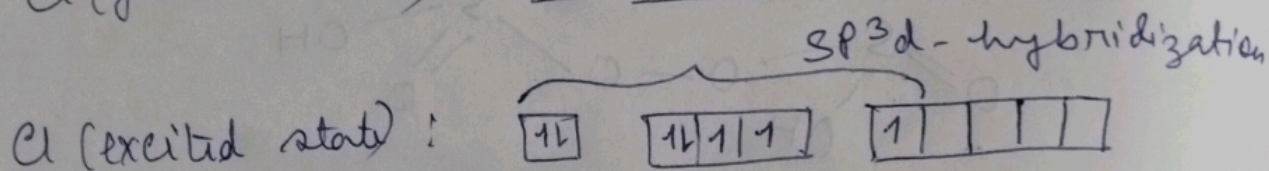
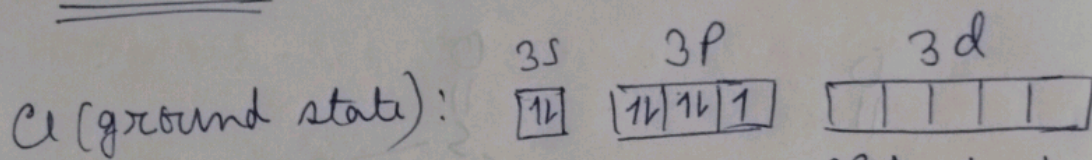
Structures of some interhalogen compound:

① Type XY: Examples ClF , BrF , IF , BrCl etc.

Structure: linear

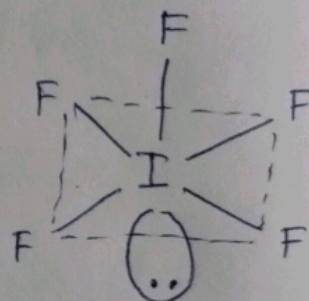
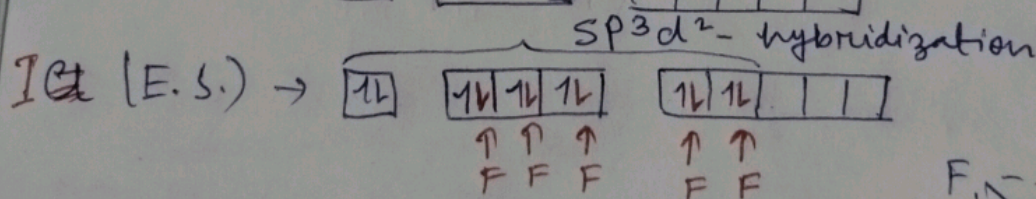
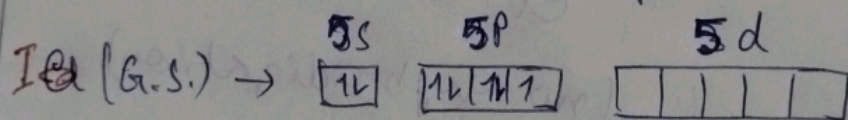


Type XY_3 eg. ClF_3 (T-shape)

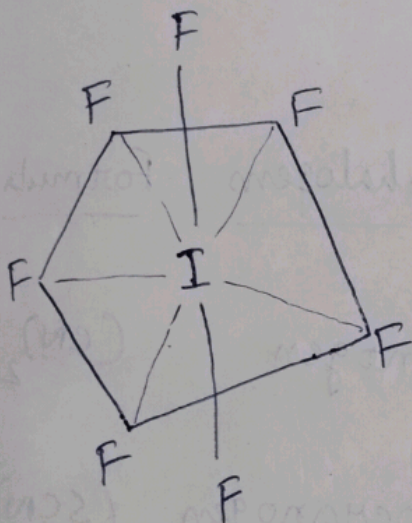
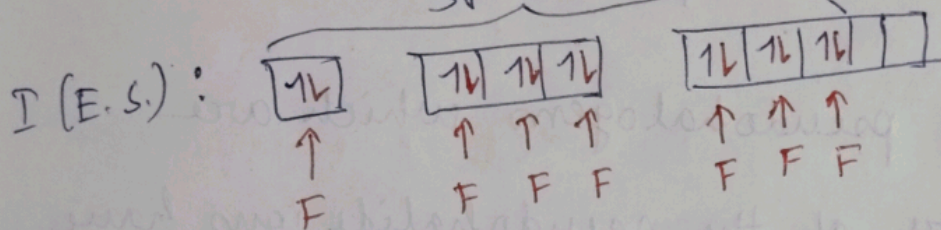
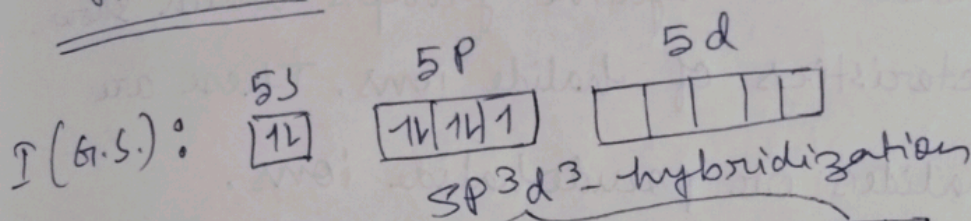


Type XY_5 : eg. IF_5 , BrF_5

Structure: square pyramidal.

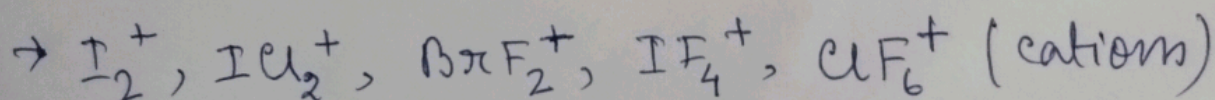
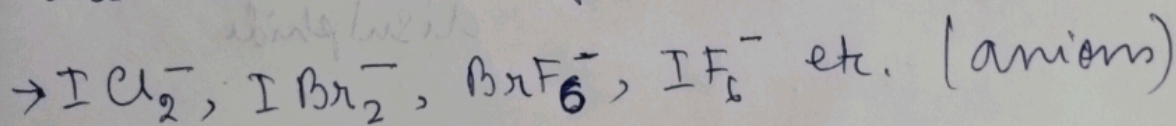


Type XY_7 (IF_7) Pentagonal bipyramidal



Polyhalide ions

In addition to neutral interhalogens, some interhalogen and polyhalogen anions and cations are also known, eg.



Pseudohalides and pseudohalogens:

There are several uni-negative groups which show certain characteristics of halide ions. These are called pseudohalides or pseudohalide ions.

So far, four pseudohalogens which are covalent dimers of the pseudohalide ions have been isolated. They are:

<u>Pseudohalide ion</u>	<u>Formula</u>	<u>Pseudohalogen</u>	<u>Formula</u>
Cyanide	CN^-	Cyanogen	$(\text{CN})_2$
Thiocyanate	SCN^-	Thiocyanogen	$(\text{SCN})_2$
Selenocyanate	SeCN^-	Selenocyanogen	$(\text{SeCN})_2$
Azidothiocarbonate	SCSN_3^-	Azidothiocarbon disulphide	$(\text{SCSN}_3)_2$

Some similarities of pseudohalogens with halogens:

- (1) Pseudohalogens are volatile like halogens
- (2) With hydrogen, the pseudohalide ions, like halide ions gives acid.
- (3) Pseudohalides of Ag, Pb and Hg [eg. AgCN , $\text{Pb}(\text{CNS})_2$, HgCNS] are insoluble like corresponding halides (eg. AgCl , PbCl_2 , Hg_2Cl_2)

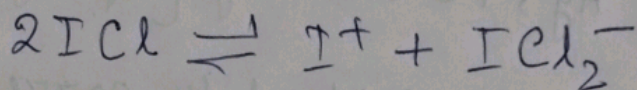
Basic character of iodine:

The ionization energy of elements decreases down the group. ~~Though, halogens~~ Thus, the non-metallic character of halogens decreases down the group and the last element, Iodine behaves as metalloid.

It can form I^+ and I^{3+} ion.

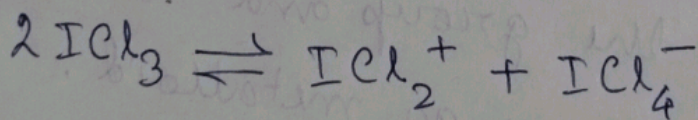
Evidence for the existence of I^+ ion:-

On electrolysis of molten ICl , a mixture of iodine and chlorine is liberated at the anode while only iodine is liberated at the cathode. This suggests that ICl ionizes as



Evidence for the existence of I^{3+} ion:-

On electrolysis of molten ICl_3 , a mixture of iodine and chlorine are liberated at both the electrodes. This suggests ionization of ICl_3 as:



This indicates that ICl_2^+ and ICl_4^- ions contain iodine in the form of I^{3+} ions.