

Unit - I :- P-Block :- Group - 13

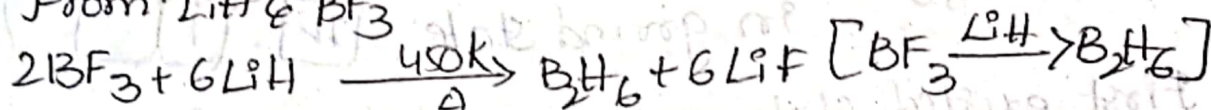
Electron deficient compounds: The compounds containing less no. of e⁻s than required for bonding are called as e⁻ deficient compounds.

Ex: Diborane (B₂H₆), Al₂Cl₆ etc.

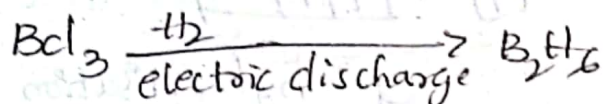
Diborane (B₂H₆)

→ preparation of Diborane:-

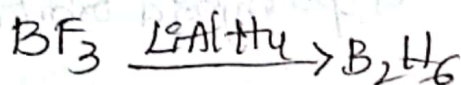
i, From LiH & BF₃



ii, From electric discharge



iii, From BF₃ and LiAlH₄



Structure of Diborane

* In B₂H₆ two planar BH₂ groups are present.

* These 2-BH₂ groups are linked through 2H₂ atoms.

* The 4-hydrogens attached to 2 BH₂ groups are called as 'Terminal Hydrogens' (H_t) & the 2 hydrogens linking the 2 BH₂ groups are called as 'Bridge hydrogen' (H_b).

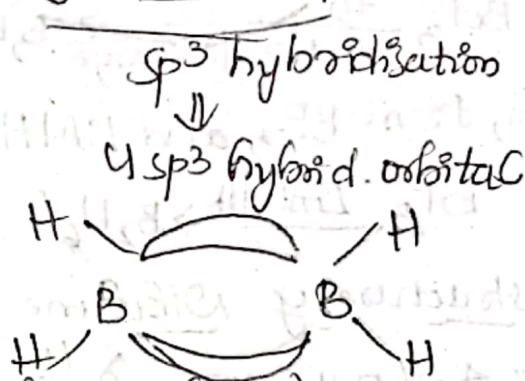
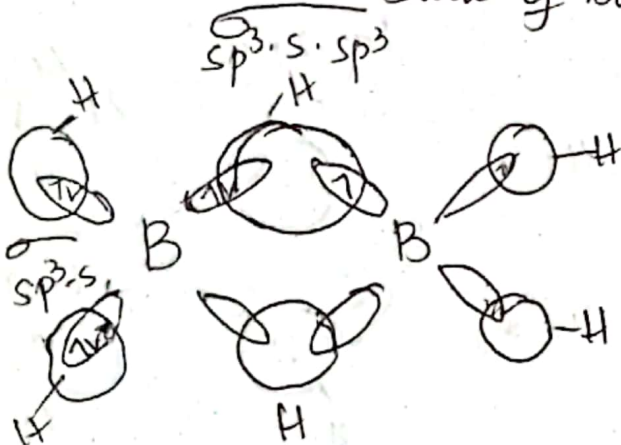
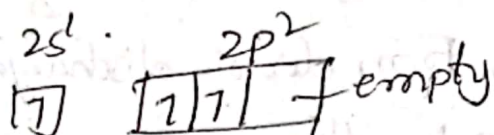
In Diborane, each boron atom undergoes sp³ hybridisation in its 1st excited state to form 4 sp³ hybrid orbitals, out of these 4-sp³ hybrid orbitals, 3 orbitals have unpaired electrons and the 4th sp³ hybrid orbital is vacant. Now in each boron atom, two sp³ hybrid orbitals with unpaired e⁻s overlap

with 1s orbitals of 2-hydrogen atoms to form two normal $2C-2e^-$ bonds (B-H bonds). The 3rd sp^3 hybrid orbital of each boron atom with unpaired e^- , the 1s orbital of two ^{bridged} hydrogen atoms to form 2 normal $2C-2e^-$ bonds & and the empty sp^3 hybrid orbital of other boron atom overlaps with each other to form B-H-B bond (bridge bonds)

* The valency e^- configuration of B ($Z=5$) $\rightarrow 1s^2 2s^2 2p^1$ in ground state



First excited state of boron - $2s^1$

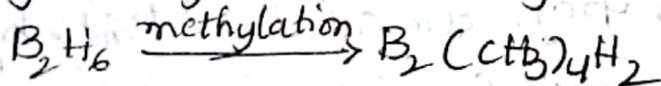


\rightarrow Totally :- 4 B-H bonds ($2C-2e^-$ bonds) &
2 B-H-B bonds ($3C-2e^-$ bonds)

Evidences for above structure

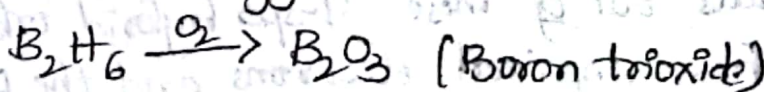
* IR & Raman

* Methylation of Diborane to form Tetra-methyl diborane

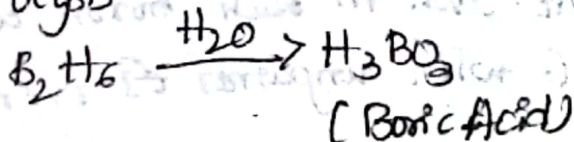


Chemical reactions

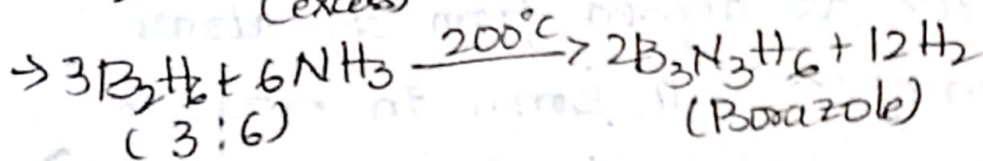
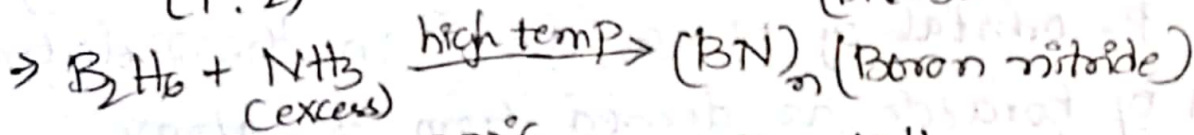
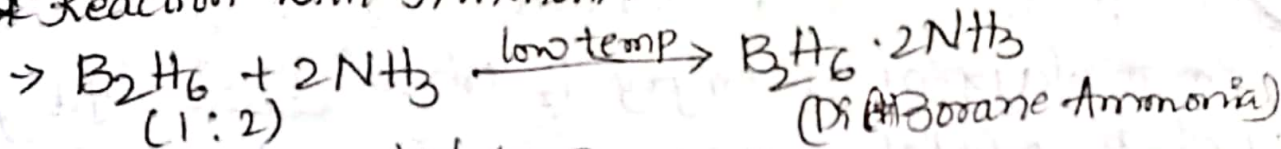
* Reaction with oxygen



* Hydrolysis



* Reaction with Ammonia



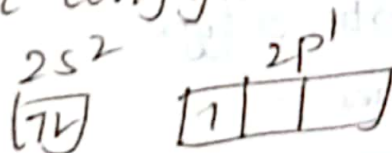
Borazole, Borazine (or) Inorganic benzene

preparation structure of borazole

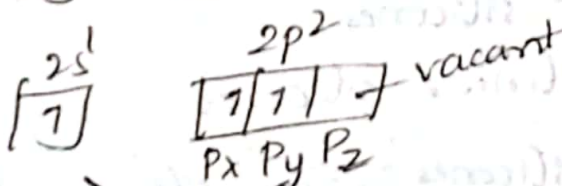
\rightarrow Borazole is iso-electronic benzene. The structure of borazole is similar to that of benzene & borazole has cyclic delocalised π -electron cloud similar to benzene (Dative π -electron cloud) due to this borazole is called Inorganic benzene.

\rightarrow Borazole is a planar molecule in which boron and nitrogen atoms are sp^2 hybridised in 1st excited state.

\rightarrow The valency electronic configuration of B ($Z=5$) in ground state

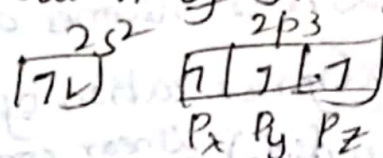


1st excited state

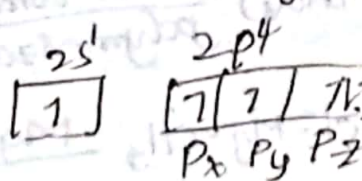


$sp^3 \rightarrow 3 sp^2$ hybrid orbitals

\rightarrow The valency e^- configuration of Nitrogen ($Z=7$) - G.S



1st excited state



Fully filled P_z -orbital

$sp^2 \rightarrow 3 sp^2$ hybrid orbitals

→ In borazole, the π bonding is dative & it arises from overlapping of empty p_z orbital of B & fully filled p_z orbital of N. So, the e^- in the π -electron cloud of borazole are derived from 3N-atoms

→ The function of σ & π bonds in borazole is ~~an~~

Evidences for structure of borazole

→ X-ray spectra

→ Electron diffraction spectra

Group-14 Silicones

Silicones :- The organo silicon polymers containing -Si-O-Si- linkages are called as silicones.

Ex: silicone rubbers, silicone oils, silicone resins

Classification of silicones :- Based on structure silicones are classified into 3 types.

i, Linear silicones

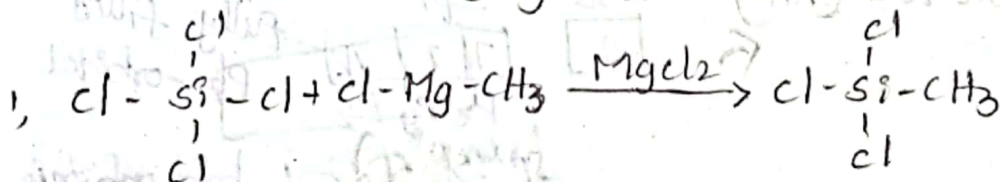
ii, cyclic silicones

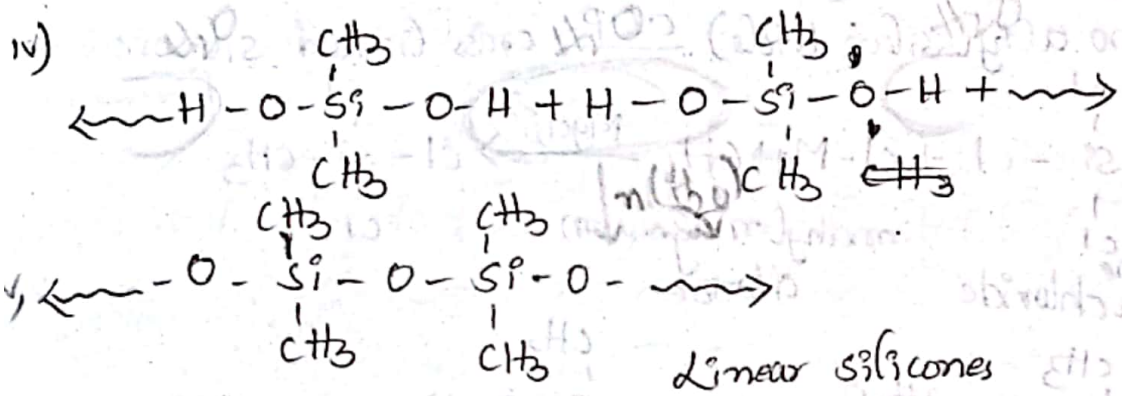
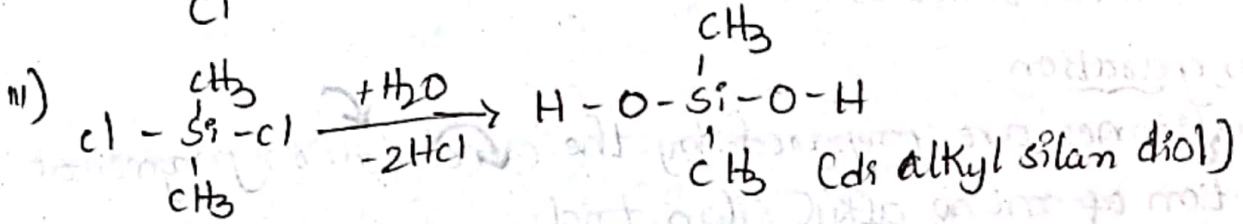
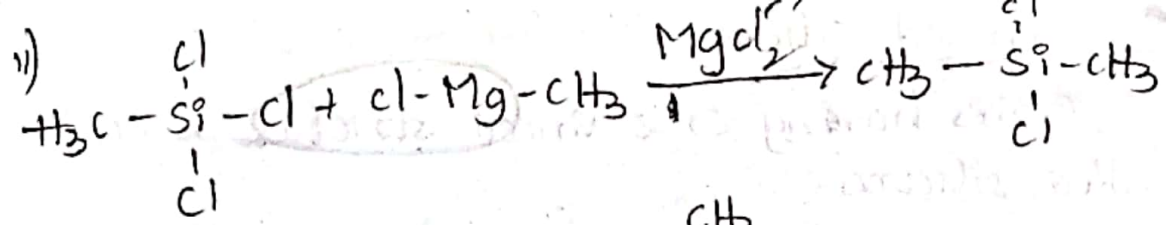
iii, cross-linked silicones

Linear silicones :- The silicones having linear structure are called as linear silicones.

Preparation :- Linear silicones are prepared by the condensation polymerization of 'Di alkyl silicon diols'

$n(\text{Di alkyl silan diols}) \xrightarrow[\text{Polymerization}]{\text{Linear condensation}}$ linear silicones

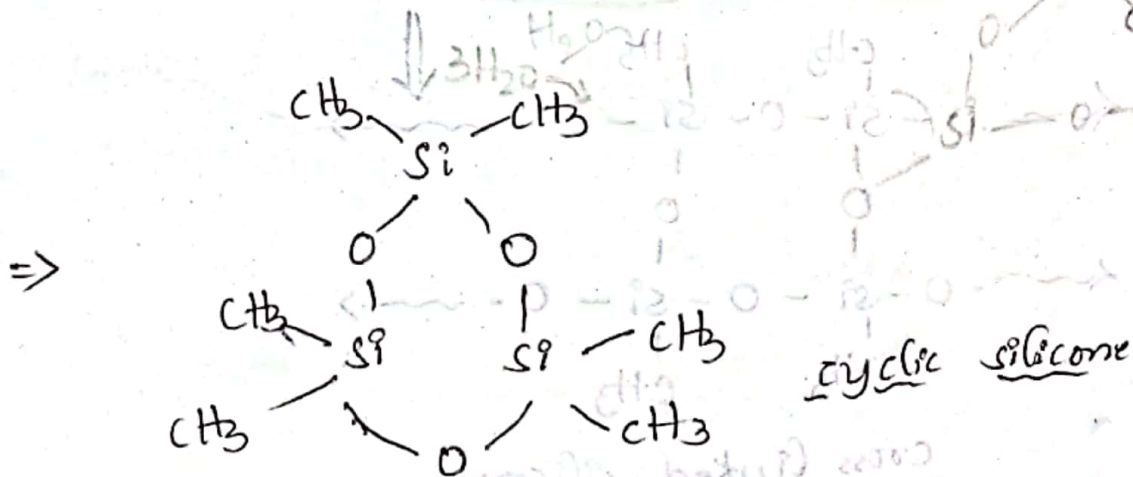
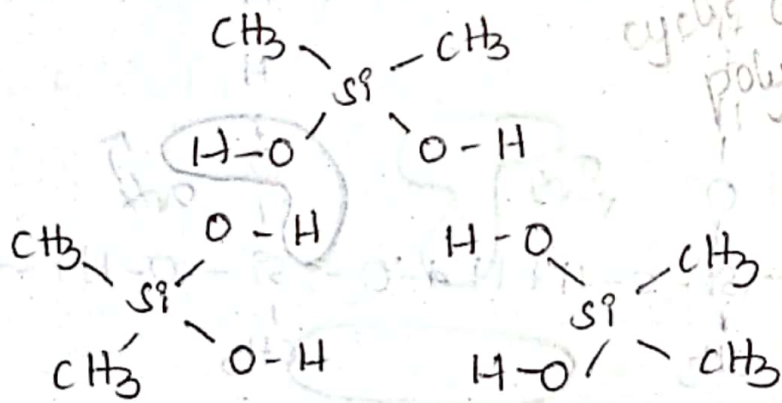
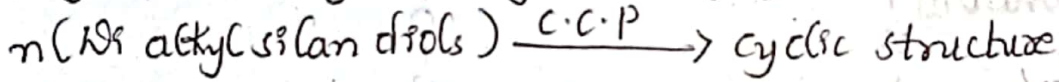




Preparation of cyclic silicones

The silicones having cyclic structure is called cyclic silicones.

cyclic silicones are prepared by cyclic condensation polymerization of di-alkyl silan diols



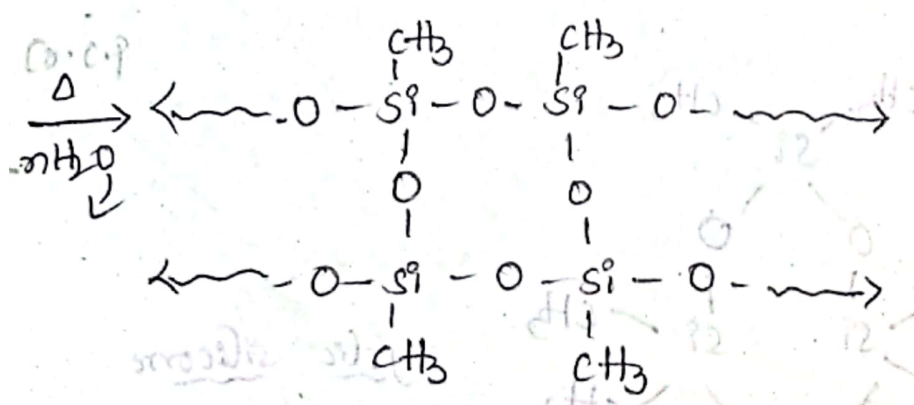
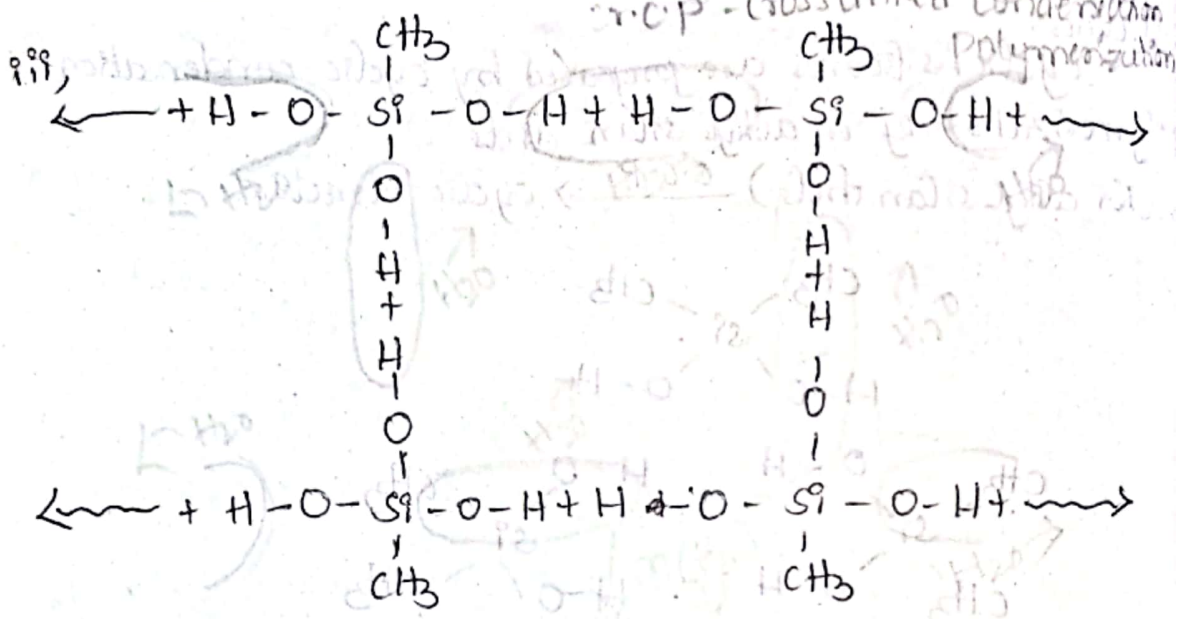
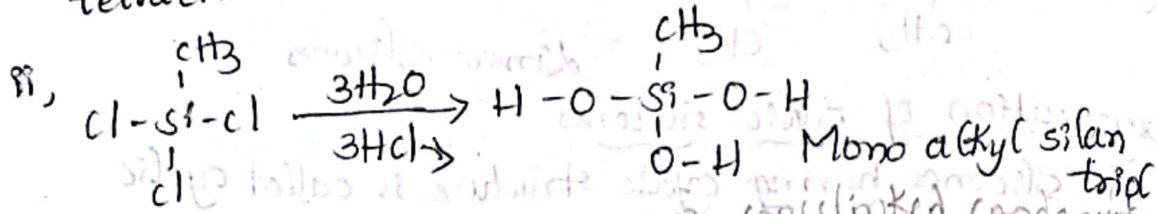
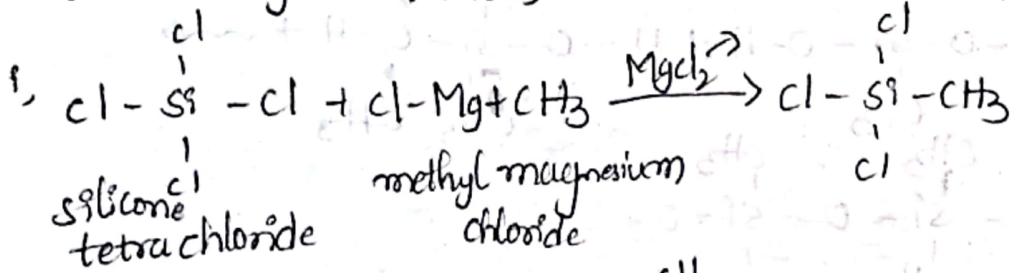
cross linked silicones

The silicones having cross linked structure is called cross linked silicones.

preparation

silicones are prepared by the condensation polymerization of mono alkyl silan triols

$n(\text{mono alkyl silan triols}) \xrightarrow{\text{C.C.P.}}$ cross linked silicone



cross linked silicone

Uses :- Applications of silicones

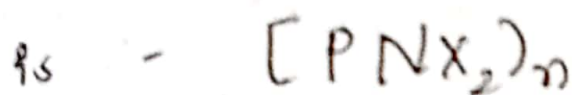
- silicones are used in preparation of rubbers
- silicones are used in preparation of water proof rain coats and papers
- silicones are used as oil & greases in air crafts (to the reason for use, it doesn't freeze at 40°C)
- silicones are used in preparation of paints and creams
- silicones are used in preparation of insulation materials and seals due to their high thermal stability.

p-block ; - Group - 15 elements

phospho nitric Halides $(PNX_2)_n$
(06)

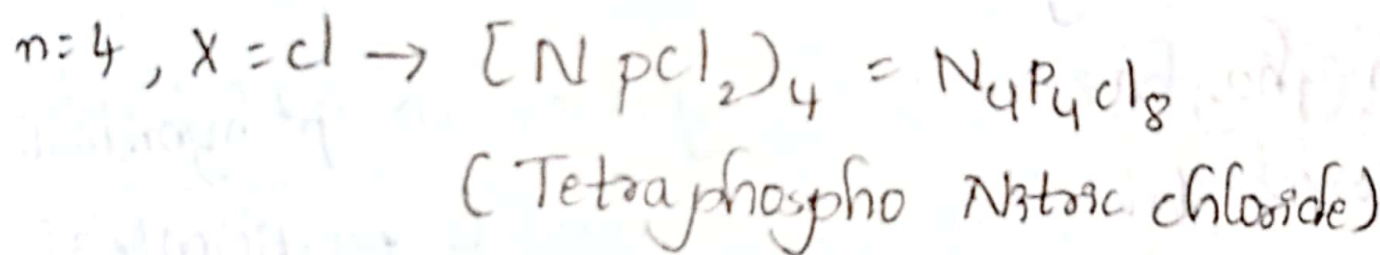
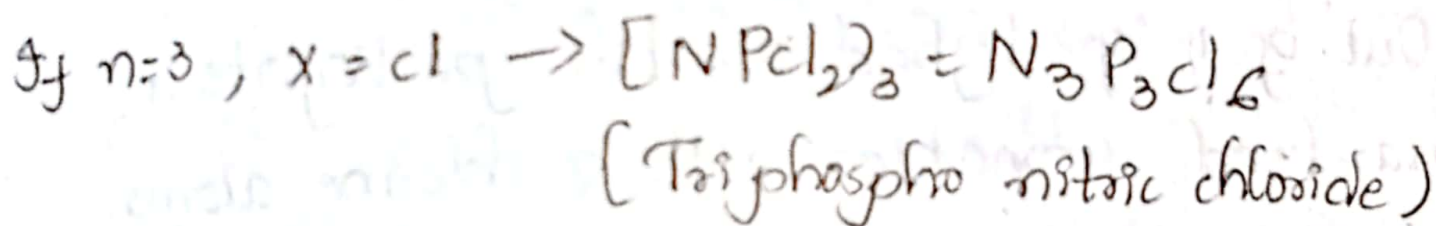
phosphazenes

General formula for phospho nitric halides



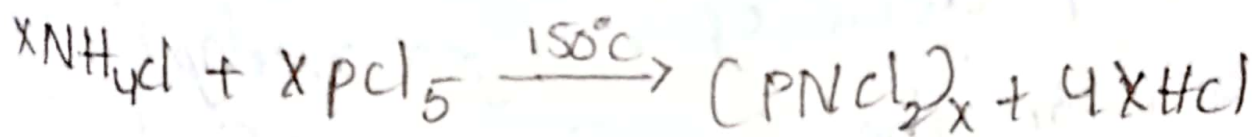
where, $X = \text{Halogens}$

F, Cl, Br, I

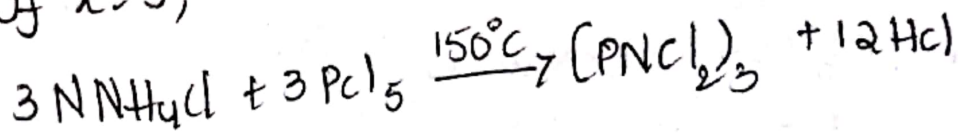


preparations of phosphazenes

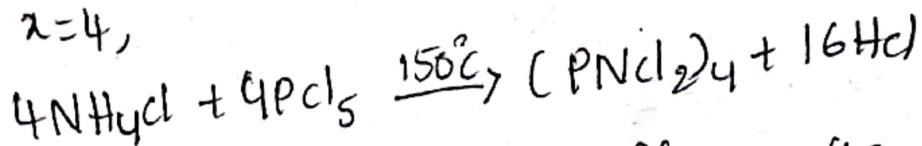
1) Heating of ammonium chloride with phosphorus pentachloride at $150^\circ C$ form phosphonitric chlorides,



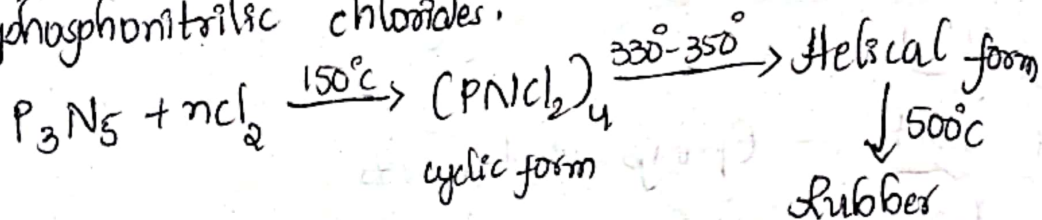
If $x=3$,



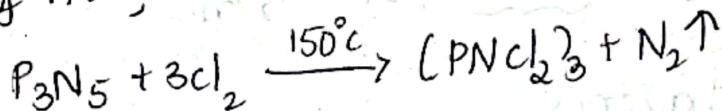
$x=4$,



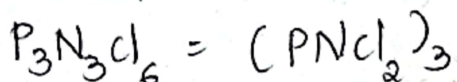
2) Heating of P_3N_5 with chlorine forms phosphonitric chlorides.



If $n=3$,



Structure of phosphazenes



In phosphazenes, phosphorous atom undergoes sp^3 hybridisation in its 1st excited state.

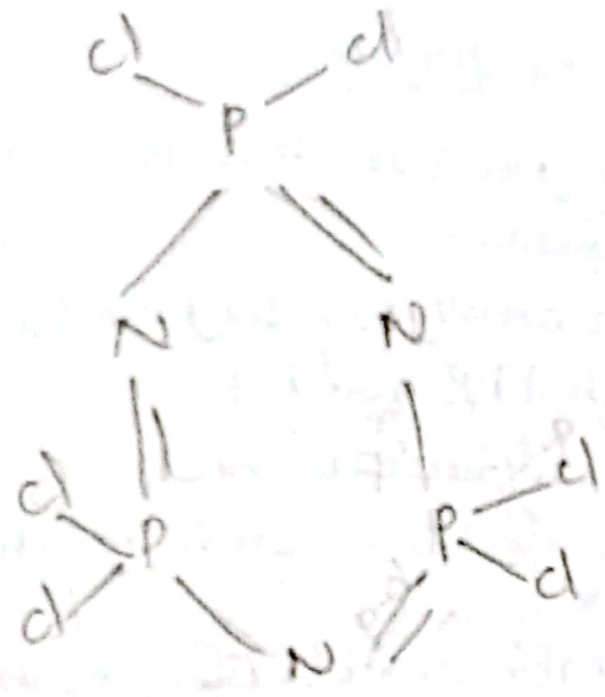
Out of 4 sp^3 hybrid orbitals participate in sigma bond formation with 2 chlorine atoms and two nitrogen atoms.

In phosphazenes, nitrogen is in sp^2 hybridisation in ground state. Two hybrid orbitals participate in sigma bond formation with 'p' atom. one hybrid orbital with lone pair remains on nitrogen.

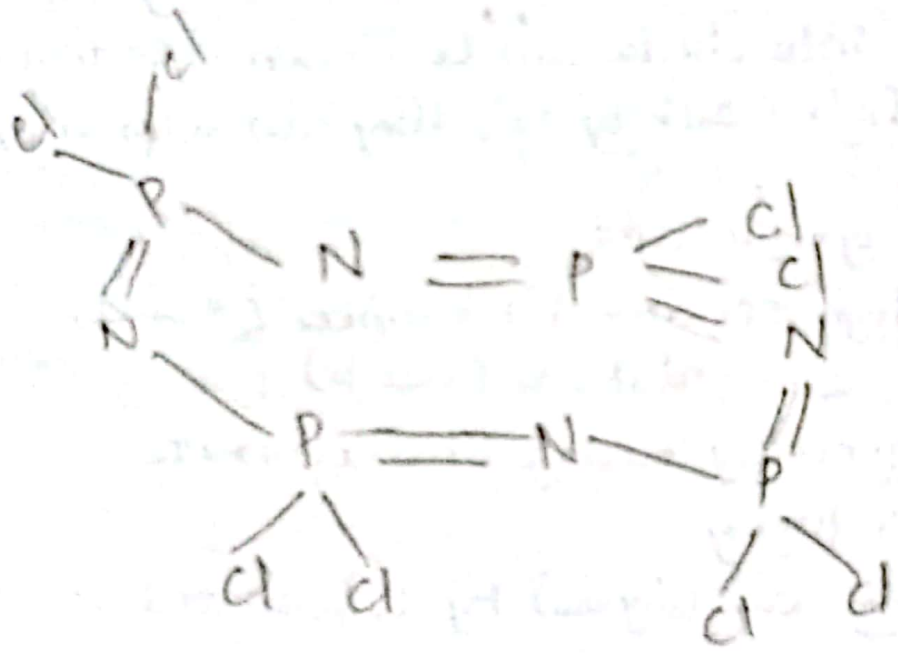
The unhybridised d orbital of phosphorous and unhybridised 'p' orbital of nitrogen overlap side wise results in the formation of π bonds.

Trimer has planar type structure where as remaining polymers have pyramidal ring structures.

Structure of $P_3N_3Cl_6$ (Trimer)



$P = sp^3$ (1st excited state)
 $N = sp^2$ (ground state)



Structure of $P_4N_4Cl_8$

phosphorous atom $\rightarrow sp^3$ hybridisation
 (1st excited state)

Nitrogenation $\rightarrow sp^2$ hybridisation
 (ground state)

π -bond $\rightarrow d-p$ overlapping

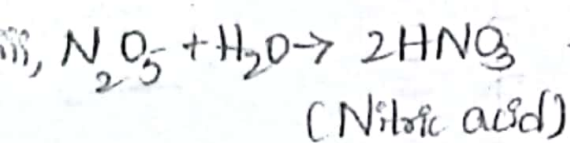
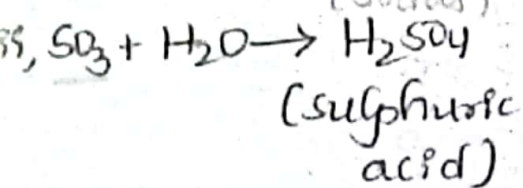
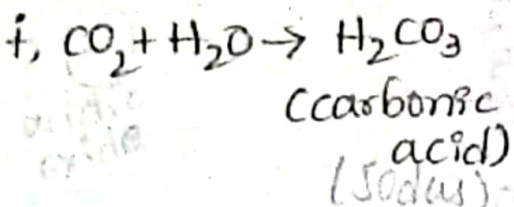
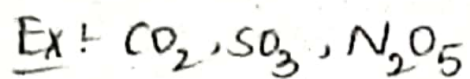
Oxides

- The Binary compounds of O_2 with the other elements are called as oxides.
- classification of oxides based on chemical behaviour.
- Oxides are classified into 4 types based on their chemical behaviour they are
 - i, Acidic oxide [Ex: CO_2, SO_3, N_2O_5]
 - ii, Basic oxide [Ex: Na_2O, CaO, BaO]
 - iii, Neutral oxide [Ex: H_2O, NO, CO, N_2O ...]
 - iv, Amphoteric oxide [Ex: SnO, ZnO, PbO, Al_2O_3]
- Basic and Amphoteric oxides are metallic oxides where as Acidic and Neutral oxides are Non-metallic oxides.

Types of Oxides

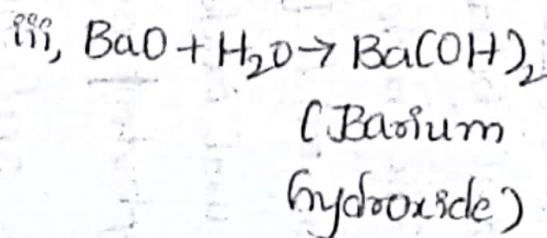
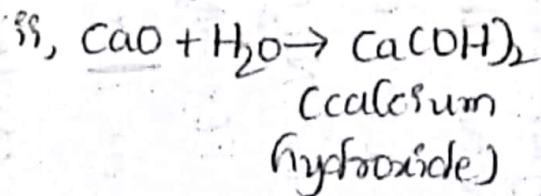
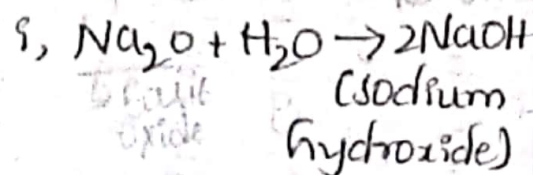
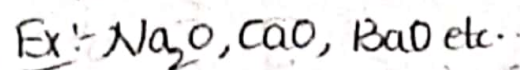
Acidic oxides

→ The oxides which reacts with water to form acids are called 'acidic oxides'



Basic oxides

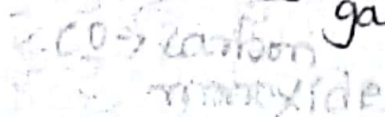
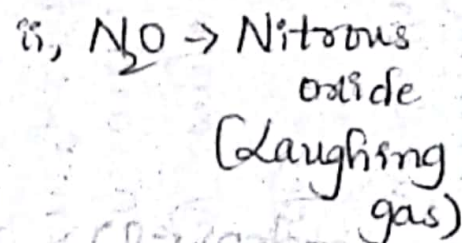
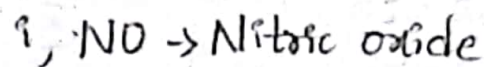
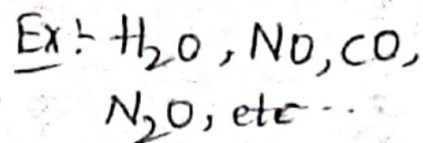
→ The oxides which reacts with water to form bases are called 'basic oxides'



Based on chemical behaviour

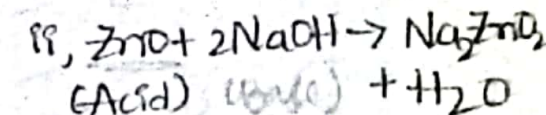
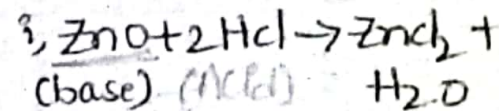
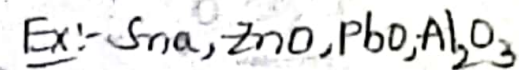
Neutral oxides

→ The oxides which are neither acids nor bases are called as 'Neutral oxides'



Amphoteric oxides

→ The oxides which have both acidic & basic characters are called as Amphoteric oxides



→ Here ZnO possess both acidic & basic characters. So 'ZnO' is an amphoteric oxide.

Classification of oxides based on O₂ content

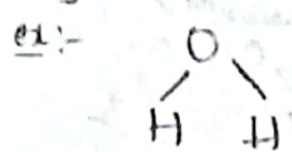
Oxides

Normal oxides

→ The oxides which have sufficient O₂ has permitted by the normal valency of the other element are called as 'Normal oxides'.

Ex: H₂O, MgO, CaO, etc..

→ Normal oxides have only M-O bonds



In normal oxides the oxidation state of O₂ is O⁻²

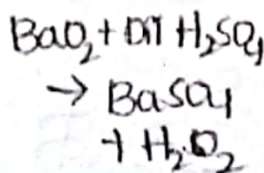
polyoxides

→ Oxides which have more O₂ has permitted by the normal valency of the other element are called as polyoxides
→ It has both M-O & O-O bonds.

peroxides

→ The polyoxides which have O₂²⁻ ion are called as 'peroxides'.

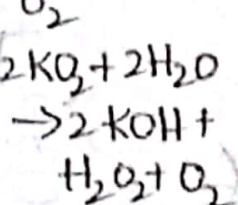
Ex: H₂O₂, BaO₂
peroxides react with dil acids to form H₂O₂



Superoxides

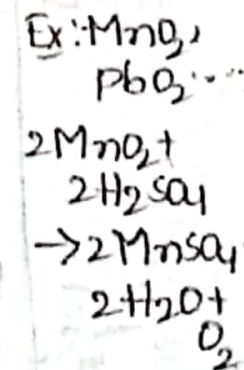
→ The polyoxides which have O₂⁻ are called as super oxides.

Ex: KO₂, CsO₂, RbO₂...
superoxides on hydrolysis gives H₂O₂ & O₂



Dioxides

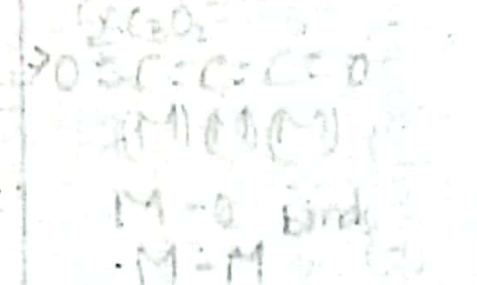
→ Dioxides are also similar to peroxides but they react with dil. acids to form H₂O & O₂



Suboxides

→ Oxides which have less oxygen has permitted by the normal valency of the other element are called as 'suboxides'.

Ex: C₃O₂, N₂O, etc..
⇒ It has both M-O and M-M bonds



Mixed oxides

→ The oxides formed by combination of 2/m normal oxides of an element are called as mixed oxides.

Ex: Fe₃O₄ (Fe₂O₃ + FeO)
⇒ Pb₃O₄ (2PbO + PbO₂)

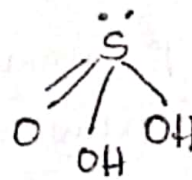
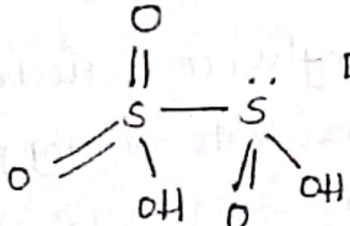
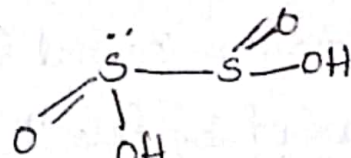
Unit - 1

P-block elements: Group - 1

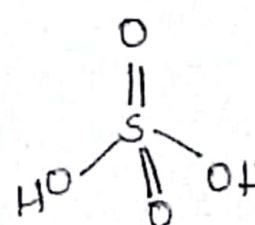
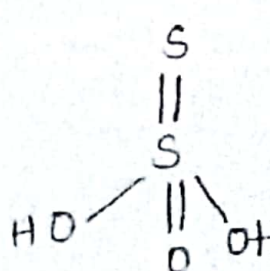
Oxoacids of sulphur

The oxoacids of sulphur are numerous and depict strong π bonding between S and O. Most exist in solution or as crystalline salts. While a few have been isolated. The oxoanions have strong p π -d π bonding and have little tendency to polymerize in contrast to silicates. The oxoacids are listed in four series:

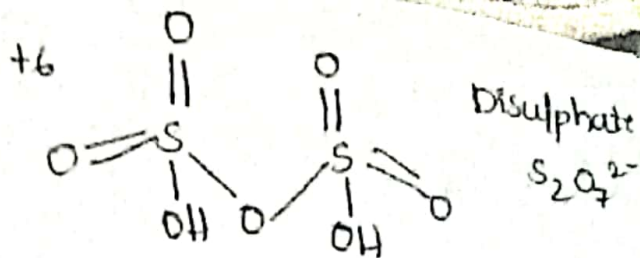
Sulphurous acid series

Formula	Name	Oxidation state	Structure	Salt
H_2SO_3	Sulphurous Acid	+4		Sulphite SO_3^{2-} Hydrogen sulphite HSO_3^-
$H_2S_2O_5$	Dipyrro sulphurous acid	+5, -3		Disulphite $S_2O_5^{2-}$
$H_2S_2O_4$	Dithionous Acid	+3		Dithionite $S_2O_4^{2-}$

Sulphuric acid series

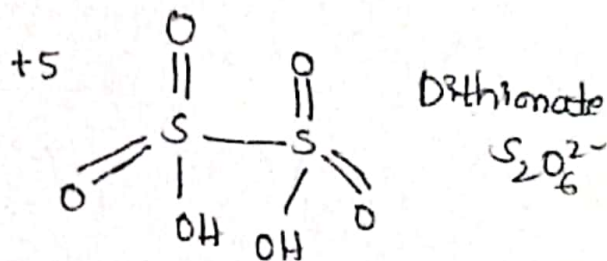
H_2SO_4	Sulphuric Acid	+6		Sulphate SO_4^{2-} Hydrogen sulphate HSO_4^-
$H_2S_2O_3$	Thiosulphuric Acid	+6 -2		Thiosulphate $S_2O_3^{2-}$

$H_2S_2O_7$ Pyro or Sulphuric Acid

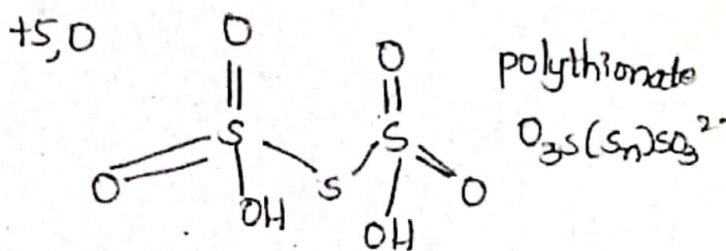


Thionic acid series

$H_2S_2O_6$ Dithionic acid

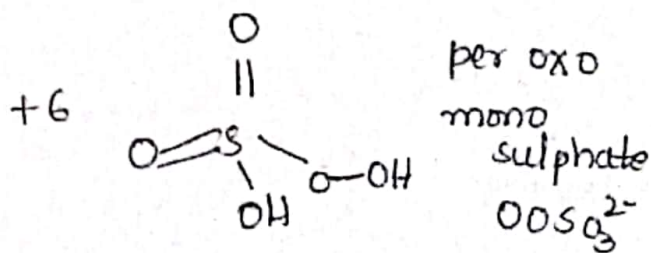


$H_2S_{10}O_{26}$ polythionic acid

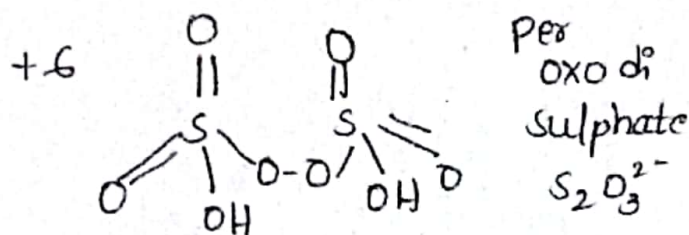


Per oxo acid series

H_2SO_5 per oxo mono sulphuric acid



$H_2S_2O_8$ per oxo di sulphuric acid



Unit - 1 - p-block

Group - 17 :- pseudohalogen compounds

A pseudo halogen can be defined as 'A molecule consisting of 2 or more electronegative atoms, which resemble the halogen atoms. The corresponding univalent anion which resemble the halide ion in their behaviour are called as 'pseudohalogens'

pseudo halogens

cyanogen - $(\text{CN})_2$

Thiocyanogen - $(\text{SCN})_2$

Oxycyanogen - $(\text{OCN})_2$

Hydrozoic acid - NH_3H

pseudohalides

cyanide - CN^\ominus

Thiocyanate - SCN^\ominus

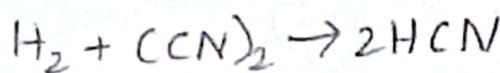
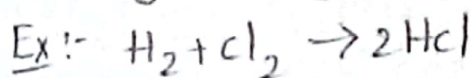
Oxycyanate - OCN^\ominus

Azide - N_3^\ominus

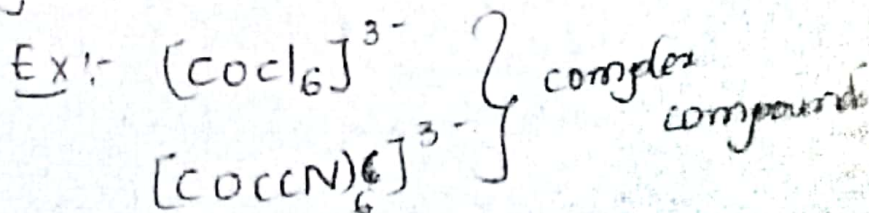
Similarities between pseudohalogens & halogens

* Similar to halogens, pseudohalogens are also diatomic molecules. *bimolecular*

* Similarities between pseudohalogen combines with hydrogen to form mono basic acids.



* Similar to halides, pseudo halides also form complexes.



Interhalogen compounds :- $(ns^2 np^5)$

→ The binary compounds formed by the combination of halogen among themselves are called as Interhalogen compounds.

→ Halogens VIIA [F, Cl, Br, I,]

Ex: ClF_3 , IF_7 , BrF_5

Types of Interhalogen compounds

→ Based on the molecular formula Interhalogen compounds are classified into 4 types

<u>AX</u>	<u>AX₃</u>	<u>AX₅</u>	<u>AX₇</u>
ClF	ClF ₃	IF ₅	IF ₇
BrF	BrF ₃	BrF ₅	
BrCl	I ₂ Cl ₄		
I ₂ Cl ₄			
IBr			

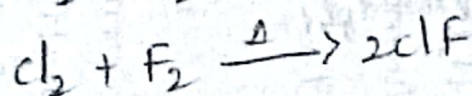
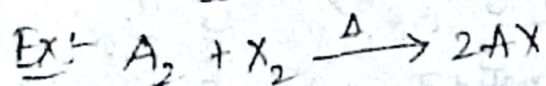
Total no. of stable inter halogen compounds are - 11

→ The main reason for the formation of interhalogen compounds is the large electro negativity and size differences among the different halogens.

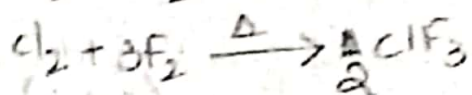
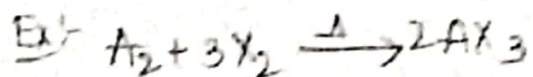
Methods for preparation of Inter halogen compounds

→ Method - I (By direct combination of halogen)

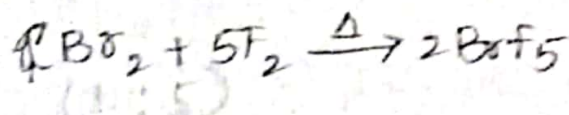
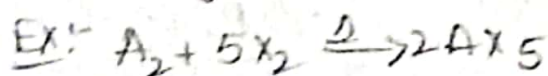
i, AX :- Type (1:1 ratio)



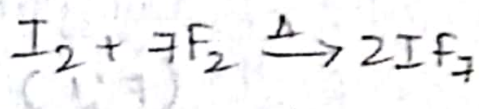
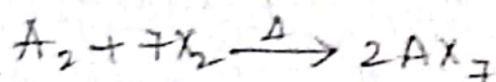
ii, AX_3 type :- (1:3 ratio)



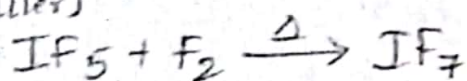
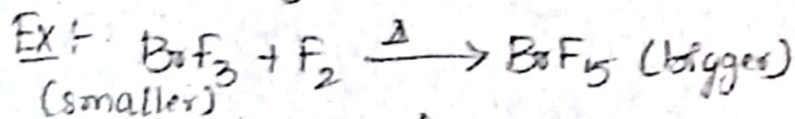
iii, AX_5 type :- (1:5 ratio)



iv, AX_7 type :- (1:7 ratio)



→ Method - II :- preparation of bigger inter halogen compounds from smaller inter halogen compounds



Structures of Interhalogen compounds

i, Structure of AX type Interhalogen compounds :-

→ In AX -type Interhalogen compounds, the central halogen atom 'A' undergoes sp^3 hybridisation in ground state to form $4sp^3$ hybrid orbitals.

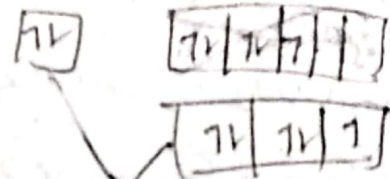
→ out of these $4sp^3$ hybrid orbitals, 3 hybrid orbitals are fully filled and the remaining sp^3 hybrid orbital is half-filled.

→ Now the half-filled sp^3 hybrid orbital of central halogen atom 'A' overlaps with the half-filled p_z orbital of halogen 'X' to form 1 σ bond.

→ So, AX type Inter halogen compounds have linear shape, and the bond angle is 180° .

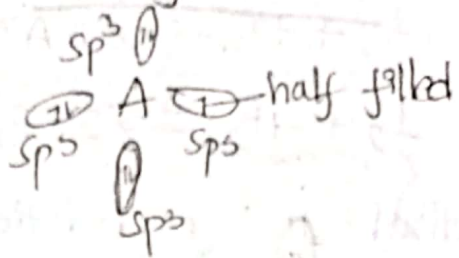
→ The valency electronic configuration of central halogen atom - 'A' in ground state - $ns^2 np^5$

Hybridisation:- Inter mixing of 2 atomic orbitals is called as hybridisation

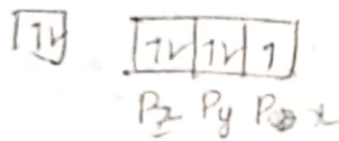


sp^3 hybridisation

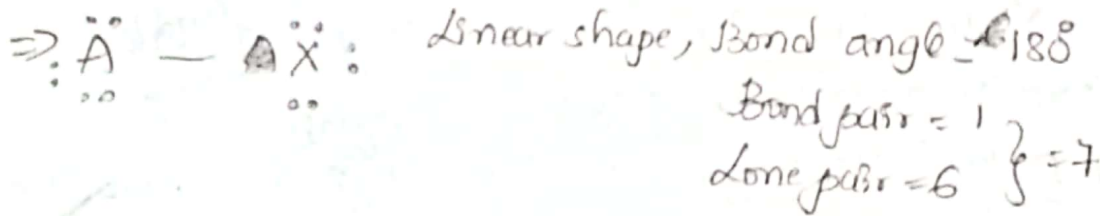
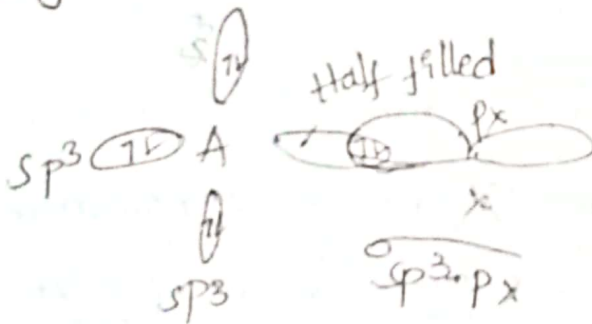
4 sp^3 hybrid orbitals



→ The valency electronic configuration of halogen - 'X' in ground state - $ns^2 np^5$



Bonding



ii) Structure of AX₃ type of Inter halogen compound (ClF₃)

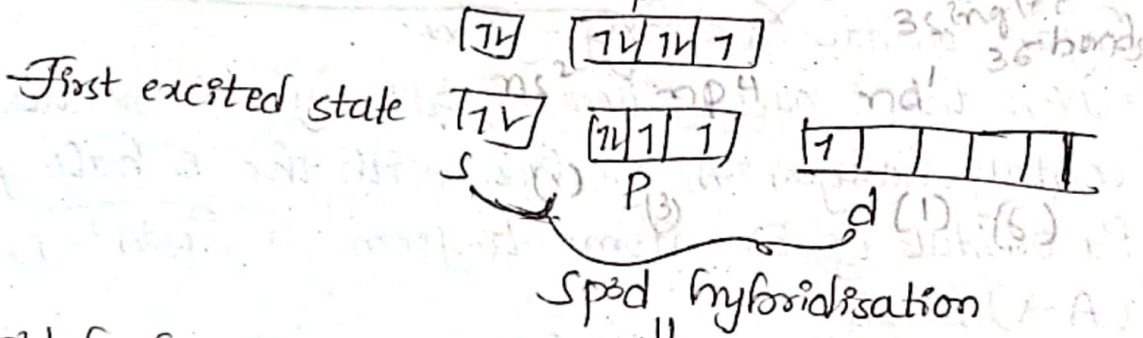
→ In AX₃ type of Inter halogen compounds the central halogen atom - 'A' under goes sp^3d hybridisation in 1st excited state to form 5 sp^3d hybrid orbitals.

→ out of these 5 sp³d hybrid orbitals 2 hybrid orbitals are fully filled, and the remaining 3 hybrid orbitals are half-filled.

→ Now, the 3 half filled sp³d hybrid orbitals of halogen 'A' overlaps with the 3 half filled P_z- orbitals of 3-x halogen atoms to form 3 sp³d p_z (A-x) bonds.

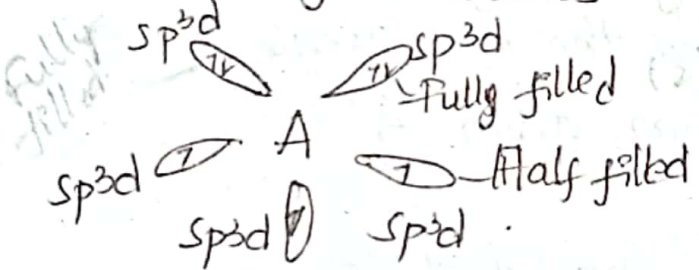
→ so AX₃ type inter halogen compounds have T-shape, and the bond angle is ≈ 87.5°.

→ The valency E.C of central halogen atom 'A' in ground state is equal to ns² np⁵

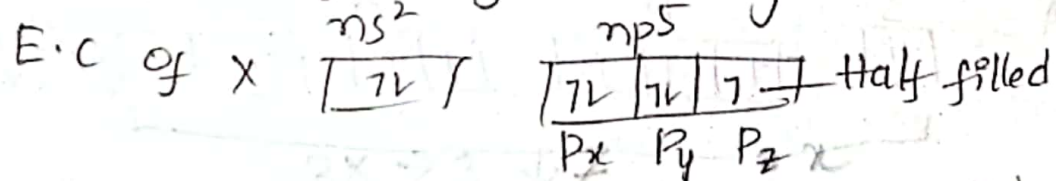


5 sp³d hybrid orbitals

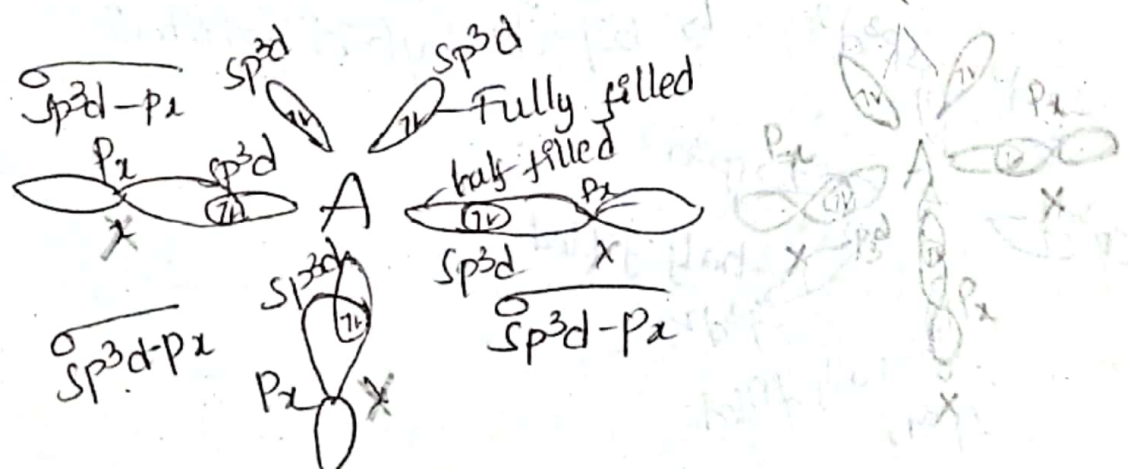
5 sp³d hybrid orbital



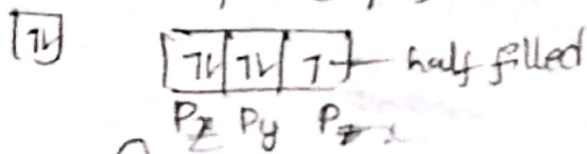
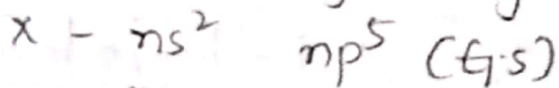
→ The valency E.C of halogen 'x' in ground state



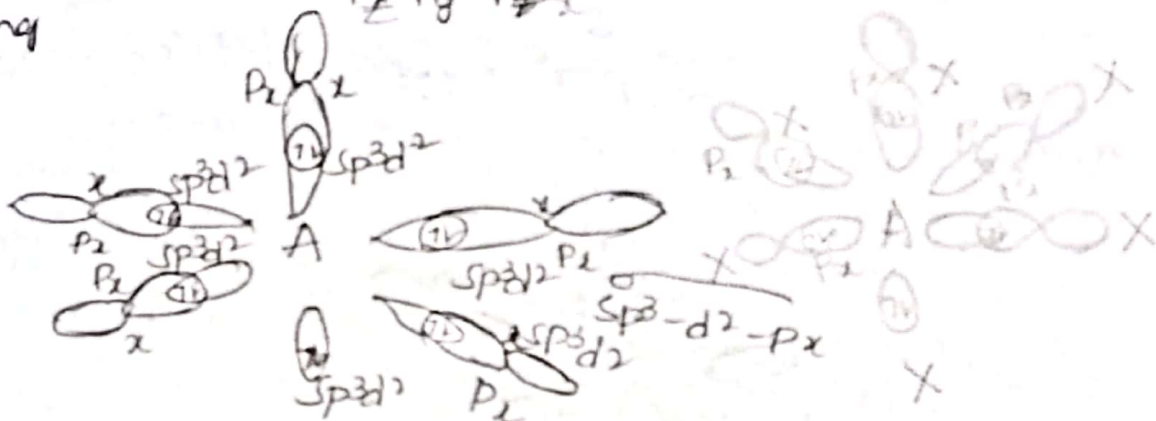
Bonding



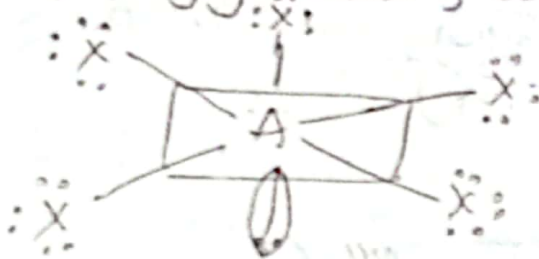
→ The valency E.C of halogen 'X' is $ns^2 np^5$



Bonding



→ shape - square pyramidal ; bond angle = 90°

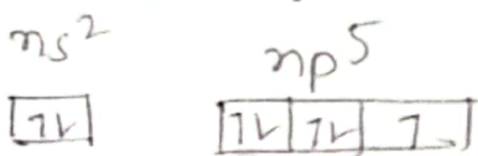


Bond pairs - 5
 Lone pairs - 15
 16

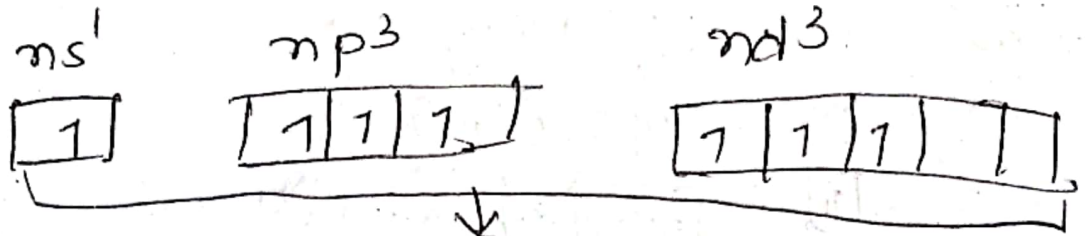
Structure of AX₇ type inter halogen compound

→ In AX₇ type of inter halogen compound the central atom 'A' undergoes sp^3d^3 hybridisation, in 3rd excited state to form seven sp^3d^3 hybrid orbitals having unpaired electrons overlap directly with the 7 p-orbitals of seven other halogen atoms forming seven σ bond. The shape of the molecule is 'pentagonal bi-pyramidal'.

→ The central atom - 'A' electronic configuration of valency electronic configuration in ground state.

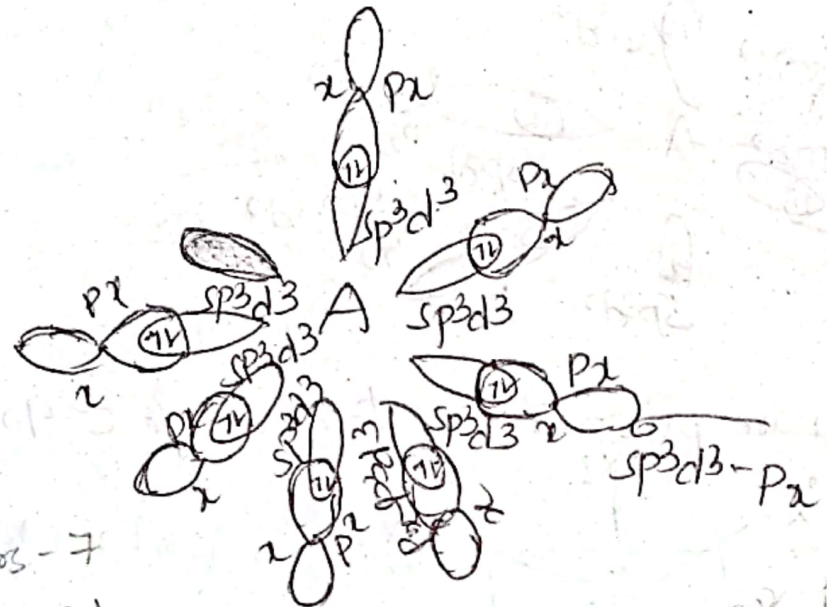


The valency electronic configuration of central atom - A in 3rd excited state.

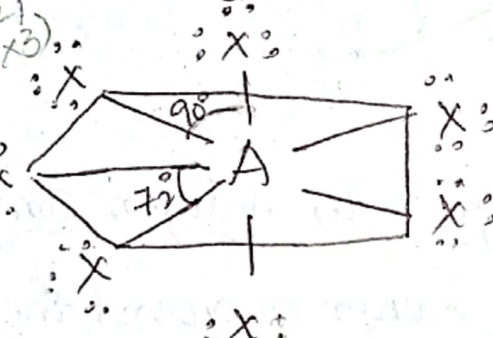


sp^3d^5
 \Downarrow
 7 sp^3d^5 hybrid orbitals

Bonding



Bond pairs - 7
 Lone pairs - 2
 (7x3)



→ shape pentagonal bipyramidal & bond angle is 72° & 90°