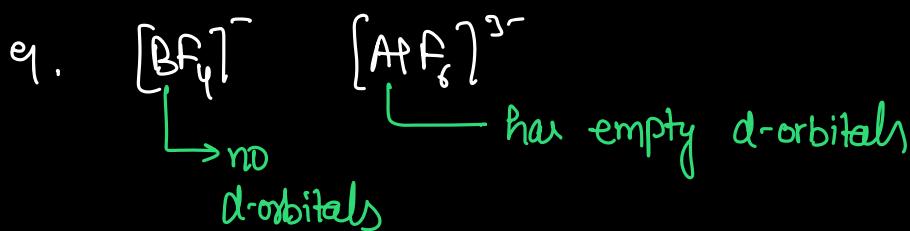
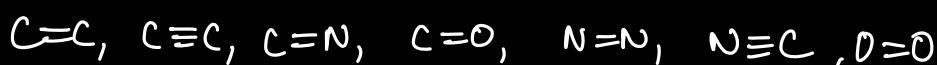


P-Block \rightarrow G: 13 & 14

1. Inert Pair effect

G-13 :	$ns^2 np^1$	\rightarrow 3 valence e^-	$\rightarrow +3, +1$	stability of lower O.S. \uparrow down the group.
G-14 :	$ns^2 np^2$	\rightarrow 4 , ,	$\rightarrow +4, +2$	
G-15 :	$ns^2 np^3$	\rightarrow 5 , ,	$\rightarrow +5, +3$	
G-16 :	$ns^2 np^4$	\rightarrow 6 , ,	$\rightarrow +6, +4$	
G-17 :	$ns^2 np^5$	\rightarrow 7 , ,	$\rightarrow +7, +5$	
G-18 :	$ns^2 np^6$	\rightarrow 8 , ,		

- P-Block \rightarrow
 - metals $\xrightarrow{\text{oxides}}$ Basic
 - non-metals $\xrightarrow{\text{oxides}}$ acidic
 - metalloids $\xrightarrow{\text{oxides}}$ amphoteric
- First member shows anomalous behavior
 - \downarrow
 - small size
 - high E.N.
 - absence of d-orbitals
- forms π -bonds



Al is the most abundant metal & 2nd most abundant element in the earth crust

# <u>BORON family</u>	\rightarrow orthoboric acid	$- H_3BO_3$
	\rightarrow Borax	$- Na_2B_4O_7 \cdot 10H_2O$
	\rightarrow kernite	$- Na_2B_4O_7 \cdot 4H_2O$

Boron exists in many allotropic forms. Boron has unusually high m.p. due to very strong crystalline lattice.

2453K

IE	801	* 577	* 529	558	589
	2427	1816	1979	1820	1971
	3659	2744	2962	2704	2877
	B	Al	Ga	In	Tl

semimetal
(extremely hard)
(Black)

B.P. \downarrow

Atomic radius ($r_{Al} > r_{Ga}$)

IE (I, II, III) - DUDU

density \uparrow

M.P. \downarrow upto Ga & then \uparrow

EN. : First \downarrow then \uparrow

M.P. of Ga = 303K

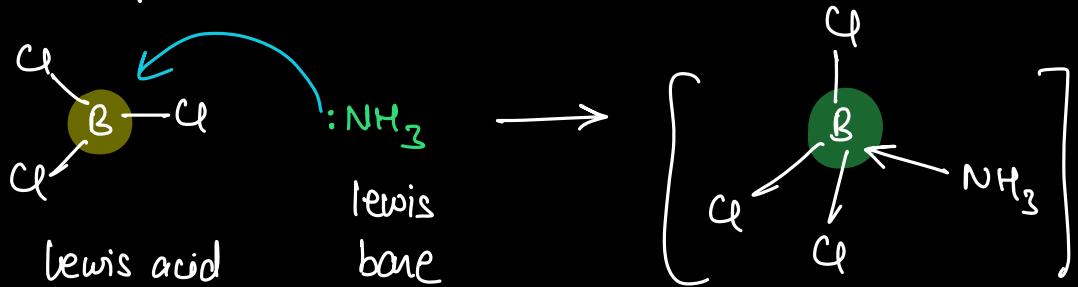
* Compounds in +1 O.S. \Rightarrow More ionic
Compounds in +3 O.S. \Rightarrow More Covalent

*	B	Al	Ga	In	Tl
$M^{3+} M$	-	-1.66	-0.56	-0.34	+1.26
$M^+ M$	-	+0.55	-0.79 (acid) -1.39 (alkali)	-0.18	-0.34
	Al exists only as Al^{3+}		Ga exists as Ga^+ and Ga^{2+} but Ga^+ is more stable in alkali medium		Tl^{+3} is not stable \therefore converts to Tl^+ .

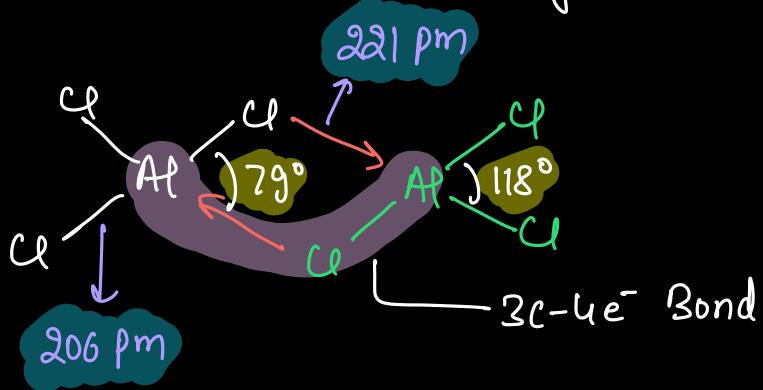
* Tl^+ is more stable than Tl^{+3}



- G-13 compounds \rightarrow e⁻ deficient \rightarrow lewis acid



$\text{AlCl}_3 \rightarrow$ achieves stability via dimer formation



- * In Trivalent state, most of compounds are covalent, undergo hydrolysis in water

* Reactivity Towards air

- Crystalline Boron \rightarrow very unreactive
 Powdered Boron \rightarrow React on heating
- $$2E + 3O_2 \xrightarrow{\Delta} E_2O_3(s)$$
- $$2E + N_2 \rightarrow 2EN(s)$$

- B_2O_3 — acidic
- Al_2O_3, Ga_2O_3 — Amphoteric
- In_2O_3, Tl_2O_3 \rightarrow Basic

* Reactivity with acids & alkalies

- BORON \rightarrow ND Rxn
- $Al + nCl \rightarrow AlCl_3 + H_2 \uparrow$
- $Al + NaOH \rightarrow Na[Al(OH)_4] + H_2 \uparrow$
- $Al + HNO_3 \rightarrow Al_2O_3$ layer formed
 \downarrow
 Renders it passive

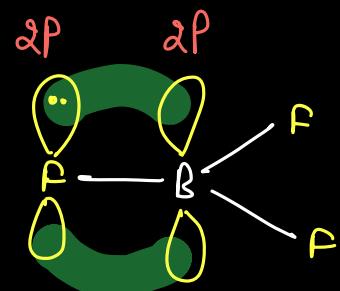
Reactivity Towards halogens

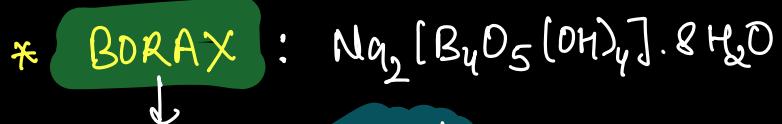
- form bihalides $\gamma.$ $AlCl_3$
 BCl_3
- Al has strong affinity of O_2 :



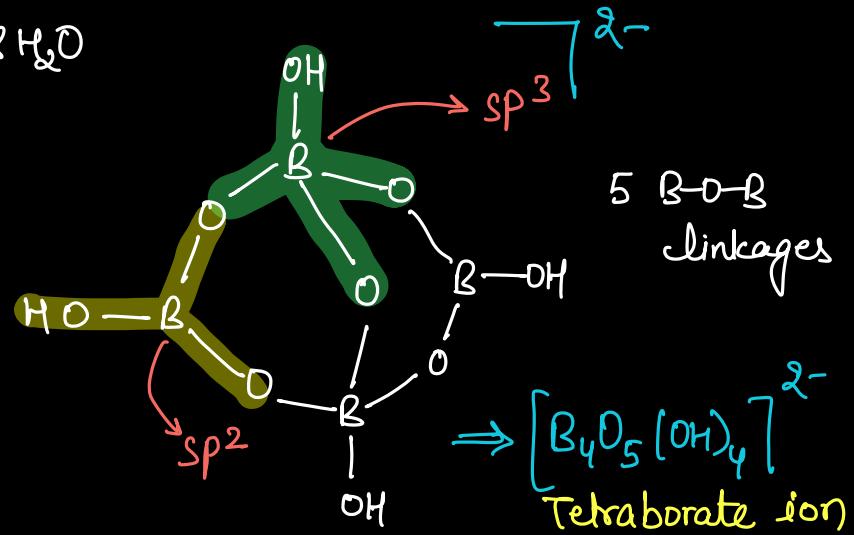
* TlI_3 consists of Tl^+ & I_3^-

* **acidity** : $BF_3 < BCl_3 < BBr_3 < BI_3$
 \uparrow
 Back Bonding





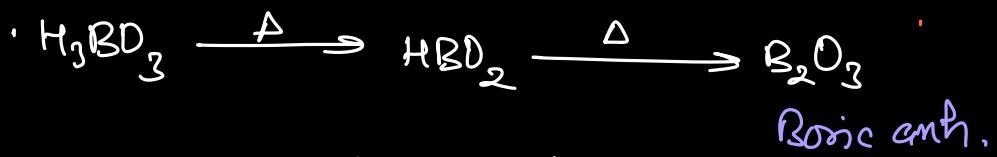
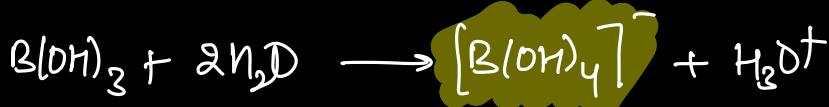
- also called **Tincal**
- white crystalline solid



- $\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \longrightarrow \frac{4\text{H}_2\text{BO}_3}{\text{weak acid}} + \frac{2\text{NaOH}}{\text{strong base}}$ } alkaline soln
- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} \frac{2\text{NaBO}_2}{\text{sod. metaborate}} + \frac{\text{B}_2\text{O}_3}{\text{Boric anh}}$
- Salt + Borax Powder $\xrightarrow[\text{Pt wire loop}]{\Delta \text{ on}}$ colored beads



- * Orthoboric acid
 - weak monobasic acid
 - not a proton donor but OH^- acceptor



- white crystalline solid
- slippery touch
- sparingly soluble in water

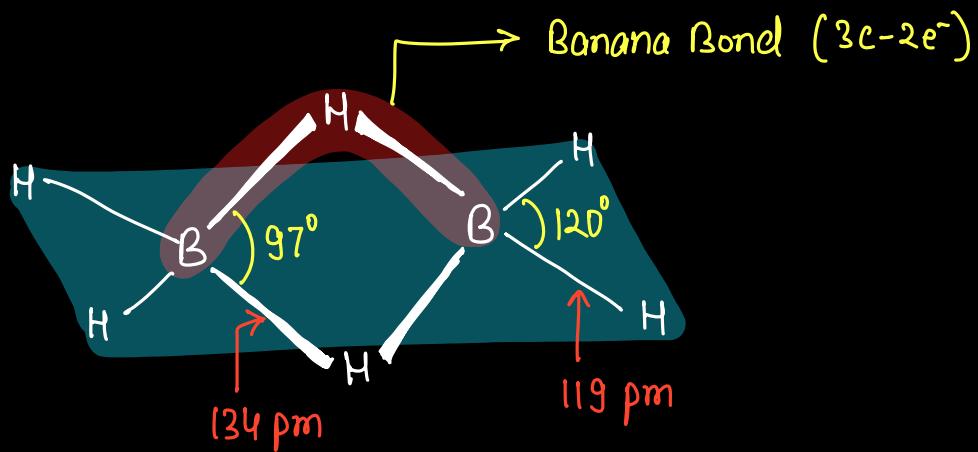
layer structure with
planar BO_3 units

- * Diborane B_2H_6
 - colorless, highly toxic gas
 - burns spontaneously

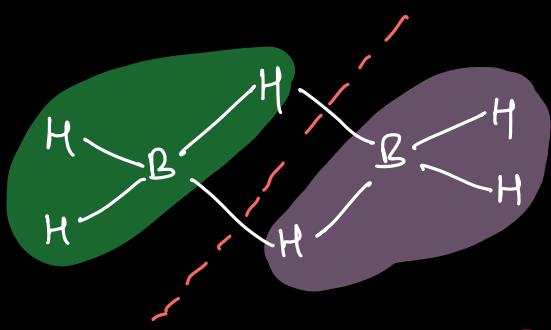
simplest Borane



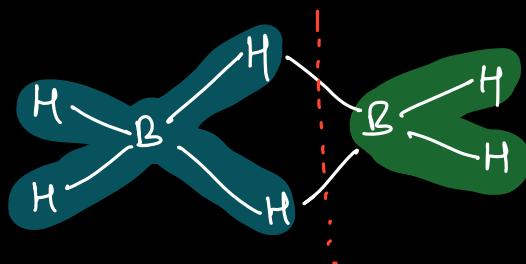
- $\text{B}_2\text{H}_6 + 3\text{O}_2 \longrightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$ $\Delta H_c = -1978 \text{ kJ/mol}$ = Good fuel
- B_2H_6 is e^- deficient \therefore electrophilic



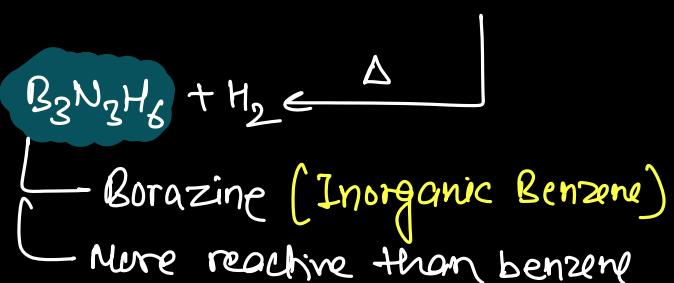
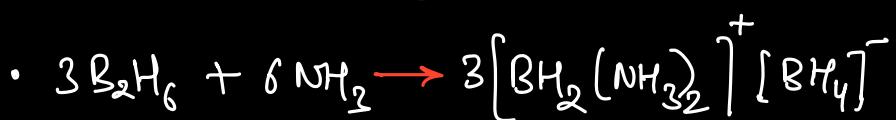
BORON IS 2nd only to carbon in the number of hydrides that it forms.



Symmetrical Cleavage with Bigger Nuc:-



Unsymmetrical Cleavage with Compact Nuc:-



Uses → Boron Fibre = Bullet proof vests
= light composite material for aircraft

^{10}B = absorbs neutrons

Borax & Boric acid → heat resistant glass
→ glass wool
→ fibreglass
↓
as flux for soldering

Carbon Family :

Non-metals		Metalloid	Metals
C	Si	Ge	Sn
$\text{C}^{12}, \text{C}^{13}$ = stable C^{14} = radioactive	↓ ceramics electronics glass cement		Pb ↓ SnO_2

Ionic & covalent radii ↑

IE ↓ upto Sn then ↑ for Pb
($\text{IE}_1, \text{IE}_2, \text{IE}_3$ & IE_4)

E.N. ↓ first then almost const.

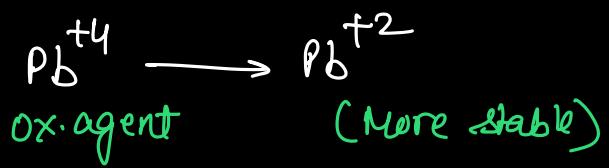
M.P. ↓ upto Sn then ↑

R.P. ↓

density ↓ first then ↑

	C	Si	Ge	Sn	Pb
E.N.	2.5	1.8	1.8	1.8	1.9
M.P.	4373 K	1693	1218	505	600
R.P.	—	3550	3123	2896	2024
density	3.51	2.34	5.32	7.26	11.34

Element	O.S.
C	+4, +2, -4
Si	+4, -4
Ge	+4, -4
Sn	+2, +4
Pb	+2, +4



* **Oxides** \rightarrow MO 9. CO , SiO , GeO

\rightarrow MO_2 9. CO_2 , SiO_2 , GeO_2 , PbO_2 , SnO_2

CO_2 , SiO_2 , GeO , GeO_2 = acidic

SnO , SnO_2 , PbO , PbO_2 = Amphoteric

CO = Neutral

* Reactivity Towards water

- C, Si, Ge \Rightarrow No Rxn
- Sn $\xrightarrow{\text{Steam}}$ $\text{SnO}_2 + \text{H}_2$
- Pb \rightarrow unaffected due to PbO layer on its surface

* Reactivity towards halogens

halides \rightarrow MX_2

GeX_4 is more stable than GeX_2
 PbX_2 than PbX_4

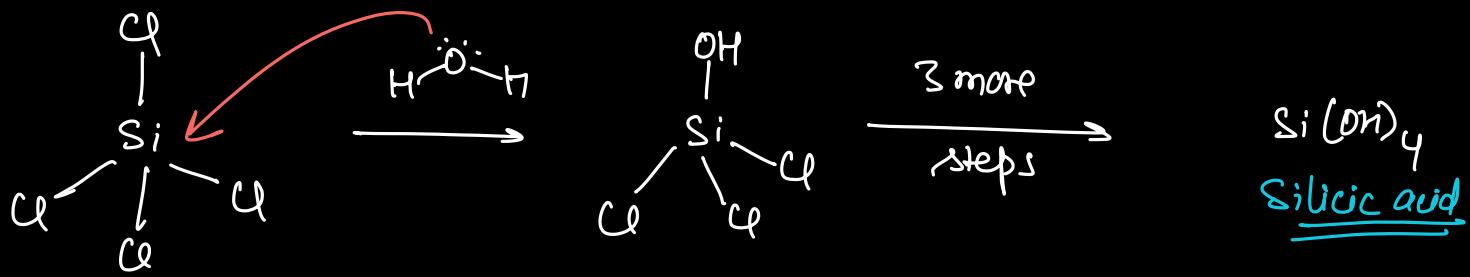
\rightarrow MX_4 (Mostly covalent) SnF_4 & PbF_4 are ionic

* PbI_4 doesn't exist — b'coz weak Pb-I bond can't compensate for excitation of 6s e^-

G.S. $6s$
 $\boxed{11} \quad \boxed{111} \quad \boxed{}$

F.S. $\boxed{1} \quad \boxed{1111}$

* Except CCl_4 , other MCl_4 are easily hydrolysed.



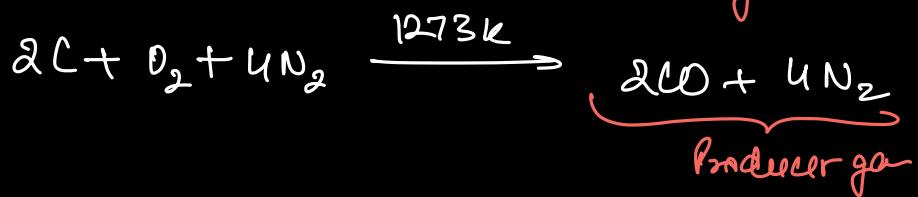
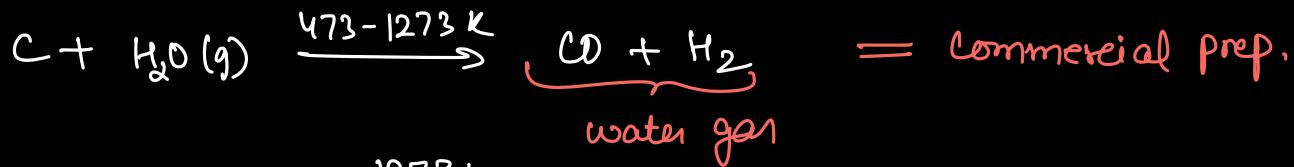
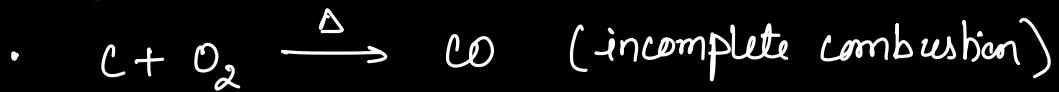
* Catenation: $C \gg Si > Ge \approx Sn$ Pb doesn't show catenation

- **diamond**
 - all C are sp^3
 - higher density than graphite
 - less stable than graphite
 - Non conductor of electricity

- **Graphite**
 - all C are sp^2 → free e^- → conducting
 - layered structure → slippery
 - used as lubricant

- **Fullerenes**
 - C_{60} has 20 hexagons + 12 pentagons
 - C_{60} is aromatic

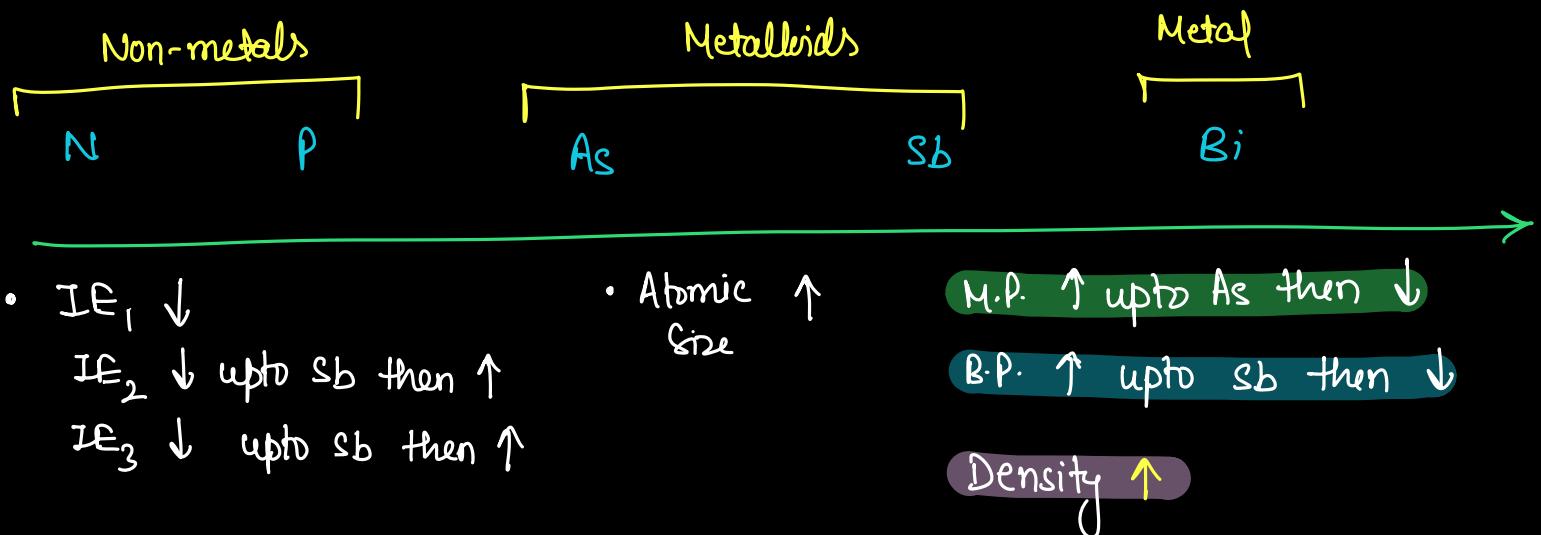
CO → colorless, odorless, insoluble in water



* Carboxyhaemoglobin is 300 times more stable than oxy-haemoglobin

Nitrogen Family

- Fluorapatite : $\text{Ca}_5(\text{PO}_4)_3 \cdot \text{CaF}_2$ → Strong layer on teeth enamel

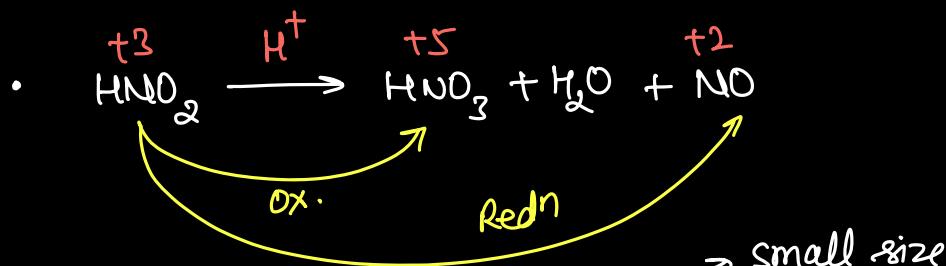


• $\boxed{11} \boxed{1111} \rightarrow$ extra stability

- * • All elements are polyatomic
• Except N, all show allotropy

Ox. States : Common O.S. = +3, -3, +5
Group O.S. = +5

• Bi^{3+} is more stable than Bi^{5+}



* Anomalous Properties of N

→ high EN
→ absence of d-orbitals

• $\ddot{\text{N}}-\ddot{\text{N}}$ bond is weaker than $\text{P}-\text{P}$ bond due to interelectronic repulsion
→ catenation is weaker

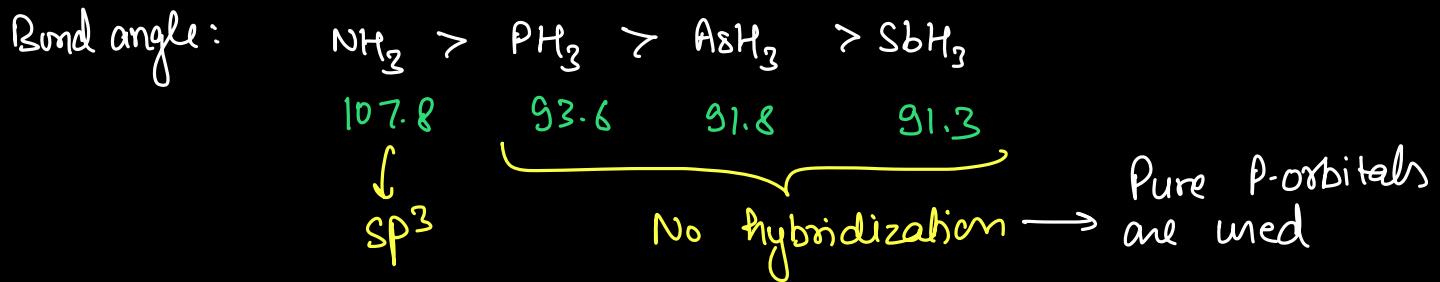
Hydrides

• Stability, Basicity : $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

M.P. : $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$
139.5 156.7 185 195.2

B.P. : $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$

185.5 210.6 238.5 254.6 290



* Oxides $\rightarrow \text{E}_2\text{O}_3$ and E_2O_5

$\text{N}_2\text{O}_3, \text{P}_2\text{O}_3$ — acidic

$\text{As}_2\text{O}_3, \text{Sb}_2\text{O}_3$ — Amphoteric

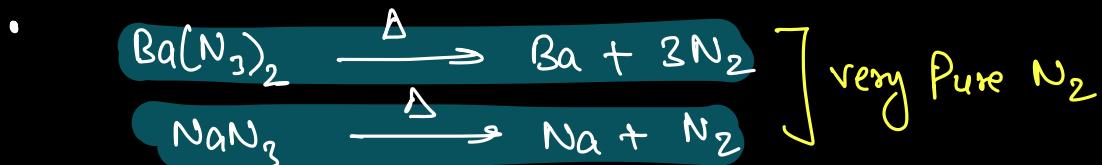
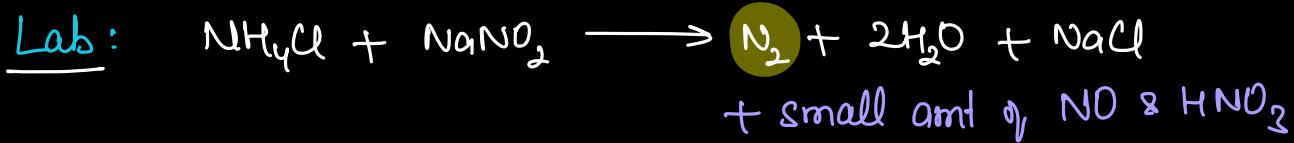
Bi_2O_3 — Basic

Halides $\rightarrow \text{Ex}_3$ and Ex_5

• Except NF_3 , all trihalides of N are unstable.

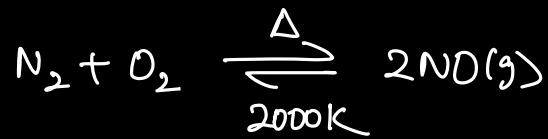
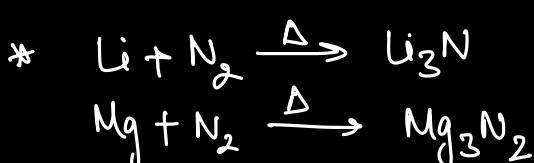
All trihalides except BiF_3 are covalent.

Preparation of N_2



* N_2 is relatively inert \rightarrow high B.E of $\text{N}\equiv\text{N}$
 \rightarrow non-polar
 \rightarrow L.P. is in σ bonding MO

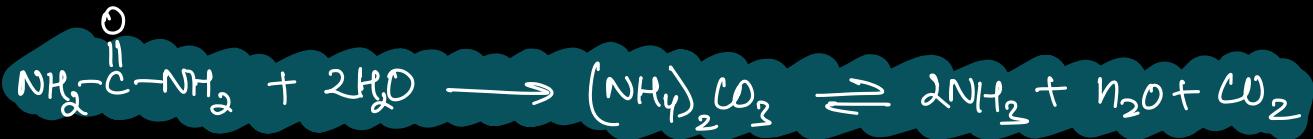
* Isotopes: ^{14}N & ^{15}N



Uses: ① Manufacture of NH_3

- ② Inert atmosphere
- ③ Liquefied N_2 is refrigerant

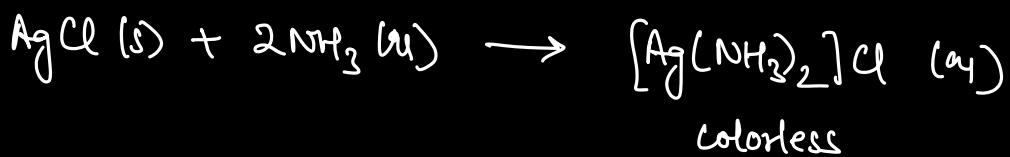
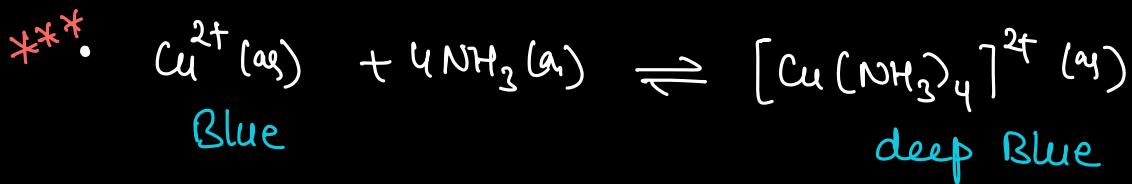
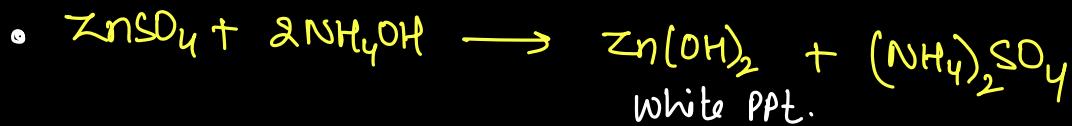
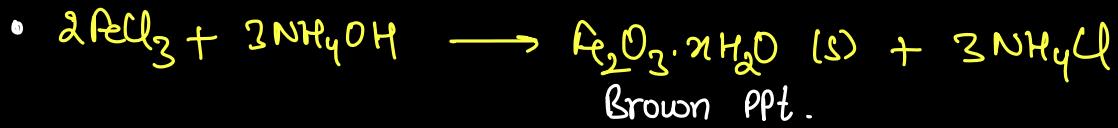
NH_3 → Formed in soil by decay of nitrogenous organic matter.



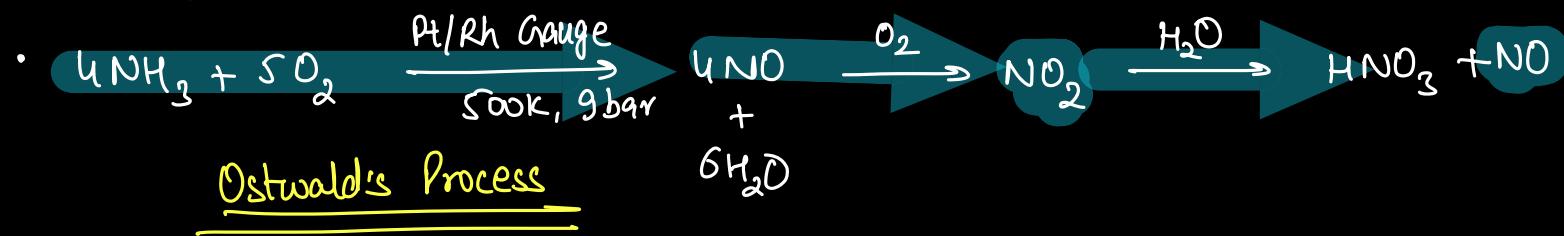
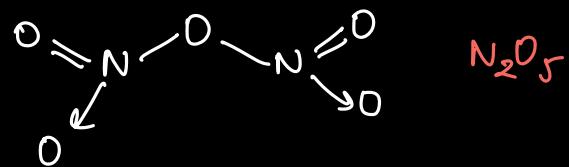
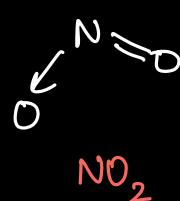
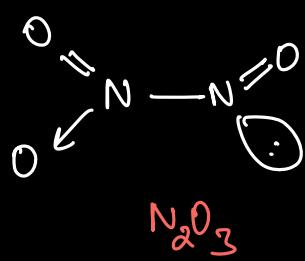
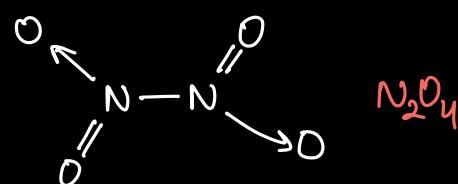
↳ favored at low T & high P
700K 200 atm

↳ Iron oxide (catalyst) + Al_2O_3, K_2O (Promoter)

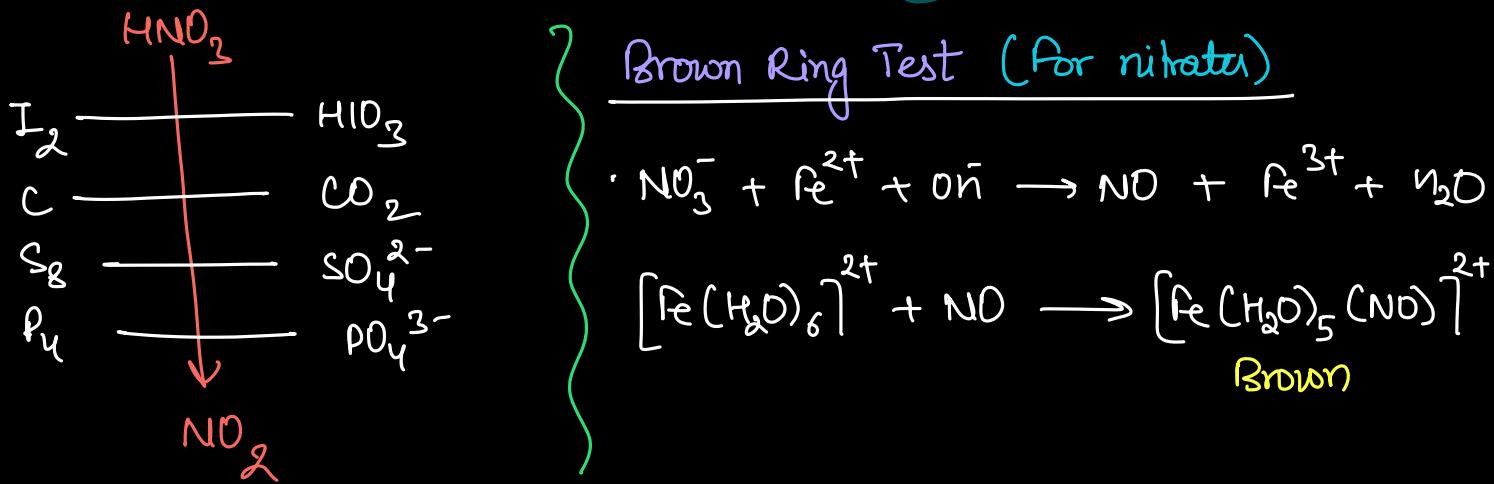
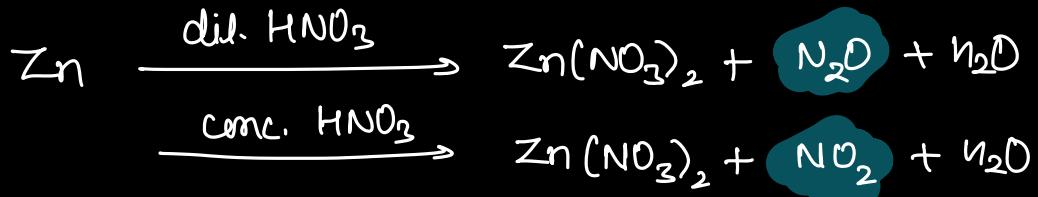
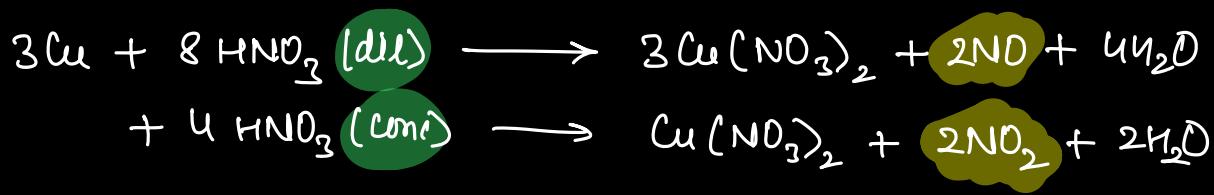
→ colorless gas with pungent odour.



Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{ K}} 2\text{N}_2\text{O}_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{ K}} 4\text{NO}_2 + 2\text{PbO}$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$	colourless solid/liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic



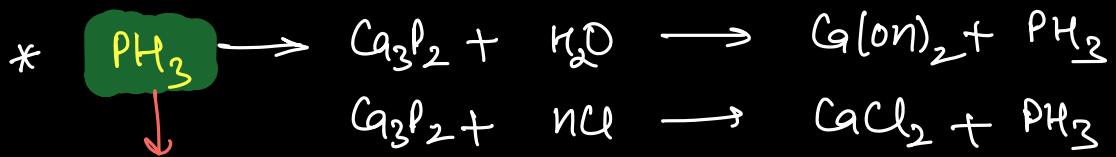
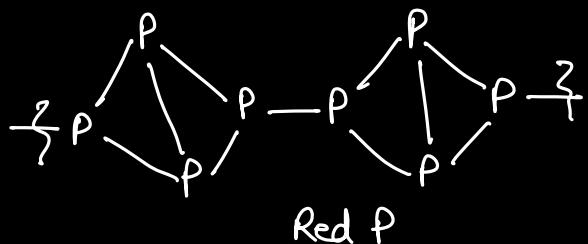
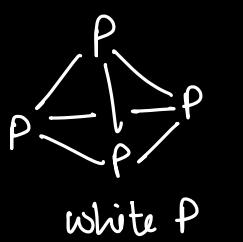
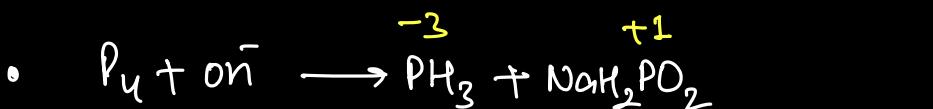
* HNO_3 attacks most metals except Au & Pt.



white — toxic, unstable , glows in dark

Red — Non toxic, stable

Black \longrightarrow Most stable $\rightarrow \alpha \& \beta$ form



Non-flammable
M1

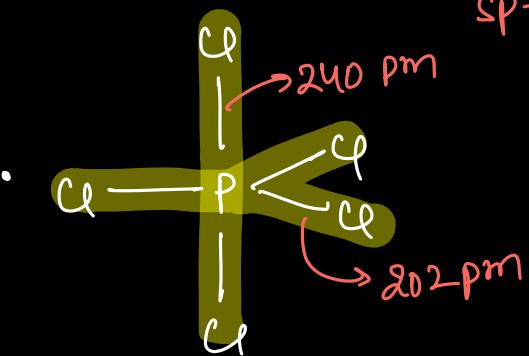
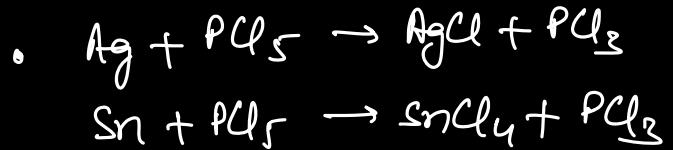
but contains imp. of P_2H_4 or P_4

HI

Removes
impurities

- Colorless gas with rotten fish smell & highly poisonous
- explodes on contact with ox. agents like HNO_3 , Cl_2 & Br_2 (vap)
- Slightly soluble in water

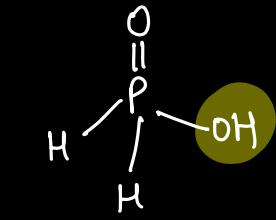
PCl_5 exists as $[\text{PCl}_4]^+ | \text{PCl}_6^-$ in solid state



- * PCl_3 hydrolyses in the presence of moisture to give HCl
 \therefore it fumes in moisture.



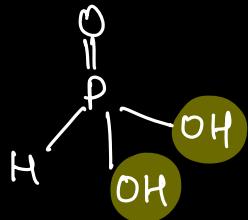
* Oxoacids of P



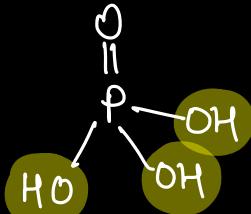
Hypophosphorous acid



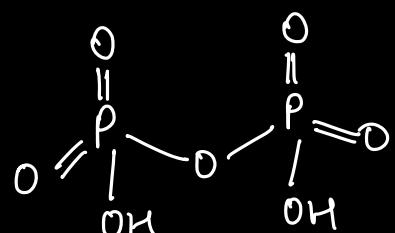
Good
Red. agent



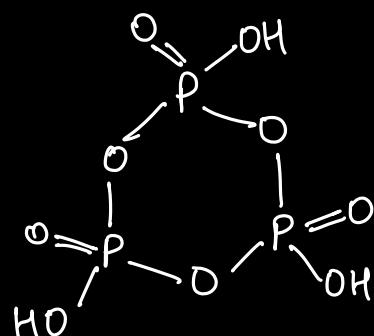
Orthophosphorous acid



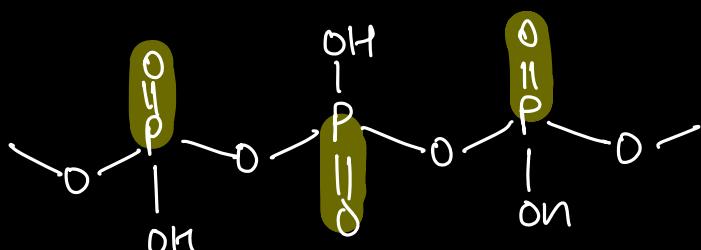
Phosphorous acid



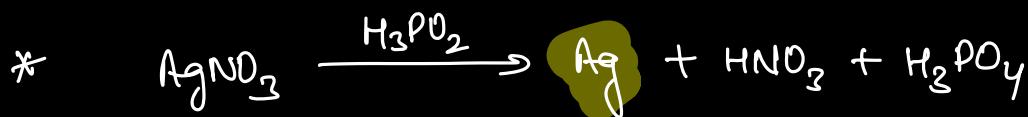
Pyrophosphorous acid



Cyclotriphosphorous acid



Polymetaphosphorous acid



Oxygen family \rightarrow Group O.S. = +6

-2 \longrightarrow +6

O

S

Se

Te

Po

Atomic size \uparrow

IE \downarrow

density \uparrow

Ionic radius \uparrow

M.P. \uparrow upto Te then \downarrow

B.P. \uparrow upto Te then \downarrow

• Acidity: $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

thermal stability: $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

All hydrides except H_2O are reducing agents and Red. Power \uparrow down the group.

• M.P. & B.P. of H_2O are highest \longrightarrow H-bonding

H_2O

H_2S

H_2Se

H_2Te

Bond angle: 104°

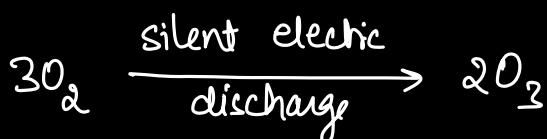
92

91

90

Industrially O_2 is obtained from air

Ozone

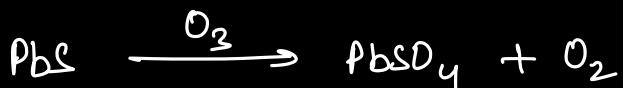


$$\Delta H = +142 \text{ kJ/mol}$$

Pale blue gas, dark blue liq, violet-black solid

Conc. $> 100 \text{ ppm}$ \rightarrow headache & nausea

ox. agent



When O_3 reacts with $KI \rightarrow I_2$ is released which can be titrated against hypo soln. This method is used for estimation of O_3 .

depletion of O_3 layer in upper atmosphere.

Uses

Germicide

disinfectant

Sterilising water

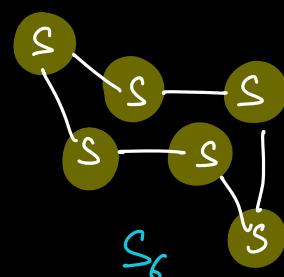
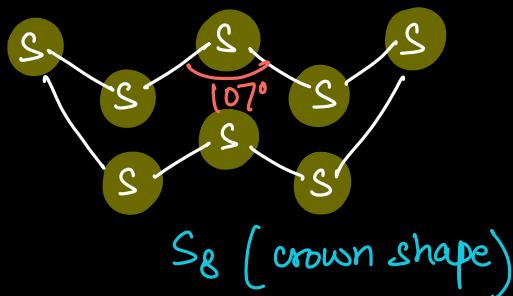
Bleaching oils, ivory, flour, starch etc.

to prepare $KMnO_4$

Sulphur

Yellow Rhombic (α) \rightarrow stable at R.T.

Monoclinic (β)



at $\approx 1100 \text{ K}$
if breaks into S_2 .

* S_2 is paramagnetic like O_2

* Imp Rxn

→ SO_2 is formed as by-product of roasting

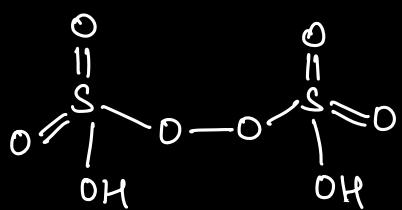
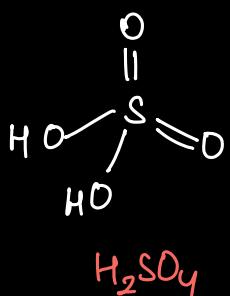
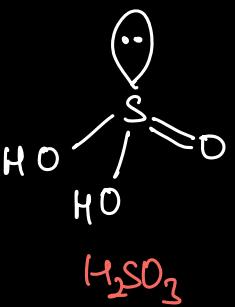
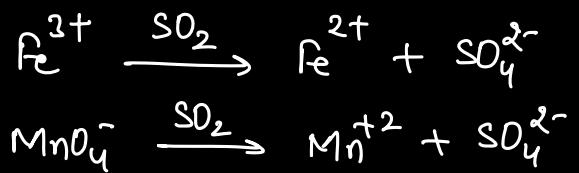


→ SO_2 is colorless gas with pungent smell & highly soluble in H_2O

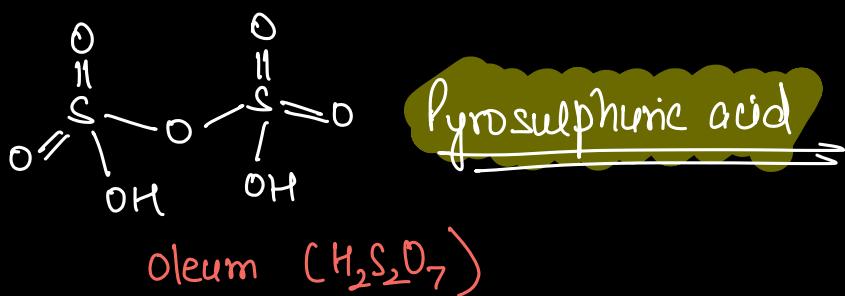
$$\hookrightarrow \text{NaOH} + \text{SO}_3 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$



*** Moist SO_2 acts as a Red. agent :



$\text{H}_2\text{S}_2\text{O}_8$ (Peroxo disulphuric acid)

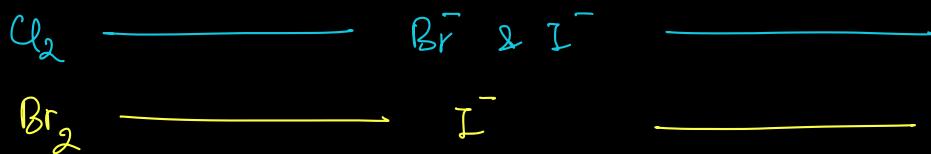


Halogen Family

- $\text{F} \longrightarrow \text{CaF}_2$ (Fluorspar)
- $\longrightarrow \text{Na}_3\text{AlF}_6$ (Cryolite)
- $\longrightarrow 3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ (Fluoroapatite)
- Sea-water is mainly NaCl soln (2.5% by mass) + Iodides + Bromides

F	Cl	Br	I	At
Size \uparrow	$\text{IE} \downarrow$		M.P. \uparrow B.P. \uparrow	density \uparrow
E.A: $\text{Cl} > \text{F} > \text{Br} > \text{I}$				
B.E: $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$				
Bond Length: $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$				
E° : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$	2.87	1.36	1.09	0.54
				Ox. Power: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

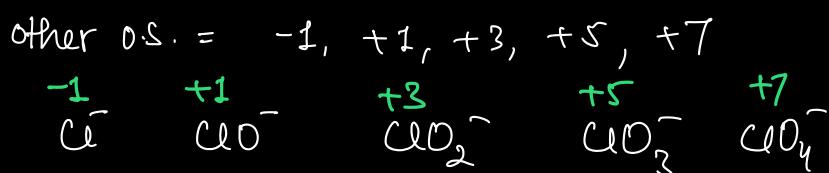
F_2 can displace Cl^- , Br^- , I^- from their soln.



• Colors of halogens

- F_2 — Yellow
- Cl_2 — Greenish Yellow
- Br_2 — Red (liq.)
- I_2 — violet (solid)

Ox. State : Group Ox. state = +7



• F only shows -1 O.S.

Properties of HX

Acidity: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

M.P.: $\text{HCl} < \text{HBr} < \text{HF} < \text{HI}$

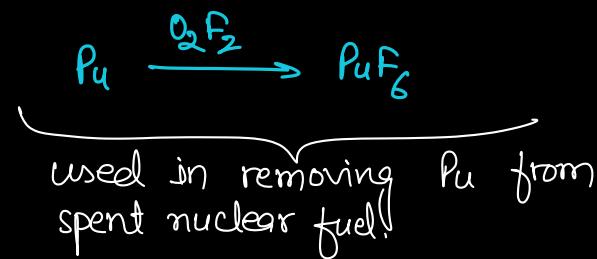
B.P.: $\text{HCl} < \text{HBr} < \text{HF} < \text{HI}$

Red. Power: $\text{HI} > \text{HBr} > \text{HCl}$

• F forms OF_2 & O_2F_2 (Fluorides)

stable at RT

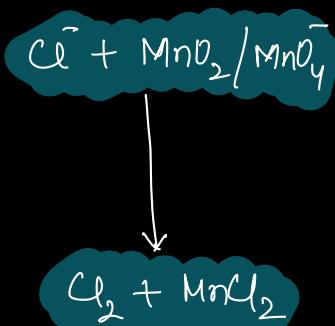
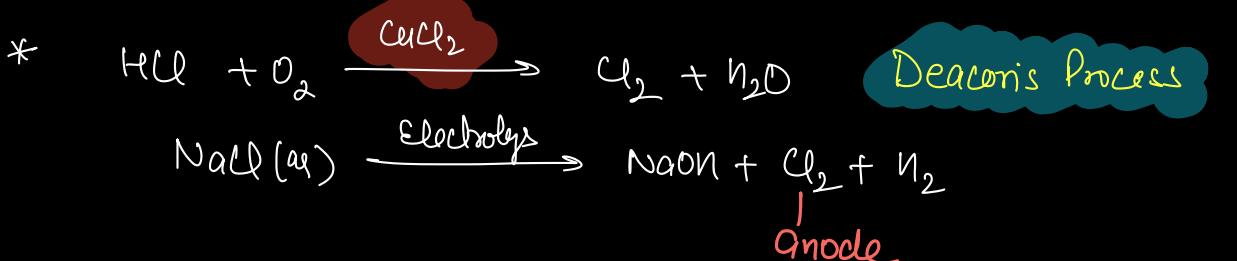
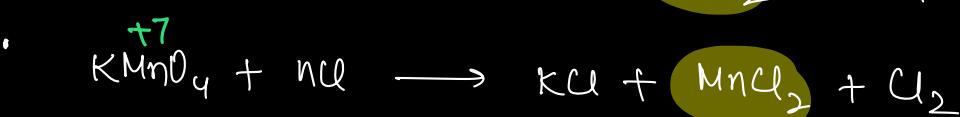
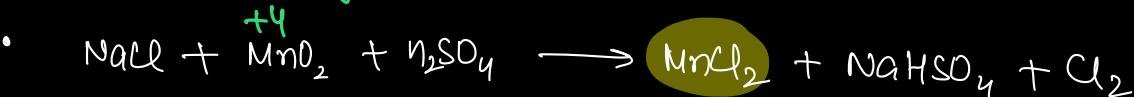
Strong fluorinating agents

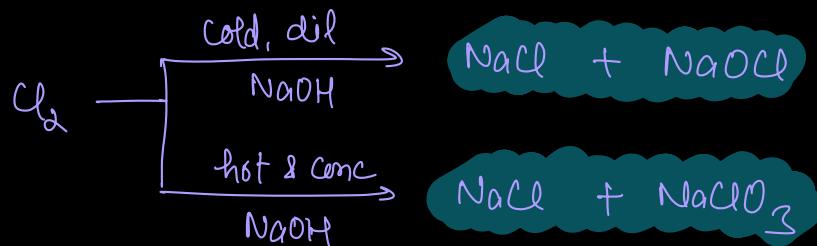
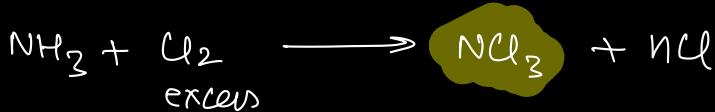
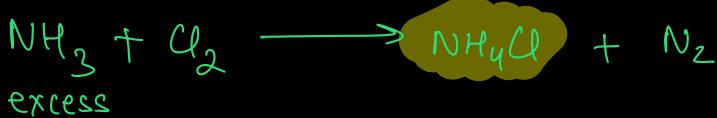


Cl_2 : Greenish yellow gas with pungent & suffocating odour.

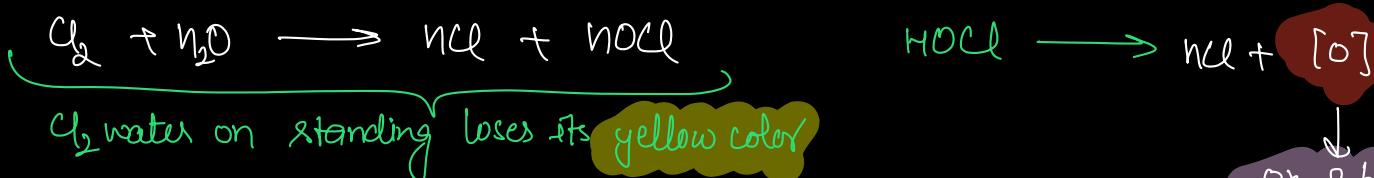
: Soluble in water

Preparation Rxn:





Composition of Bleaching Powder: $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$

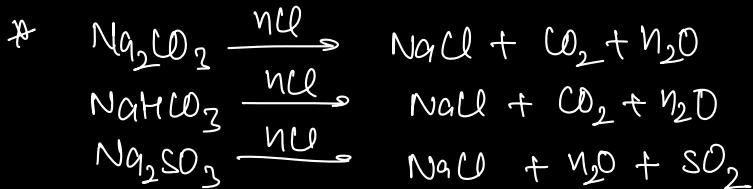
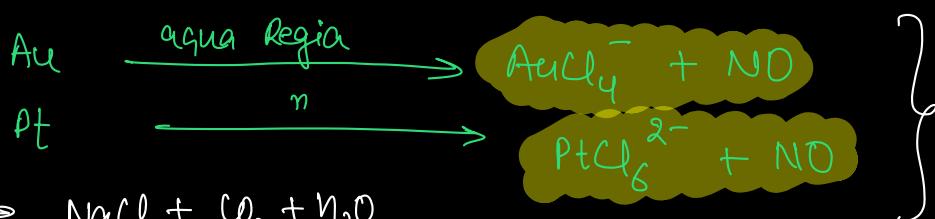


↓
Ox. & bleaching properties

Colored substance + [O] \rightarrow Colorless substance

HCl

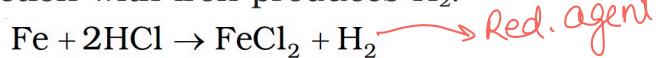
- colorless pungent smelling gas
- conc HCl + conc. HNO_3 = Aqua Regia \rightarrow can dissolve noble metals like Au & Pt



When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

Example 7.18

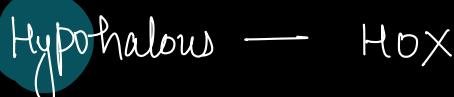
Its reaction with iron produces H₂.



Liberation of hydrogen prevents the formation of ferric chloride.

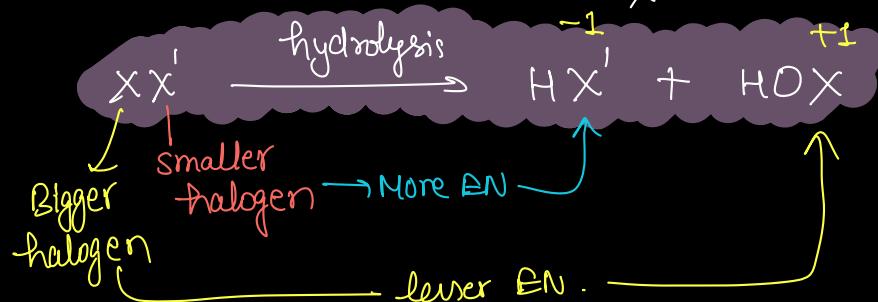
Solution

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	-	HOCIO (chlorous acid)	-	-
Halic (V) acid (Halic acid)	-	HOCIO ₂ (chloric acid)	HOBrO ₂ (bromic acid)	HOIO ₂ (iodic acid)
Halic (VII) acid (Perhalic acid)	-	HOCIO ₃ (perchloric acid)	HOBrO ₃ (perbromic acid)	HOIO ₃ (periodic acid)

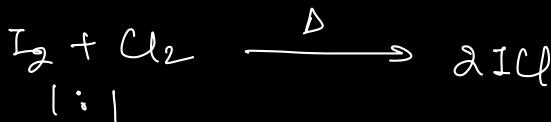
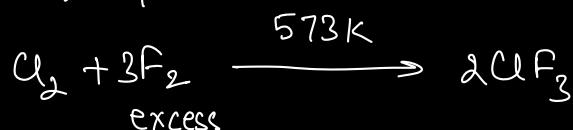


Interhalogen Compounds

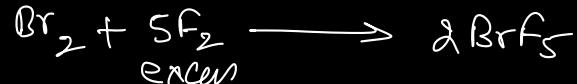
- all covalent molecules & diamagnetic
- ClF = gas ; Rest all are either liq. or solid
- M.P. & B.P. are higher than expected.
- More reactive than halogens



1 : 1



1 : 1

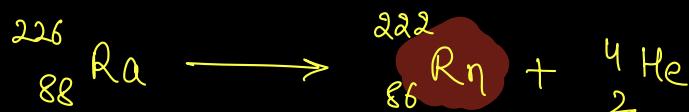


- Noble gases :
- Largest atomic radius in the period (V.D.W. radius)
 - Very high I.E
 - very low E.A

* All noble gases except Rn occur in atmosphere

He & Ne \longrightarrow pitchblende
 \longrightarrow monazite
 \longrightarrow Cleveite } Found in these minerals

\hookrightarrow Ar is major component $\approx 1\%$ by vol.



He Ne Ar Kr Xe Rn

size \uparrow I.E \downarrow ΔH_{deg} is +ve (max. endothermic value for Ne)
 density \uparrow M.P. & B.P. \uparrow \rightarrow low m.p. & b.p. bcoz of weak V.D.W. forces

* All noble gases \longrightarrow monatomic
 \longrightarrow colorless, odourless, tasteless
 \longrightarrow sparingly soluble in water

He has lowest b.p. (4.2K) of any known substance.

* O_2 than Xe have almost identical I.E,
 1175 1170 kJ/mol

