

# P Group 15    Block 15

Group 15 elements are also known as p-block elements.

# P Block (Group 15)

Group 15

## \* P-Block \*

Group - 15

### \* Nitrogen Family \*

N	}	→ Found as $\text{NaNO}_3$ (Chile Salt Peter) & $\text{KNO}_3$ (Indian Salt Peter)
	}	non metal
P	}	→ Found as apatite family $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaX}_2$ $x = \text{F, Cl, Br, OH}$
	}	metalloids
As	}	Fluxapatite
Sb	}	
Bi	}	metal

### \* Electronic Configuration

Nitrogen Family  $\rightarrow [\text{IG}] ns^2 np^3$  (Half filled configuration)  
 extrastable configuration

2nd period N  $\rightarrow [\text{He}] 2s^2 2p^3$   
 3rd " P  $\rightarrow [\text{Ne}] 3s^2 3p^3$   
 4th " As  $\rightarrow [\text{Ar}] 3d^{10} 4s^2 4p^3$   
 5th " Sb  $\rightarrow [\text{Kr}] 4d^{10} 5s^2 5p^3$   
 6th " Bi  $\rightarrow [\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$

### \* Atomic Radius

N	}	considerable ↑
P	}	
As	}	Small ↑ due to poor shielding of d & f orbital
Sb	}	
Bi	}	

### \* Ionization Energy

N	}			
P	}	↓	$G_{14}$	$G_{15}$
As	}	↓	Half filled configuration	↓
Sb	}	↓	↓	↓
Bi	}	↓	↓	↓

$G_{15} > G_{14}$



\* Electronegativity

N

↓

EN  $\propto$  Size

P

↓

As

↓

Sb

↓

Bi

\* Physical properties

→ All members are polyatomic solid but Nitrogen is diatomic

→ B.P → ↑ from top to bottom -  $N < P < As < Sb > Bi$  gas

→ M.P → ↑ upto Arsenic & ↓ upto Bismuth  $N < P < As > Sb > Bi$

→ Allotropy - Except nitrogen all show allotropy because nitrogen do not catenation because  $N-N$  is weak

\* General Oxidation state

-3

↓

Tendency to show -3 oxidation state ↓ down the Group # Bi never forms -3 oxidation state

+3

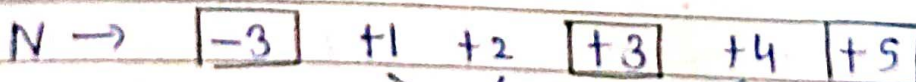
↓

due to inert pair effect stability of +3 oxidation state ↑ down the group

+5

↓

due to inert pair effect stability of +5 oxidation state ↓ down the group Only BiF5 is formed



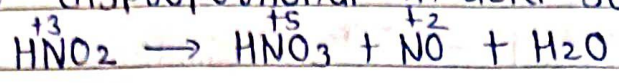
When reacts with oxygen



In Oxo acids

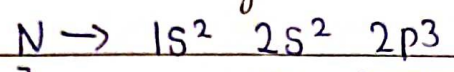


# In Nitrogen, all oxidation state from +1 to +4 tend to disproportionate in acid solution

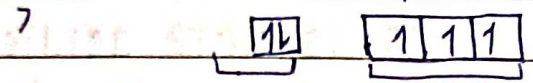


# In phosphorous all intermediate oxidation state disproportionate into +5 and -3 in acid/base rxn

\* Covalency



→ max covalency of Nitrogen is 4



→ But other members of Nitrogen

1 coordinate bond (lone pair)      3 covalent bond      family forms more than 4 bond because of vacant d orbital eg -  $\text{PF}_6^-$

\* Anomalous Property of Nitrogen.

- Small size.
- High electronegativity
- High Ionization potential
- no vacant d orbital
- Nitrogen forms π-π multiple bond  $\text{N} \equiv \text{N}$ ,  $\text{C} \equiv \text{N}$ ,  $\text{C} \equiv \text{O}$  but other members can form dπ - π or dπ-dπ

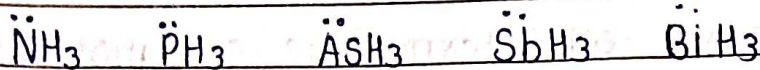
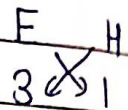
→ N	P	As	Sb	Bi
$\text{N} \equiv \text{N}$	P-P	As-As	Sb-Sb	Bi <sup>&lt;</sup> metal

→  $\ddot{\text{N}}-\ddot{\text{N}} < \text{P}-\text{P}$  (so catenation is weak in nitrogen) lone pair repulsion



\* Chemical Reaction.

1) Reaction with Hydrogen  $\rightarrow$   $\text{EH}_3$  Hydride

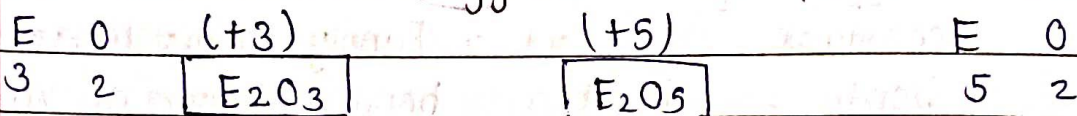


Stability  $1 > 2 > 3 > 4 > 5$

Reducing Nature -  $5 > 4 > 3 > 2 > 1$

Basic order -  $1 > 2 > 3 > 4 > 5$

2) Reaction with Oxygen -  $\text{E}_2\text{O}_5$  is more acidic than  $\text{E}_2\text{O}_3$



as we go |  $\text{N}_2\text{O}_3$  } Acidic.

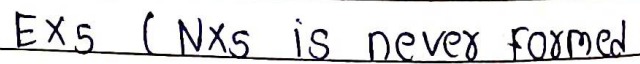
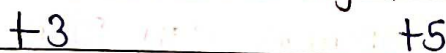
down acidic |  $\text{P}_2\text{O}_3$  }

character |  $\text{As}_2\text{O}_3$  } Amphoteric

decreases |  $\text{Sb}_2\text{O}_3$  }

↓  
 $\text{Bi}_2\text{O}_3$  } Basic

3) Reaction with Halogen



$\rightarrow$   $\text{EX}_5$  is more covalent than  $\text{EX}_3$  - (Fajan's Rule) because max. covalency of Nitrogen is 4)

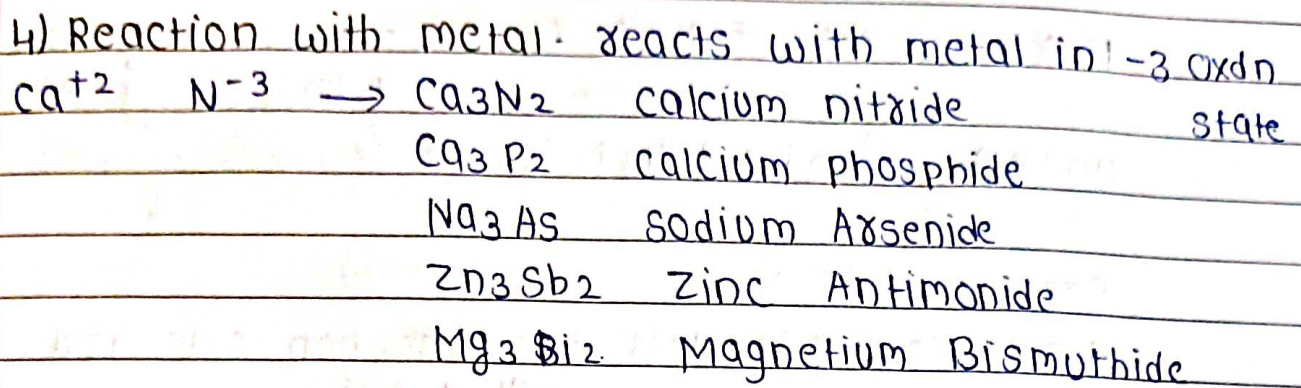
$\rightarrow$  Nitrogen trihalides are unstable, but only  $\text{NF}_3$  is found to be stable.

$\rightarrow$   $\text{NCl}_3$  is explosive.

#  $\text{BiF}_3 \rightarrow$  ionic

# Rest trihalides are covalent





### \* Compounds of Nitrogen

1) Dinitrogen ( $\text{N}_2$  gas)

Preparation  $\rightarrow$  liquification & fractional distillation of air  
commercially  $(\text{liq N}_2 + \text{liq O}_2) \rightarrow$  mixture

$\downarrow$   $\downarrow$

B.P  $77.2\text{K}$   $90\text{K}$

$\downarrow$  distills out first & liquid  $\text{O}_2$  is obtained

(ammonium  $\text{NH}_4^+$ )

Laboratory Preparation  $\rightarrow$  अम्ली अजान करती है

Preparation

nitrite

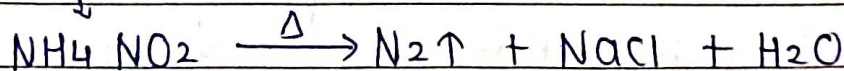
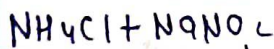
dichromate

Azide  $\rightarrow$  very pure

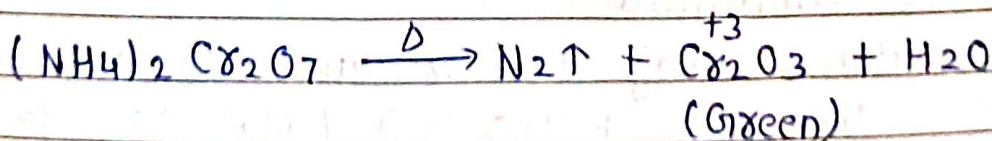
$\text{NH}_4\text{NO}_2$

$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

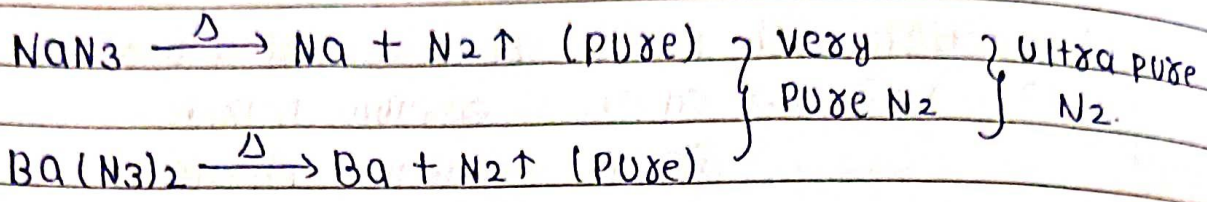
$(\text{Na}, \text{Ba})$  Nitrogen



( $\text{NO}$  and  $\text{HNO}_3$  is also formed here and removed by passing gas through aq.  $\text{H}_2\text{SO}_4$  containing  $\text{K}_2\text{Cr}_2\text{O}_7$ .)



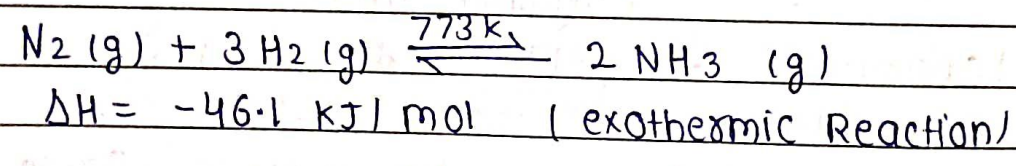




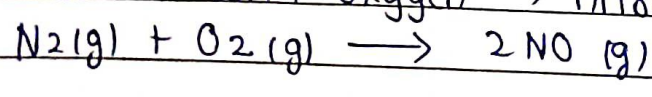
### Properties of N<sub>2</sub>

- colourless, odourless, tasteless, non toxic acid.
- Two stable isotope N<sup>14</sup> & N<sup>15</sup>
- N<sub>2</sub> is usually inert (non reactive) at room temp because of high bond energy (N≡N)
- when T ↑ reactivity ↑
- N<sub>2</sub> + metal → ionic nitride  
 Li + N<sub>2</sub> → Li<sub>3</sub>N ; Mg + N<sub>2</sub> → Mg<sub>3</sub>N<sub>2</sub>
- N<sub>2</sub> + nonmetal → covalent nitride

# N<sub>2</sub> reacts with Hydrogen → Ammonia (Haber's process)



# N<sub>2</sub> reacts with oxygen → nitric oxide (NO)



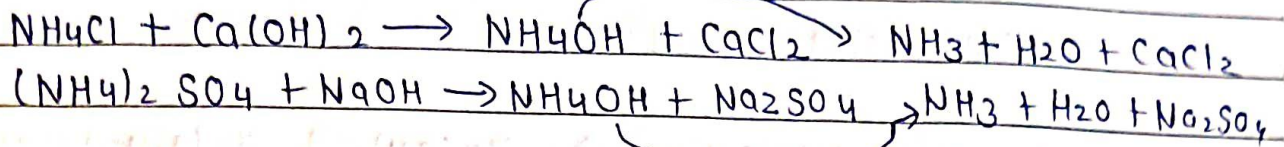
Uses - manufacture of NH<sub>3</sub> ↗ Fertilizer, calcium cyanamide (CaCN<sub>2</sub>)  
 $\text{Ca}^{+2} \text{CN}_2^{-2}$   
 $\text{Ca}^{+2} [\text{N} = \text{C} = \text{N}]$

### 2) NH<sub>3</sub> Ammonia

Preparation - decay of nitrogenous organic matter eg-urea  
 $\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \xrightarrow{\text{urea}} (\text{NH}_4)_2\text{CO}_3 \xrightarrow{\Delta} \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$

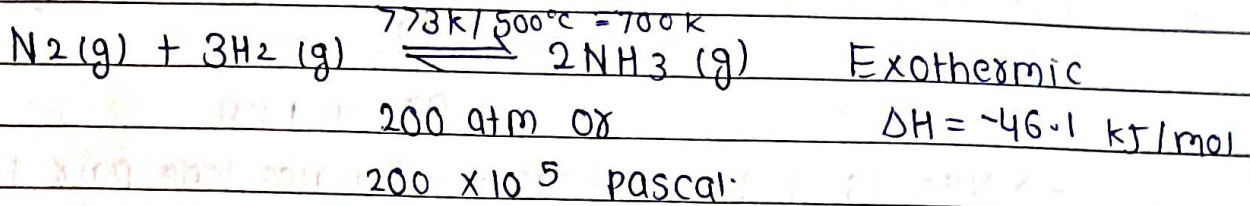


On small scale



On large scale

Haber's Process



Catalyst  $\rightarrow$  Iron Oxide +  $\text{K}_2\text{O}$  +  $\text{Al}_2\text{O}_3$

earlier  $\rightarrow$  Iron (Fe) + MO (promoter)

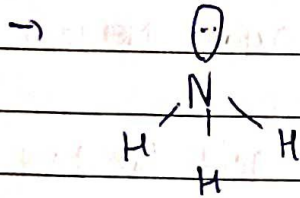
According to Lechatelier's principle  $\rightarrow$

High Pressure  
& low Temp

Favors  $\text{NH}_3$  Formation

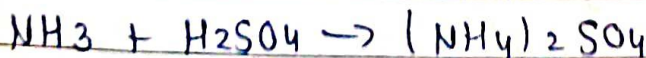
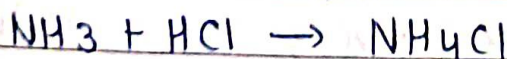
\* Properties

- $\rightarrow$  colorless, pungent color.
- $\rightarrow$  solid / liquid state  $\rightarrow$  it shows Hydrogen bonding



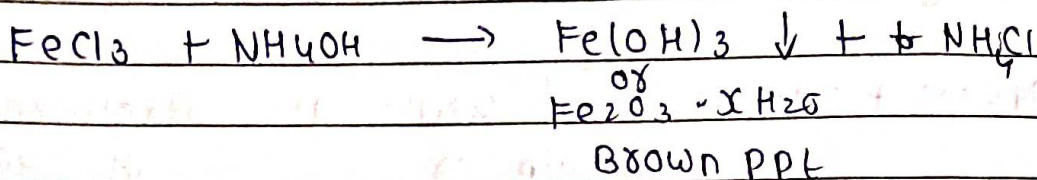
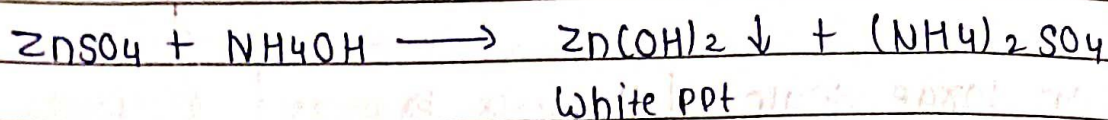
- $\rightarrow$  3  $\sigma$  bond. + 1 lone pair
  - $\rightarrow$   $\text{sp}^3$  ; tetrahedral
  - $\rightarrow$  Highly soluble in  $\text{H}_2\text{O}$ . it aqueous is weakly basic
- $$\text{NH}_3(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$$
- weak base

- Reaction with acid

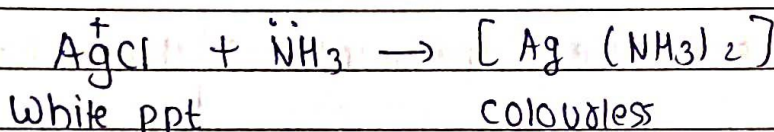




→ Reaction of aq. ammonia  $\text{NH}_4\text{OH}$  with metal salt metal forms precipitate



→  $\text{NH}_3$  is a Lewis base → donates lone pair to metal ion  
 $\text{Cu}^{2+} + \text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$  → complex compound  
 blue deep blue

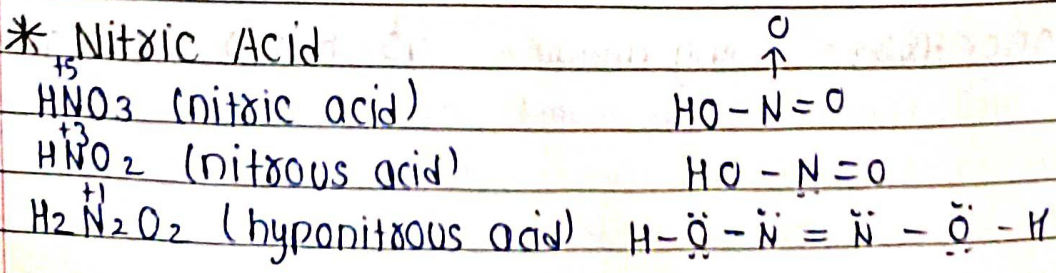
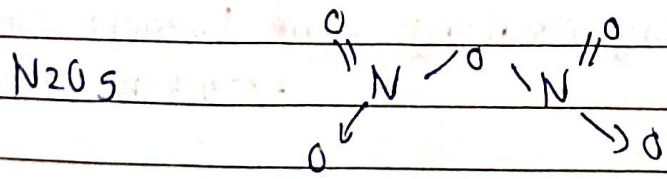
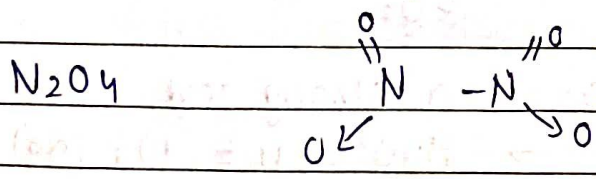
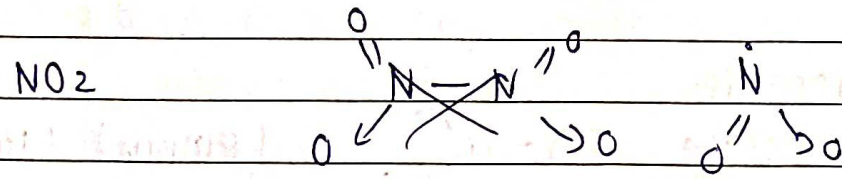
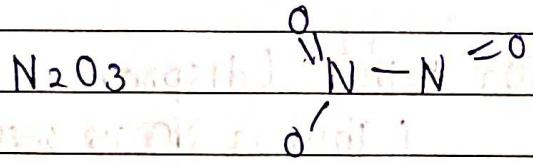
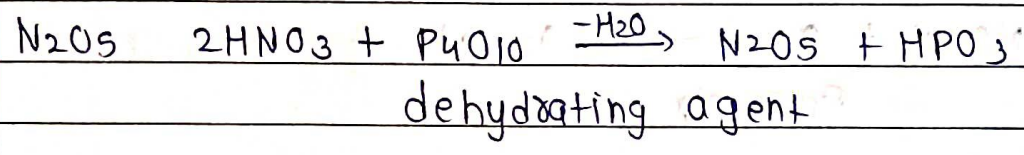
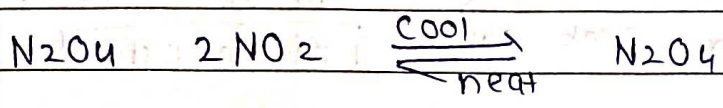
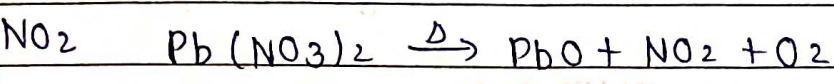
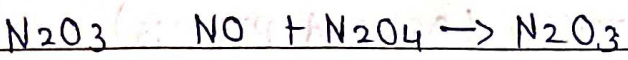
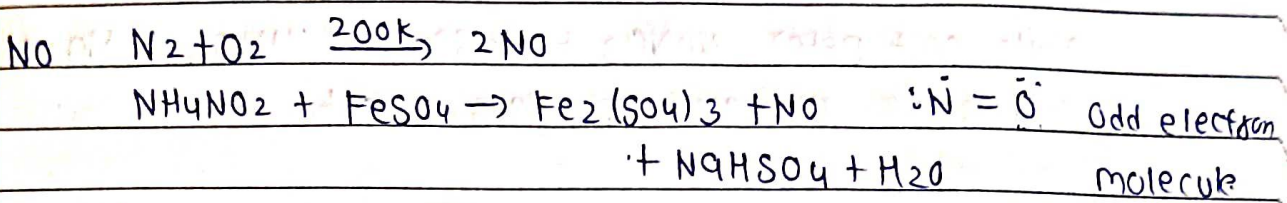
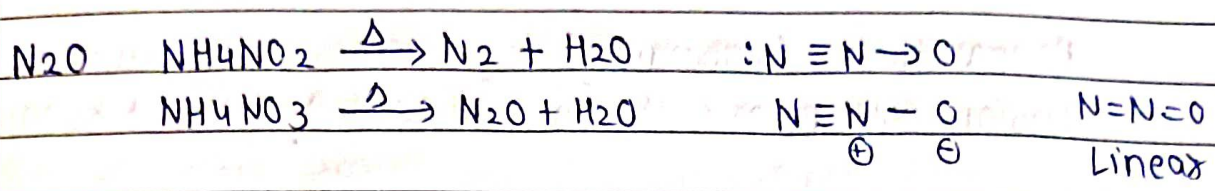


→ Liq.  $\text{NH}_3$  → Refrigerant

### \* Oxides of Nitrogen

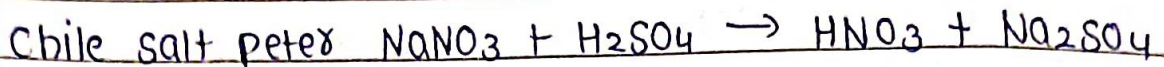
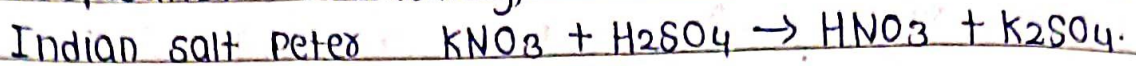
+1	$\text{N}_2\text{O}$	dinitrogen oxide or nitrous oxide	Neutral	colourless
+2	$\text{NO}$	nitrogen monoxide or nitric acid	Neutral	colourless
+3	$\text{N}_2\text{O}_3$	dinitrogen trioxide	Acidic	blue
+4	$\text{NO}_2$	Nitrogen dioxide	Acidic	brown
+4	$\text{N}_2\text{O}_4$	dinitrogen tetroxide	Acidic	colourless
+5	$\text{N}_2\text{O}_5$	dinitrogen pentoxide	Acidic	colourless







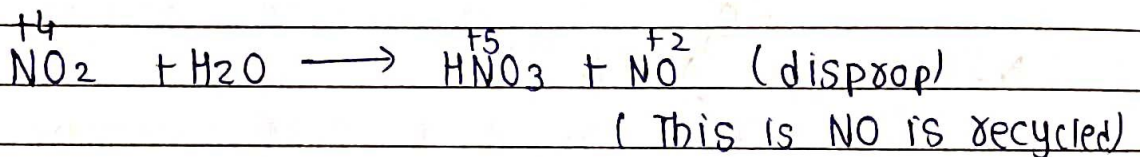
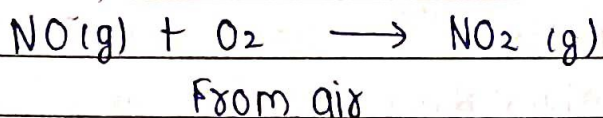
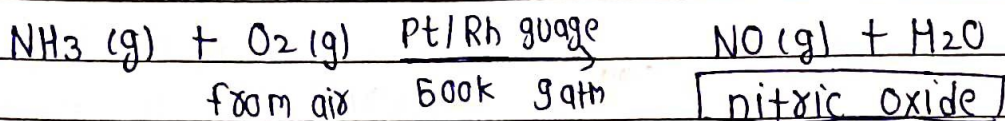
## Preparation (Laboratory)



This is prepared in glass retort

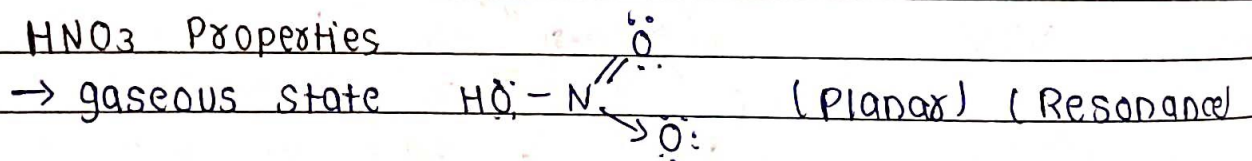
## # Large Scale preparation (Ostwald process)

→ Catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen

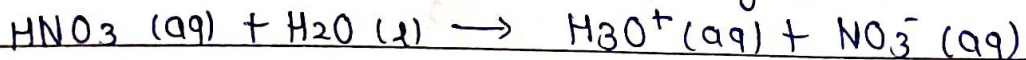


## $\text{HNO}_3$ Properties

→ gaseous state

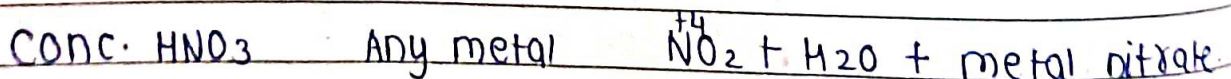


→ In aq. soln of  $\text{HNO}_3$  is a strong acid.

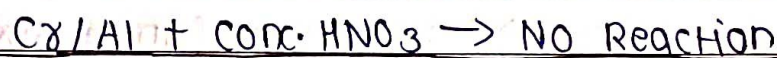
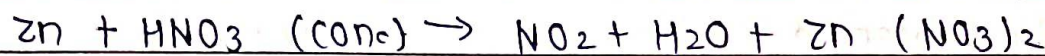
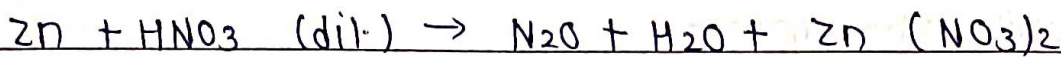
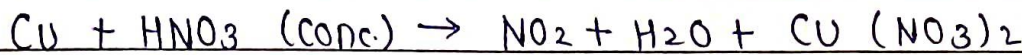
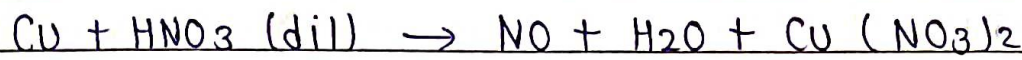
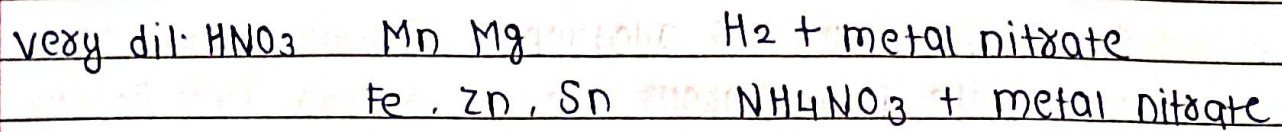
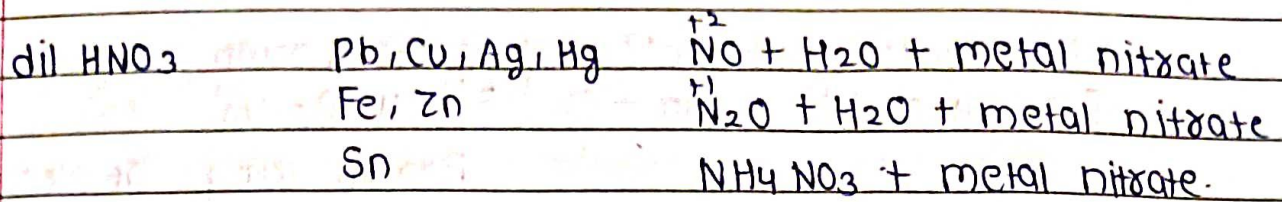


→ Conc.  $\text{HNO}_3$  → Strong oxidising agent (reacts with all metals except noble metal Au, Pt)

## Reaction with $\text{HNO}_3$

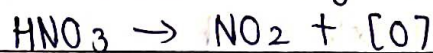




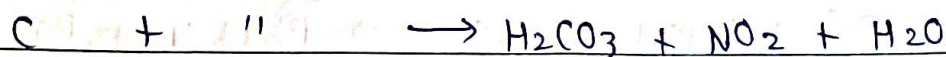


metal becomes  $\leftarrow$  Oxide layer formation  
 on metal surface  
 Passive

conc.  $\text{HNO}_3 \rightarrow$  Strong Oxidising Agent



NON metal + conc.  $\text{HNO}_3 \rightarrow$  Oxo acid



\* Brown Ring Test.

$\rightarrow$  Test for nitrate ( $\text{NO}_3^-$ )  $\rightarrow$  oxidation

$\rightarrow$   $\text{NO}_3^-$  reacts with  $\text{Fe}^{+2}$  and converts into  $\text{Fe}^{+3}$

$\rightarrow$  dil. Ferrous Sulphate is added to aq. soln containing nitrate ion & carefully conc.  $\text{H}_2\text{SO}_4$  is added to side walls of test tube.



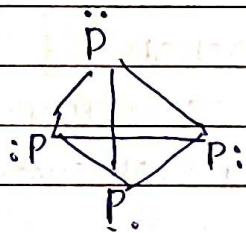
→ NO reacts with  $Fe^{+2}$  and forms Brown ring complex  
 $[Fe(H_2O)_6]^{+2} + NO \rightarrow [Fe^+(H_2O)_5NO^+]$   
 Brown Ring Complex

\* Phosphorous - 3 allotope

- 1) White phosphorous
- 2) Red "
- 3) Black "

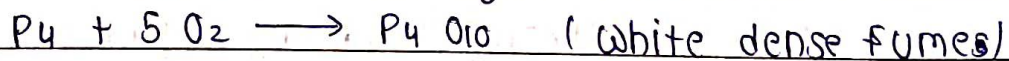
1) White phosphorous

→  $P_4$  molecule

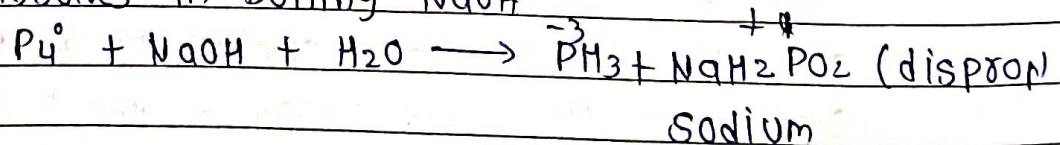


- Tetrahedral ( $sp^3$  hybridization)
- less stable (angle strain)
- most reactive betw white, red, & black

→ Catches fire in air to give dense fumes of  $P_4O_{10}$



- Translucent white waxy solid
- Poisonous, insoluble in  $H_2O$ , soluble in  $CS_2$
- Glows in dark
- dissolves in boiling NaOH



2) Red phosphorous

Hypophosphite

- Heating of white phosphorous at 573 K in inert atmosphere
- Iron grey lustre
- odourless, non poisonous
- insoluble in  $H_2O$  and  $CS_2$
- more stable than white phosphorous
- less reactive than white phosphorous
- do not glow in dark
- Polymer of  $P_4$



### 3) Black phosphorous

Red phosphorous is heated under high pressure  $\rightarrow$  Black phosphorous

$\alpha$ - Black

$\beta$ - Black

$\rightarrow$  Red phosphorous is heated in a sealed tube at 803 K

$\rightarrow$  White phosphorous is heated at 473 K under high pressure

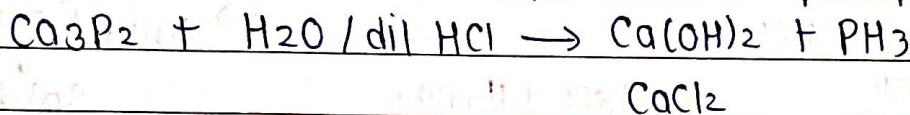
$\rightarrow$  do not oxidise in air

$\rightarrow$  doesn't burn in air upto 673 K

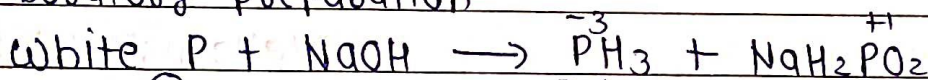
$\rightarrow$  Black phosphorous has layered str. like graphite.

### \* $\text{PH}_3$ Phosphine

$\rightarrow$  Calcium phosphide +  $\text{H}_2\text{O}$  / dil  $\text{HCl} \rightarrow$  phosphine



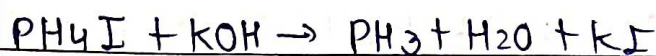
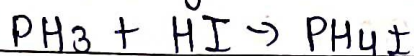
### Laboratory preparation



( $\text{P}_4$ )

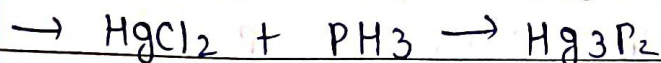
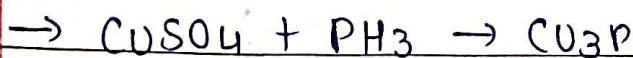
$\downarrow$   
In pure form - non inflammable  
becomes inflammable in presence  
of  $\text{P}_2\text{H}_4$  or  $\text{P}_4$  vapours

To purify  $\text{PH}_3$

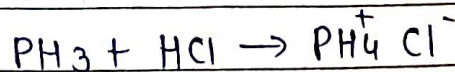


$\rightarrow$  colourless, rotten fish smell, highly poisonous

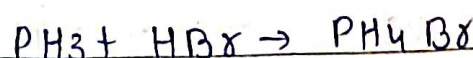
$\rightarrow$  explodes in presence of oxidizing agent ( $\text{HNO}_3$  or  $\text{Cl}_2$  /  $\text{Br}_2$  vapour)



$\text{NH}_3 \rightarrow$  weak base



$\text{PH}_3 \rightarrow$  weak base

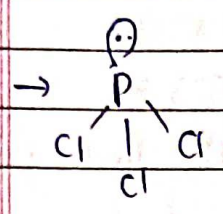
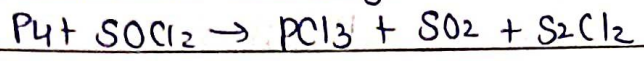
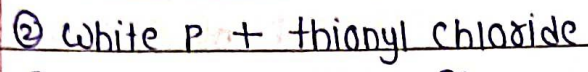
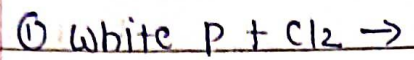




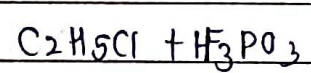
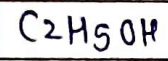
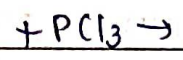
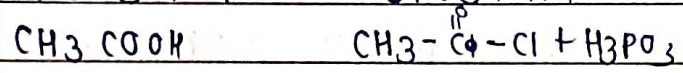
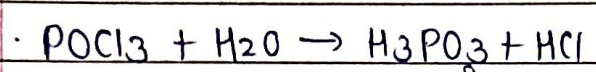
Phosphorus Halide



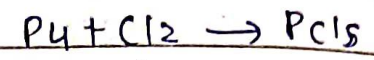
X = F, Cl, Br, I



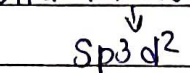
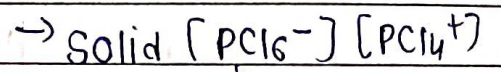
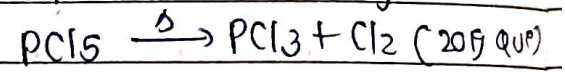
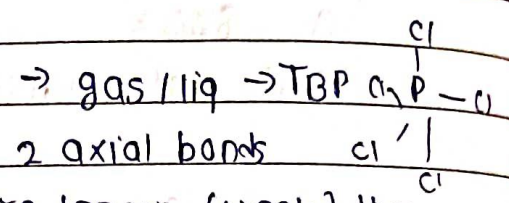
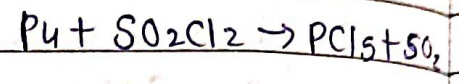
Pyramidal sp<sup>3</sup>  
colorless oily liq



X = F, Cl, Br

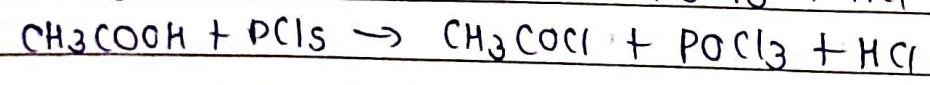
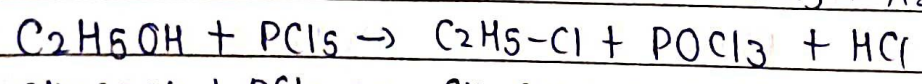
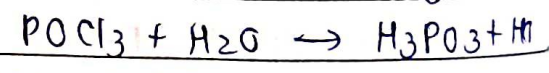
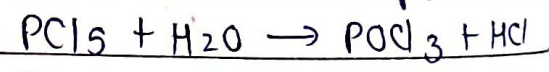


excess



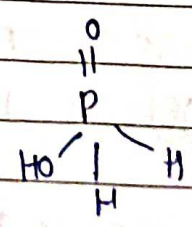
Octahedral tetrahedral

→ Yellowish white powder

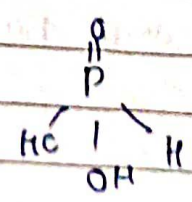


\* Oxoacid of phosphorus

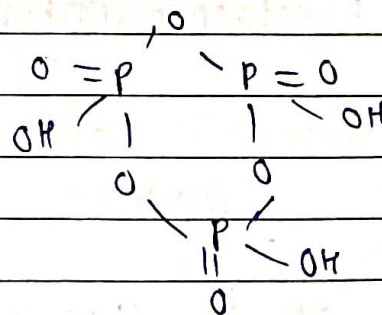
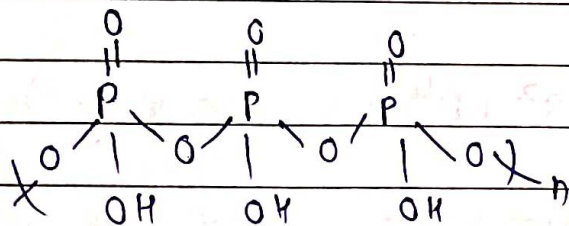
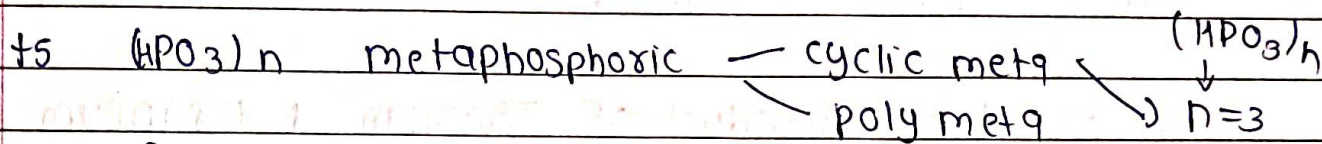
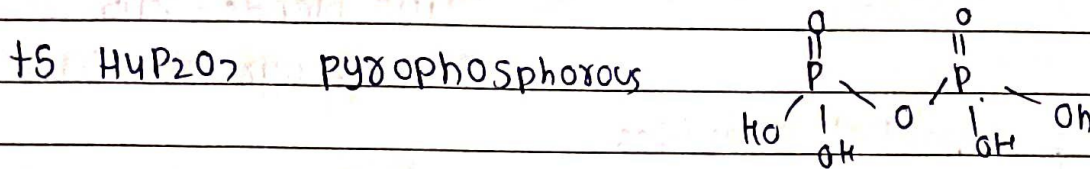
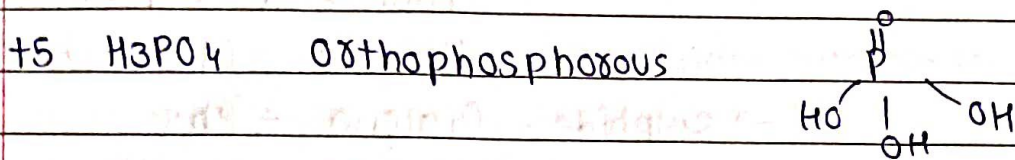
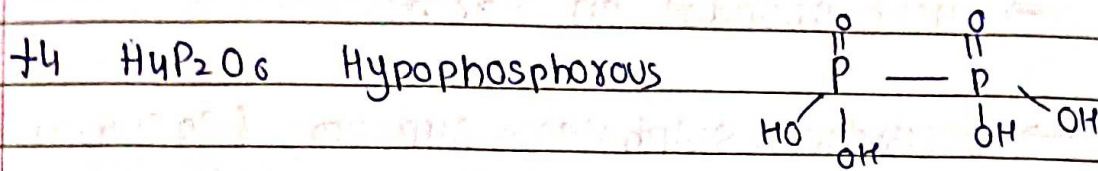
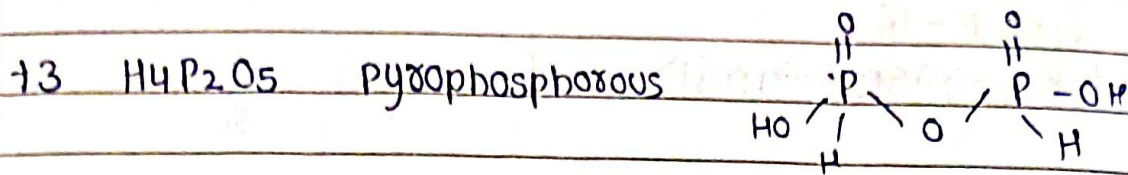
+1 H<sub>3</sub>PO<sub>2</sub> Hypophosphorous acid (Phosphinic)



+3 H<sub>3</sub>PO<sub>3</sub> Orthophosphorous (Phosphonic)









GROUP - 16

**\* Oxygen Family \***

O → most abundant on Earth

S → Occurrence → sulphates → gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )  
 Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ )  
 Baryte ( $\text{BaSO}_4$ )  
 → sulphide - Galena -  $\text{PbS}$   
 zinc blende -  $\text{ZnS}$   
 Copper pyrites -  $\text{CuFeS}_2$

Se } → metal selenides  
 Te } → metal tellurides.

Po → decay product of Thorium & Uranium

\* Electronic config -  $ns^2 np^4$

\* Atomic & Ionic -  $G_{15} > G_{16}$   
 Radius  $O < S < Se < Te < Po$  (size)

\* IE -  $G_{15} > G_{16}$

Half filled  
 config

$O > S > Se > Te > Po$  (I.E)

\* Electron gain -  $At > Ga > In > Tl > (B)$   
 enthalpy  $S > Se > Te > (O)$

Si	>	C	>	Ge	>	Sn	>	Pb
P	>	N	>	As	>	Sb	>	Bi
Cl	>	F	>	Br	>	I		



Electronegativity:  $O > S > Se > Te > Po$

metallic character:  $O < S < Se < Te < Po$

\* Physical property

$O$  } non metal  
 $S$  }  
 $Se$  } metalloid  
 $Te$  }  
 $Po \rightarrow$  metal (Radioactive)

} all show allotropy

\* MP & BP -  $O < S < Se < Te$

$\left. \begin{matrix} \text{large} \\ \downarrow \\ O_2 \quad S_8 \end{matrix} \right\}$  diff betn MP & B-P

\* Chemical property

Oxidation State

O	-2	+2	X	X
S	-2	+2	+4	+6
Se	-2	+2	+4	+6
Te	-2	+2	+4	+6
Po	X	+2	+4	X

$\rightarrow$  Stability of -2 oxidation  $\downarrow$  down the group ( $Po \rightarrow -2$ )

$\rightarrow$  Oxygen - generally shows -2 but  $OF_2$  &  $O_2F_2$

$+2$                        $+1$

$\rightarrow$  due to inert pair effect - stability of lower oxidation state (+4)  $\uparrow$  and stability of high oxidation state (+6)  $\downarrow$



\* Anomalous Behaviour of Oxygen

→ small size and high IE & high EN.

→ H<sub>2</sub>O → shows Hydrogen bond

H<sub>2</sub>S

H<sub>2</sub>Se

H<sub>2</sub>Te

Do not show H bond.

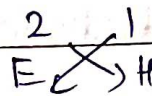
S, Se, Te - covalence more than 4

→ max. covalency is 4 (Absence of d orbital) → generally 2 bond

\* Reactivity with H - Hydroxide

H<sub>2</sub>E

O, S, Se, Te



H<sub>2</sub>O

H<sub>2</sub>S

H<sub>2</sub>Se

H<sub>2</sub>Te

H<sub>2</sub>E

① acidic character - H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te

② Thermal stability H<sub>2</sub>O > H<sub>2</sub>S > H<sub>2</sub>Se > H<sub>2</sub>Te

③ Reducing property - H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se > H<sub>2</sub>Te  
do not show Reducing property

MP & BP - H<sub>2</sub>O > H<sub>2</sub>Te > H<sub>2</sub>Se > H<sub>2</sub>S

H-Bond

Reaction with oxygen - Oxide (both EO<sub>2</sub> & EO<sub>3</sub> are acidic oxides)

EO<sub>2</sub>

O<sub>3</sub> } gas

SO<sub>2</sub>

SeO<sub>2</sub> → solid

TeO<sub>2</sub>

EO<sub>3</sub>

SO<sub>3</sub>

SeO<sub>3</sub>

TeO<sub>3</sub>

Reducing nature of dioxide

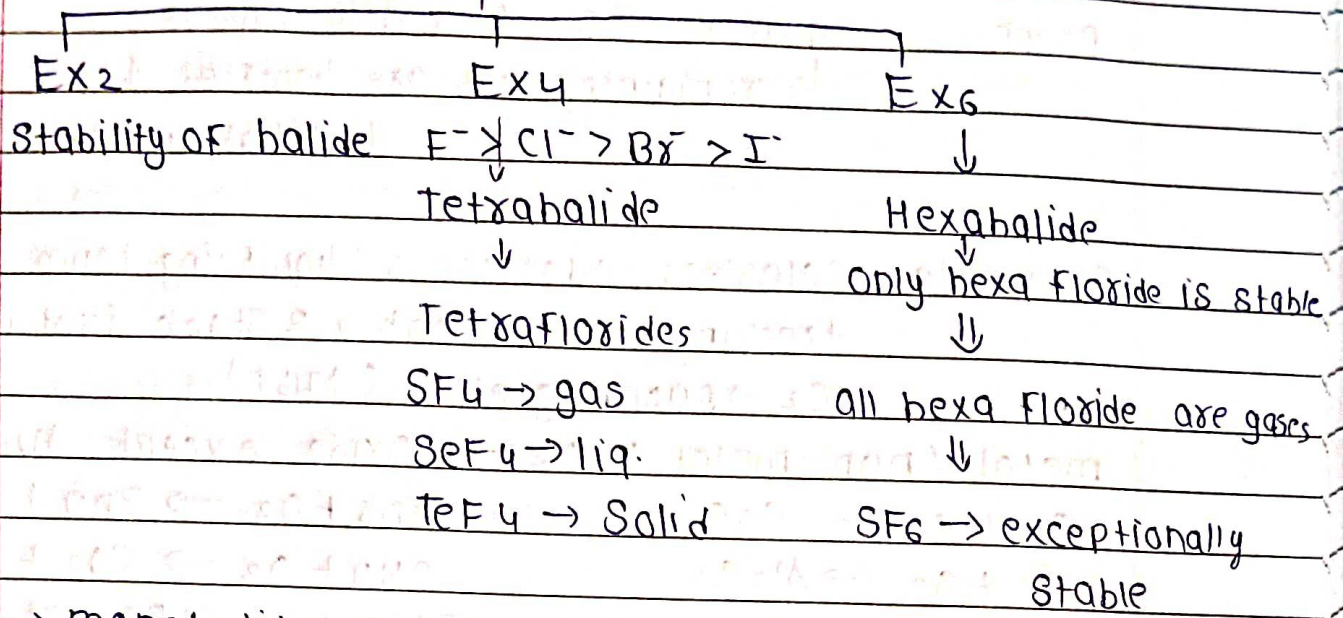
SO<sub>2</sub> > SeO<sub>2</sub> > TeO<sub>2</sub>

Reducing Agent

oxidising agent



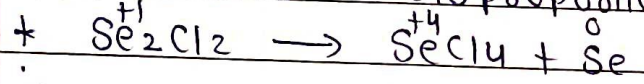
\* Reaction with Halogen → Halide



→ monohalides exists as dimer (steric reason)

eg- S<sub>2</sub>F<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, Se<sub>2</sub>Cl<sub>2</sub>, Se<sub>2</sub>Br<sub>2</sub>

These dimer → disproportionation

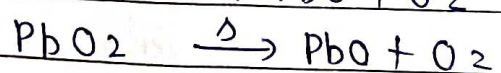
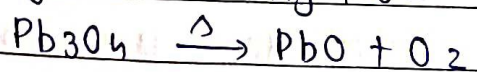
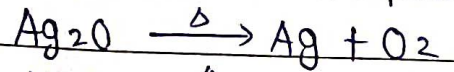


\* Dioxygen (O<sub>2</sub>)

Lab prep - ① Heating oxygen containing salt (chlorate, nitrate, permagnate)

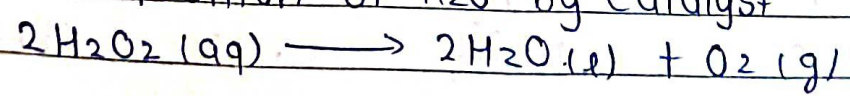
$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

② Thermal decomposition of less reactive metal oxide



↳ down in reactivity series

③ decomposition of H<sub>2</sub>O by catalyst (Finely divided metal & MnO<sub>2</sub>)



Large scale electrolysis of H<sub>2</sub>O prep

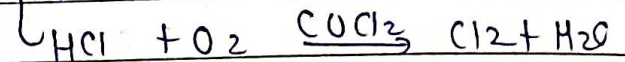
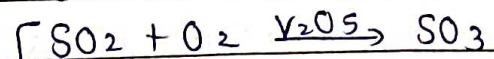
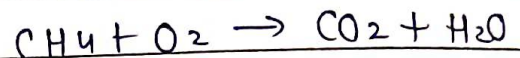
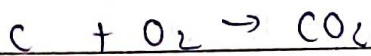
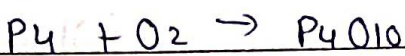
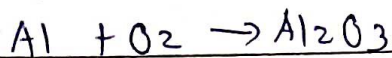
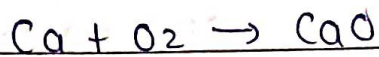
↳ H<sub>2</sub> gas → cathode  
↳ O<sub>2</sub> gas → anode



industrial  $\rightarrow$  air  
 Prepn  $\rightarrow$  remove  $\text{CO}_2$  & water vapour  
 $\hookrightarrow$  remaining gas are liquified & upon fractional distillation gives  $\text{N}_2$  &  $\text{O}_2$

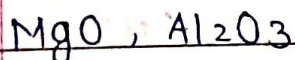
Properties: colorless, odorless; liquifying temp  $\rightarrow$  90K  
 freezing temp  $\rightarrow$  55K; 3 stable isotope  $\text{O}^{16}$ ,  $\text{O}^{17}$ ,  $\text{O}^{18}$   
 $\text{O}_2 \rightarrow$  paramagnetic (MOT)

metal / non-metal +  $\text{O}_2 \rightarrow$  Oxide except Au, Pt

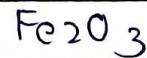
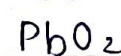
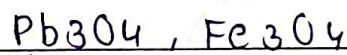


### Oxide

Simple oxide

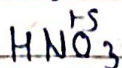
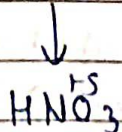
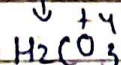
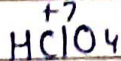
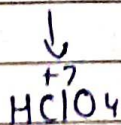
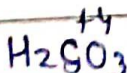
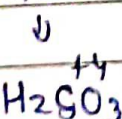
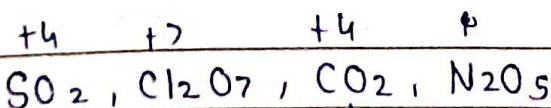
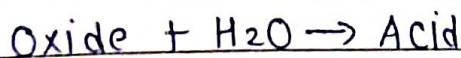


Mixed Oxide

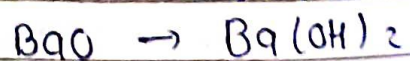
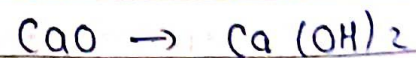
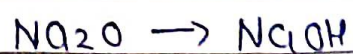
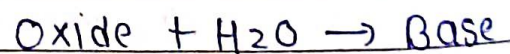


### Types of simple oxide

1) Acidic Oxide



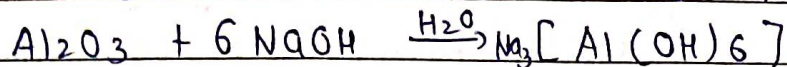
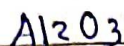
2) Basic Oxide





### 3) Amphoteric Oxide

Oxide  $\begin{cases} \text{Acidic} \\ \text{Basic} \end{cases}$



### 4) Neutral oxide

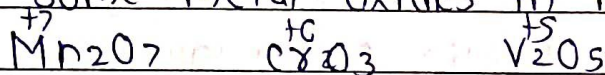
neither Acidic nor basic

$\rightarrow NO, CO, N_2O, H_2O$

Generally, metal oxide  $\rightarrow$  basic

non metal oxide  $\rightarrow$  acidic

But some metal oxides in high oxidation state - acidic

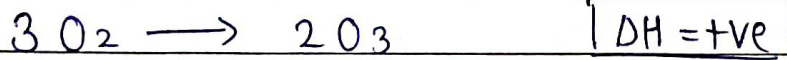


### \* Ozone

$\rightarrow$  allotrope of Oxygen

Preph - steam of Oxygen is passed through silent electric discharge

conversion of  $O_2$  to  $O_3 \rightarrow$  is only 10%.



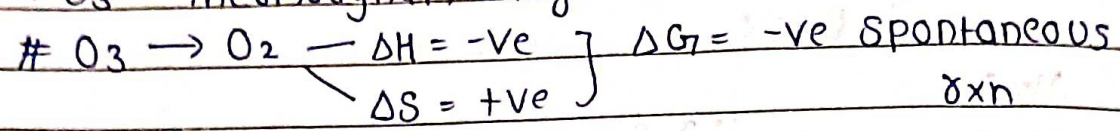
Ozonised oxygen

$\rightarrow$  since rxn  $\rightarrow$  endothermic, so silent electric discharge is used to prevent decomposition of Ozone

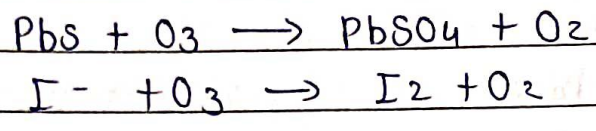
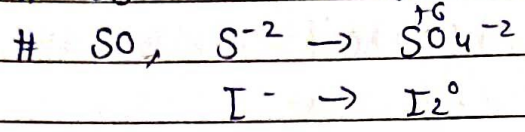
$\rightarrow$  if more than 10% ozone is required, a battery of ozonizer used. pure ozone is condensed in vessel surrounded by liq  $O_2$ .



Properties → Pure O<sub>3</sub> → Pale blue gas, dark blue liq, violet black soln  
 → O<sub>3</sub> - Thermodynamically unstable.

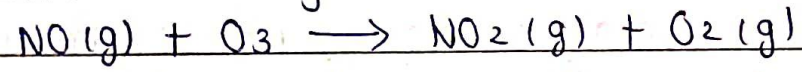


# O<sub>3</sub> → O<sub>2</sub> + [O] → Powerful oxidizing agent



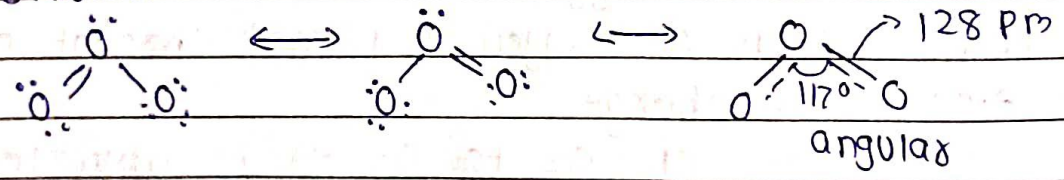
Depletion of ozone layer

→ NO gas emitted from supersonic jet aeroplane deplete ozone layer

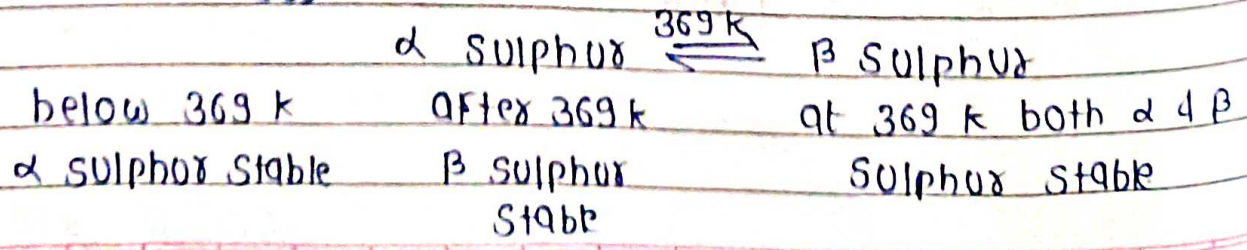
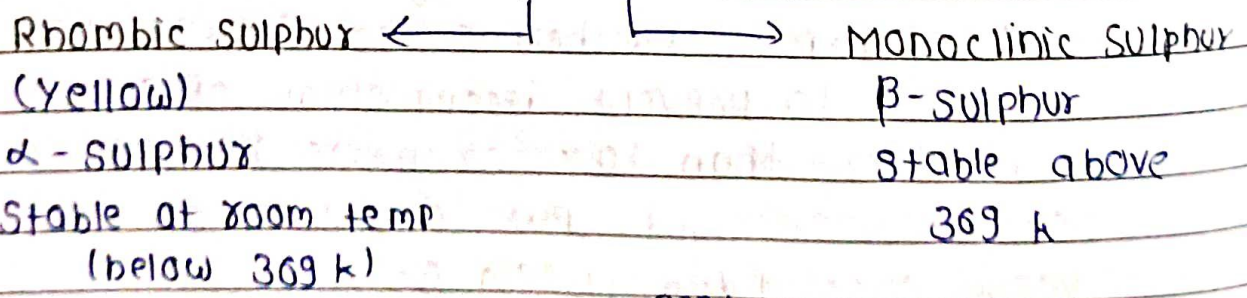


→ Use of freons deplete ozone layer  
 Aerosol spray  
 Refrigerant

→ Structure



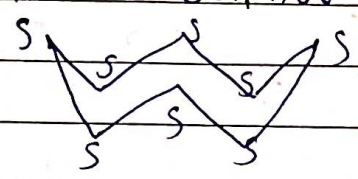
Sulphur allotrope





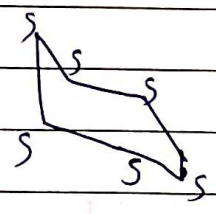
$\alpha$ - Sulphur	$\beta$ - Sulphur
Prep <sup>n</sup>	→ Soluble in $CS_2$
Roll sulphur + $CS_2 \xrightarrow{\text{evaporate}} \alpha$ -sulphur	→ melting of $\alpha$ sulphur in a dish & cooling till crust is formed
→ Insoluble in $H_2O$	→ Two holes are made in crust and remaining liq is poured out
→ partly dissolve in Benzene Alcohol, ether.	→ on removing crust needle shape $\beta$ sulphur is formed
→ Soluble in $CS_2$	

→ Both  $\alpha$  and  $\beta$  sulphur →  $S_8$  molecule



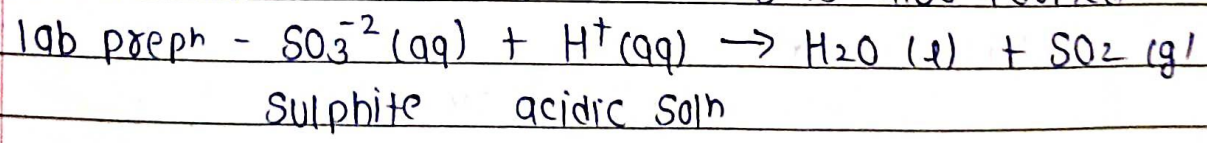
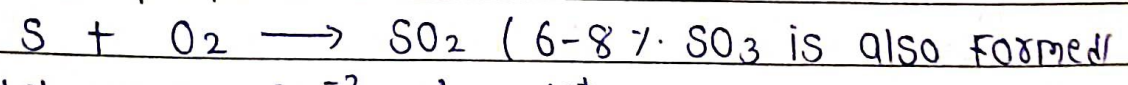
Crown shape

→  $S_6$  form  
Chair form

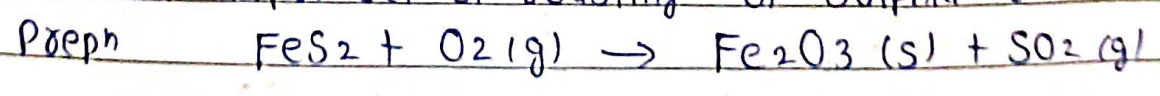


$T > 1000K$   
 $S_2$  - Paramagnetic like  $O_2$

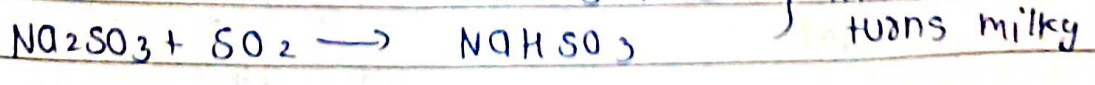
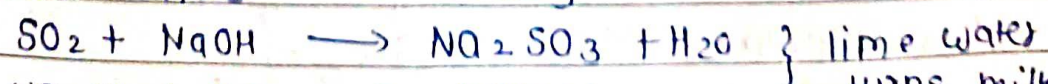
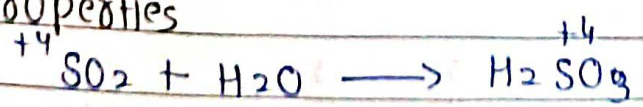
### $SO_2$ prep<sup>n</sup>



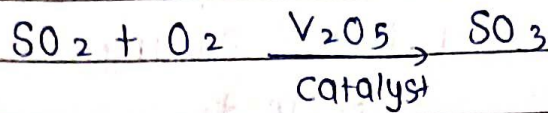
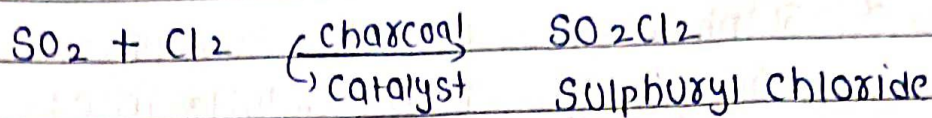
industrial byproduct of roasting of sulphide ore



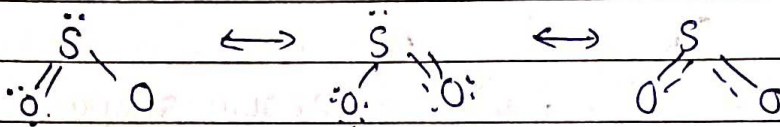
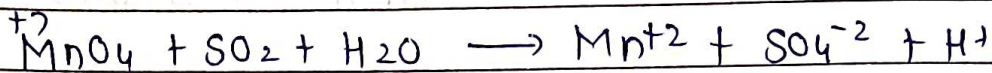
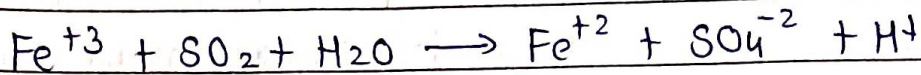
### Properties



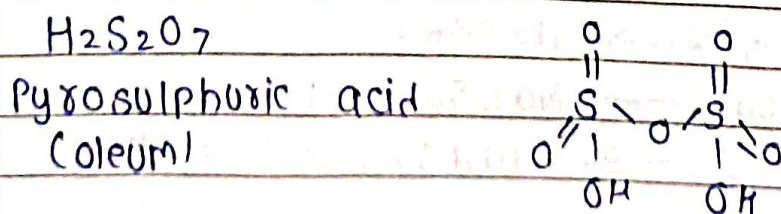
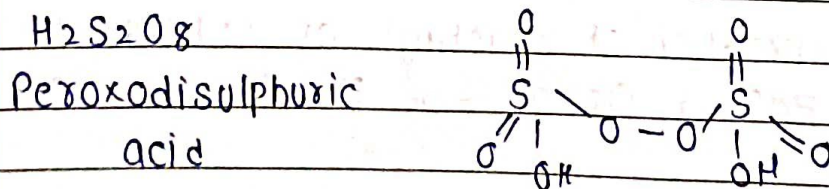
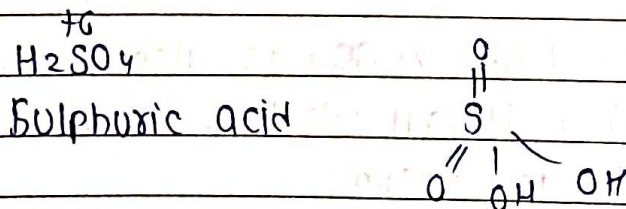
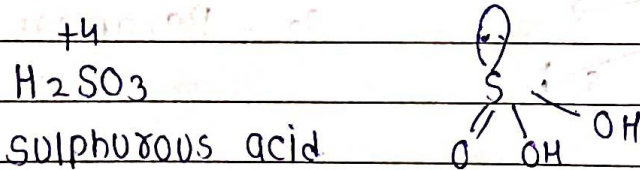




Moist  $\text{SO}_2 \rightarrow$  behave - Reducing Agent  $\rightarrow \text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$   
 Permanganate decolor



### Oxoacids of Sulphur





## Sulphuric acid

Prep contact process  $\rightarrow$  3 Step process

① Burning of Sulphur or sulphide ore  $\rightarrow$   $\text{SO}_2$  produce

②  $\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} \text{SO}_3$

③  $\overset{+6}{\text{S}}\text{O}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7$  (oleum)

# dilution of Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ) with  $\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$  of desired concn.

#  $\text{H}_2\text{SO}_4$  obtained by contact process  $\rightarrow$  96-98% pure

## Property.

$\rightarrow$  dissolves in  $\text{H}_2\text{O} \rightarrow$  releases high amount of energy

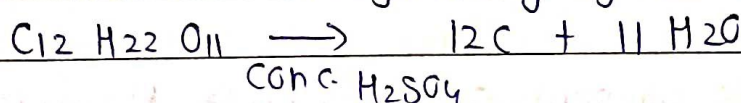
$\rightarrow$  Conc.  $\text{H}_2\text{SO}_4$  is added in  $\text{H}_2\text{O}$  slowly by const stirring

$\rightarrow$  In aq. soln

$\text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$   $K_a > 10$

$\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$   $K_a \rightarrow 1.2 \times 10^{-2}$

# Conc.  $\text{H}_2\text{SO}_4 \rightarrow$  dehydrating agent



# HOT conc.  $\text{H}_2\text{SO}_4 \rightarrow$  moderate oxidizing Agent

$\hookrightarrow$  Reduce  $\rightarrow \text{SO}_2$

$\text{Cu} + \text{Conc. H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2$

$\text{S} + \text{Conc. H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$

$\text{C} + \text{Conc. H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O}$



## GROUP-17

### \*Halogen Family\*

Greek halo means salt and genes means born i.e. salt producers.

Fluorine	F	9	$[\text{He}] 2s^2 2p^5$	फ्लोर
Chlorine	Cl	17	$[\text{Ne}] 3s^2 3p^5$	क्ल
Bromine	Br	35	$[\text{Ar}] 3d^{10} 4s^2 4p^5$	ब्रोम
Iodine	I	53	$[\text{Kr}] 4d^{10} 5s^2 5p^5$	आइ
Astatine	At	85	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^5$	आस्टी
Tennessine	Ts	117	$[\text{Rn}] 5f^{14} 6d^{10} 7s^2 7p^5$	टिसा

Note - Astatine and Tennessine are radioactive Elements.

Tennessine - It is a synthetic radioactive element.

Atomic mass is 294. Only very small amount of element could be prepared. Also its half life is in milliseconds only, so its chemistry could not be established.

### Occurrence

F → F is present as insoluble fluorides like fluorapatite (Ca<sub>5</sub>(FPO<sub>4</sub>)<sub>3</sub>) and cryolite (Na<sub>3</sub>AlF<sub>6</sub>) & in small quantities in soil, river water, plants, bone as well as teeth of animals.

→ Cl, Br, I are present as chlorides, bromide, iodide of sodium, potassium, calcium, magnesium etc.

→ The dried up seas contain sodium chloride and carnallite (KCl · MgCl<sub>2</sub> · 6H<sub>2</sub>O)

→ Iodine is also present in sea weeds (0.5% iodine) and Chile salt petre contains upto 0.2% of sodium iodide.



\* Electronic configuration - Outermost shell electronic configuration is  $ns^2 np^5$

\* Atomic and ionic radii

Size increases down the group due to increase in no. of shells, Halogens have smallest size in their respective periods due to high  $Z_{eff}$ .

\* Ionization enthalpy.

Due to low tendency to lose electron, they have high I.E. Down the group I.E.  $\downarrow$  due to  $\uparrow$  in size.

\* Electron gain Enthalpy -  $Cl > F > Br > I$

F has less electron gain enthalpy than Cl because of its small size and incoming  $e^-$  feels repulsive force from valence  $e^-$ . So some energy is absorbed to overcome the repulsive force and net energy released is decreases.

\* Electronegativity. They have very high E.N Down the Group EN  $\downarrow$ . F is most EN element in periodic table

\* Physical properties

Physical state - F, Cl  $\rightarrow$  Gases, Br - liquid, I - solid.  
MP & B.P.  $\uparrow$  down the Group with  $\uparrow$  in atomic size no.  
Colour -  $F_2$  (yellow),  $Cl_2$  (Greenish yellow),  $Br_2$  (Red)

$I_2$  (violet)

Bond dissociation Enthalpy -  $Cl-Cl > Br-Br > F-F > I-I$   
Reason for this is large electron-electron repulsion among the lone pairs in  $F_2$  molecule due to which they require less bond dissociation enthalpy than Cl, Br



□□□○

Solubility. F & Cl react with water, Br<sub>2</sub> and I sparingly soluble in water but soluble in various organic solvents such as chloroform, CCl<sub>4</sub>, CS<sub>2</sub> etc.

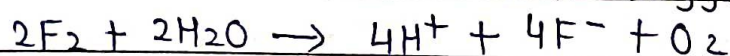
- Q. Why Fluorine is stronger oxidizing agent than Chlorine?
- i) low enthalpy of dissociation of F-F bond.
  - ii) High Hydration enthalpy of F<sup>-</sup>

Oxidation state - All halogen exhibit -1 oxidation state Cl, Br<sub>2</sub> and I exhibit +1, +3, +5 and +7 O.S also O.S of +4 and +6 occur in oxides and oxoacids of Cl and Br

The F atom has no d orbital in its valence shell and therefore cannot expand its octet. Being the most EN it shows only -1 O.S.

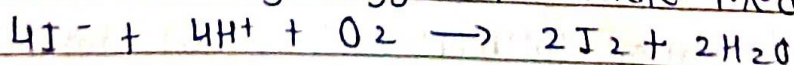
Note - A halogen oxidise halide ions of higher atomic number Ex -  $F_2 + 2X^- \rightarrow 2F^- + X_2$  (X = Cl, Br, or I)

Note - Fluorine oxidises water in oxygen



Cl and Br react with water to form corresponding hydrohalic & hypohalous acids Ex -  $X_2 + H_2O \rightarrow HX + HOX$

Reaction of I with water is non spontaneous, I<sup>-</sup> can be oxidised by oxygen in acidic medium.



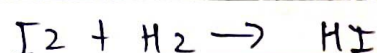
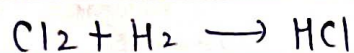
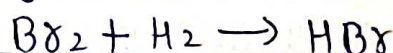
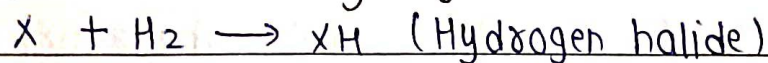


\* Anomalous behaviour of Fluorine

- IE, EN, electrode potential are higher for F than expected from the trends set by halogens
  - covalent & ionic radii, MP & BP, bond dissociation enthalpy and electron gain enthalpy is quite lower than expected.
  - Most of F reactions are exothermic.
  - only shows -1 O.S.
  - It forms only one oxoacid i.e. HOF
  - Hydrogen Fluoride (HF) is a liquid due to strong H-bonding
  - Act as strong oxidizing agent.
- Reason - Due to smaller size, higher EN and non availability of d orbital.

\* Chemical properties

Reaction with Hydrogen



Bond / strength / stability - stability of these halides ↓ down the group due to ↓ in bond (H-X) dissociation energy  
 $HF > HCl > HBr > HI$

Acidic character - ↑ down the group due to ↓ in H-X bond dissociation energy  $HF < HCl < HBr < HI$

Reducing nature - Releases H easily  
 $HF < HCl < HBr < HI$



Note - Hydrogen halides dissolve in water to form hydrohalic acids.  
 HF act as a very strong reducing agent.

Physical State - Except HF all others are gases at room temp. but HF is liquid.

Reaction with oxygen - Most of halogen oxides are unstable.  
 F forms only 2 oxides i.e.

$OF_2$  - Thermally stable at 298 K

$O_2F_2$  - It oxidise plutonium as  $PuF_6$  from spent nuclear fuel.

Cl, Br, & I form oxides in which O.S of these halogen range from +1 to +7.

Chlorine oxides -  $Cl_2O$ ,  $ClO_4$ ,  $Cl_2O_6$ ,  $Cl_2O_2$

Highly reactive oxidizing agent & tend to explode.

Note -  $ClO_2$  is used in bleaching agent.

Bromine oxides -  $Br_2O$ ,  $BrO_2$ ,  $BrO_3$  these are least stable exist only at low temp & powerful oxidising agent.

Iodine oxides,  $I_2O_5$ ,  $I_2O_4$ ,  $I_2O_7$  these are insoluble solids & decomposes on heating.

Note -  $I_2O_5$  is a very good oxidising agent and it is used in the estimation of  $CO$ .

Stability of oxides -  $I > Cl > Br$  (Due to combination of kinetic and thermodynamic factors)



Reaction towards metals.  $M + X \rightarrow MX$  (metal halides)  
 Ex -  $Mg + Cl_2 \rightarrow MgCl_2$

IF M is a monovalent metal then

Ionic character  $MF > MCl > MBx > MI$

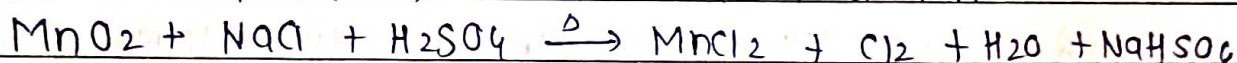
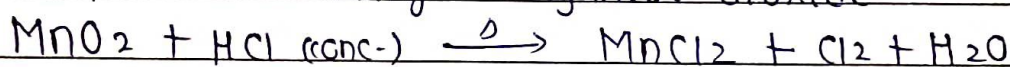
Note - Halide in Higher O.S will be more covalent than the one in lower O.S Ex  $SnCl_4$  is more covalent than  $SnCl_2$ .

Reactivity of halogen towards other halogen.

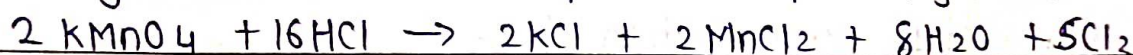
Halogen combine amongst themselves to form a no. of compounds called interhalogens

### Chlorine

i) Preparation - Using Manganese dioxide

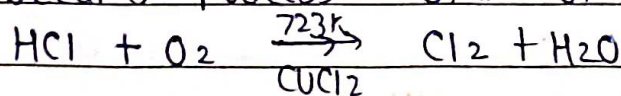


ii) By action of HCl on potassium permanganate

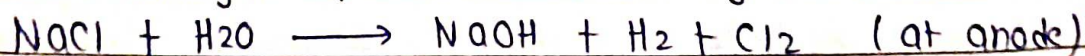


### Manufacture

i) Deacon's process - Oxidn of HCl



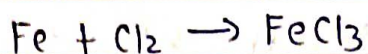
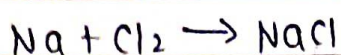
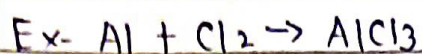
ii) Electrolytic process - Electrolysis of brine (conc. NaCl soln)



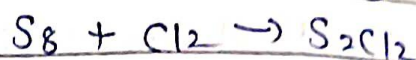
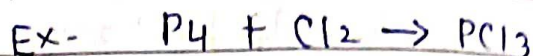
Properties: Greenish yellow gas, pungent odour & suffocating odour, easily liquified, soluble in water, 2-5 times heavier than air



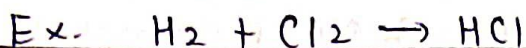
Reaction with metal



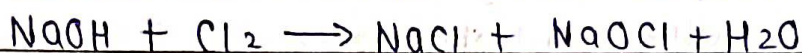
Reaction with nonmetal



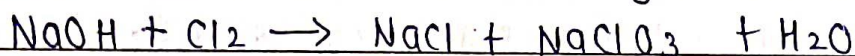
Reaction with H containing compounds



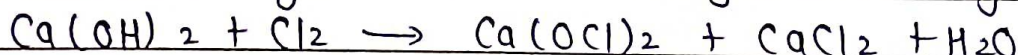
Rxn with cold & dilute alkali to produce chloride & hypochlorite



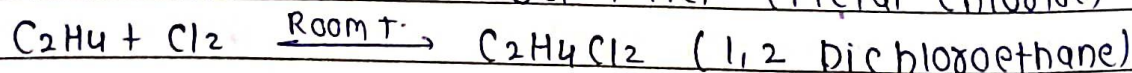
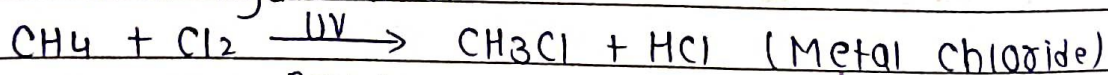
Rxn with hot & conc. alkali to give chloride & chlorate



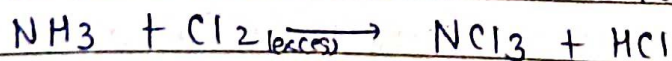
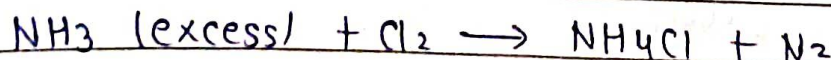
Rxn with dry slaked lime to give bleaching powder



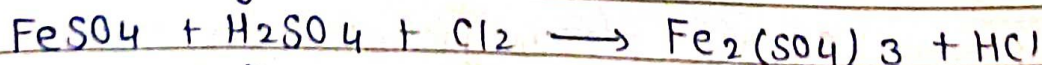
Rxn with hydrocarbon Ex -



Rxn with ammonia ex -

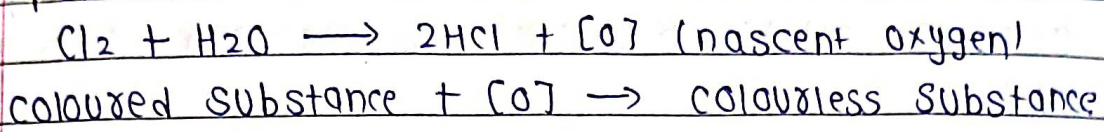


Oxidation by  $Cl_2$  Ex





Bleaching effect of  $Cl_2$  - Chlorine is a powerful bleaching agent, bleaching action is due to oxidation, which is permanent i.e.



Uses: For bleaching wood pulp, cotton and textiles, extraction of gold and platinum, manufacture of dyes drugs, organic compounds such as  $CCl_4$ ,  $CHCl_3$ , DDT, refrigerant, used in sterilising drinking water

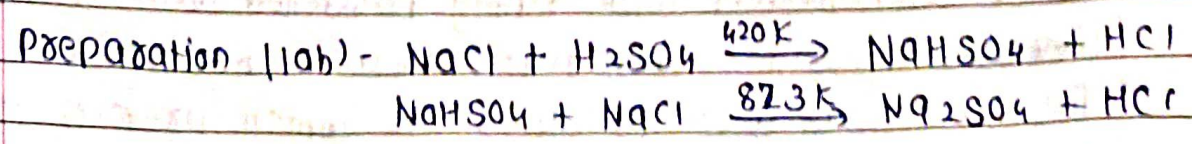
Q) Name two poisonous which can be prepared from  $Cl_2$ ?  
Phosgene ( $COCl_2$ ), tear gas ( $CCl_3NO_2$ ) Mustard gas ( $CClK_2CH_2SCH_2CH_2Cl$ )

Q)  $Cl_2 + NaOH \rightarrow NaCl + NaClO_3 + H_2O$ . Is this reaction a disproportionation reaction?  
Yes chlorine forms a oxidation state is changed to an +5 oxidation states

Note- Chlorine was discovered by Scheele in 1774 by action of HCl on  $MnO_2$ . In 1810 Davy established its elementary nature & suggested name chlorine on account of its colour (Greek chloros - greenish yellow)

\* Hydrogen Chloride (HCl)

Glauber prepared this acid in 1648 & Davy in 1810 showed that it is compound of H and Cl.

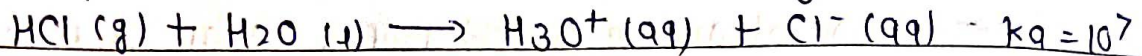




HCl can be dried by passing through concentrated  $H_2SO_4$

Properties: Colourless, pungent smelling gas, easily liquified, extremely soluble in water, freezes to a white crystalline solid.

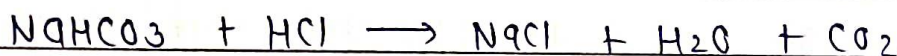
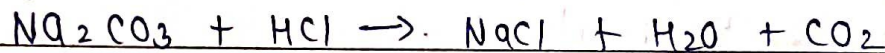
Its aqueous soln in water is called hydrochloric acid



High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water



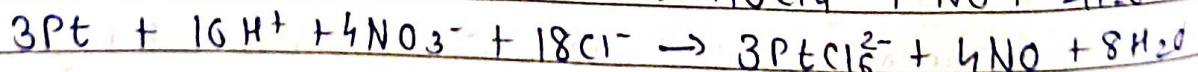
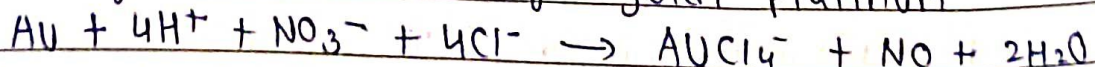
Hydrochloric acid decomposes salts of weaker acid



Uses - Used in manufacture of chlorine &  $NH_4Cl$ , glucose, extracting glue from bones & purifying bone black. In medicine and as a laboratory reagent.

Aqua regia

When 3 parts of conc. HCl and 1 part of conc.  $HNO_3$  are mixed, aqua regia is formed which is used for dissolving noble metals eg - gold, platinum



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

The rxn with iron produces  $H_2$  which prevents form<sup>n</sup> of ferric chloride. i.e.  $Fe + 2HCl \rightarrow FeCl_2 + H_2$



## \* Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)

HO<sub>2</sub>F - Hypofluorous acid

HOBr - Hypobromous acid

HOCl - Hypochlorous acid

HOI - Hypoiodous acid

Note - Due to high EN and small size F forms only one oxoacid

Halic (III) acid (Halous acid)

HOClO - Chlorous acid

Halic (V) acid (Halic acid)

HOClO<sub>2</sub>

HOBrO<sub>2</sub>

HOIO<sub>2</sub>

Chloric acid

Bromic acid

Iodic acid

Halic (VII) acid (Perhalic acid)

HOClO<sub>3</sub>

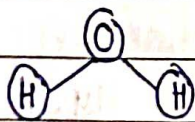
HOBrO<sub>3</sub>

HOIO<sub>3</sub>

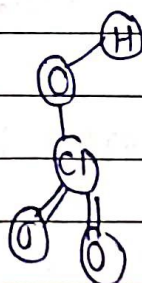
perchloric acid

perbromic acid

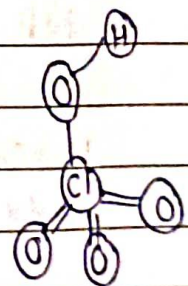
Iodic acid



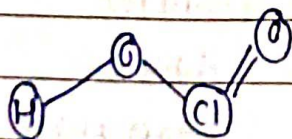
Hypochlorous acid



chloric acid



Perchloric acid



## Interhalogen compounds

When two diff halogens reacts with each other inter halogen compounds are formed. They can be assigned general composition as  $XX'$ ,  $XX'_3$ ,  $XX'_5$  and  $XX'_7$

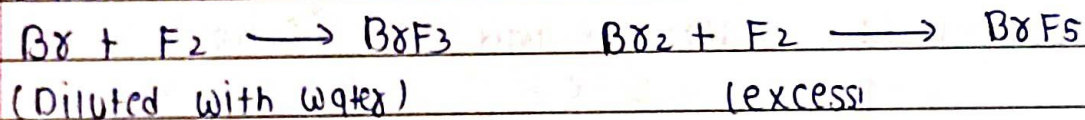
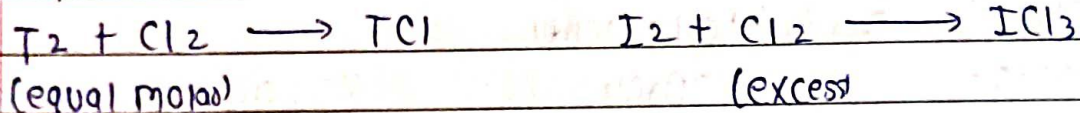
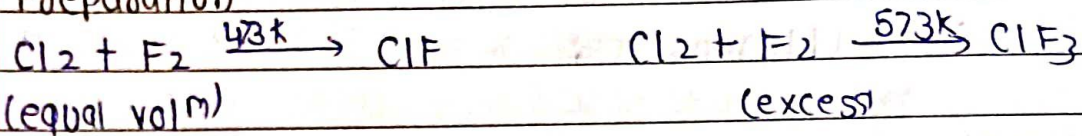


Where  $X \rightarrow$  less EN, large size, central atom  
 $X' \rightarrow$  more EN, small size. Bonded atom

Note- As ratio bet<sup>n</sup>  $X$  and  $X'$  increase the no. of atoms per molecule increases

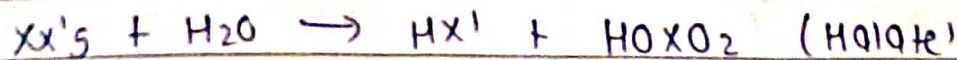
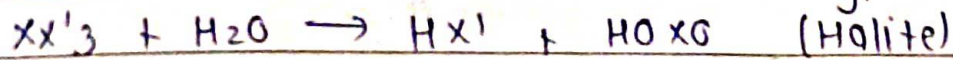
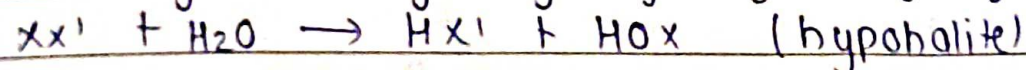
Ex- Radius ratio of iodine to fluorine is maximum so it forms  $IF_3$

### Preparation



Properties - All these molecules are covalent and diamagnetic volatile solids or liquid except  $ClF$  which is a gas MP and BP are little higher than the halogen

Interhalogen undergo hydrolysis give Hydrogen Halide



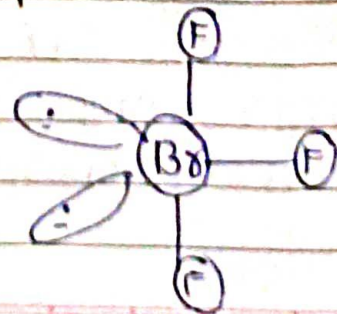
### Structure of interhalogen compound

$Bx F_3$  (yellow green liquid)

$Cl F_3$  (colourless gas)

$XX'_3$  type

Bent T-shaped



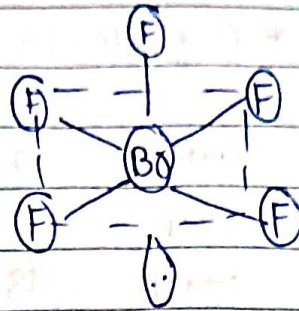


$XX_5$  type

Ex  $IF_5$  (colourless gas)

$BX_5$  ( " liquid)

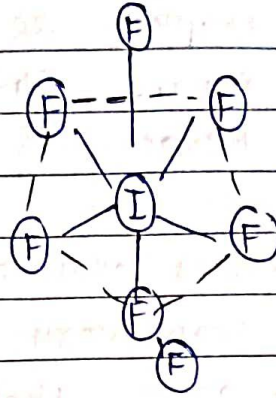
Square pyramidal shape.



$XX_7$  type

Ex  $IF_7$  (colourless gas)

Pentagonal bipyramidal



$XX$  type

Ex -  $ClF$  (colourless gas)

$ICl$  (ruby red solid  $\alpha$ -form)

(Brown red solid  $\beta$ -form)

$Cl-F$

linear

Uses - Used as non-aq. solvents, fluorinating agents  
 $ClF_3$  and  $BX_3$  are used in production of  $UF_6$  in  
excitement of  $^{235}U$ . i.e.  $U + 3ClF_3 \rightarrow UF_6 + 3ClF$



**\* GROUP-18 (Noble gases)**

He	Helium	2	1s <sup>2</sup>	हे	Noble gases or inert gases All gases are chemically unreactive
Ne	Neon	10	[He] 2s <sup>2</sup> 2p <sup>6</sup>	नानी	
Ar	Argon	18	[Ne] 3s <sup>2</sup> 3p <sup>6</sup>	आरम	
Kr	Krypton	36	[Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup>	कर	
Xe	Xenon	54	[Kr] 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>6</sup>	जिंदा	
Rn	Radon	86	[Xe] 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>6</sup>	रदोगी	

Outermost shell Electronic Configuration - ns<sup>2</sup> np<sup>6</sup>

They form very few compounds so they are called Noble gases. they react only under certain condition.

Occurrence - Except Rn and Oganesson all are present in atmosphere i.e 1% by volume in dry air, in which Argon is main constituent.

He and Ne - found in minerals of radioactive origin  
Natural gas is commercial source of Helium.

Xe and Rn - rarest elements of group.

Radon is obtained by decay product of <sup>226</sup>Ra

$${}_{88}^{226}\text{Ra} \longrightarrow {}_{86}^{222}\text{Rn} + {}_2^4\text{He}$$

Oganesson is synthetically produced by collision of <sup>249</sup>Cf atoms and <sup>48</sup>Ca ions i.e.

Oganesson - Symbol Og, atomic no 118, atomic mass 294  
electronic configuration [Rn] 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>6</sup> only  
its small amount has been produced. Its half life is 0.7 milliseconds.



Electronic configuration - general E.C -  $ns^2 np^6$  except He which has  $1s^2$

Atomic radii -  $\uparrow$  down the group with  $\uparrow$  in atomic no. However it is higher than corresponding halogens.

Ionisation Enthalpy - Due to stable electronic configuration they have very high I.E. However it  $\downarrow$  down the group with  $\uparrow$  in atomic size.

Electron gain Enthalpy - Since they have stable configuration they have no tendency to accept the electron & therefore have large +ve values of electron gain enthalpy.

MP and B.P - They have low MP and BP because weak vander waal forces are present betn their atoms -

Down the grp MP & BP  $\uparrow$  due to  $\uparrow$  in atomic size leads to increase in vanderwaal forces.

Some physical properties - Monoatomic gases, colourless, odourless, tasteless, sparingly soluble in water.

Note - He has the lowest B.P (4.2K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastic.

#### \* Chemical Properties

They are least reactive, their inertness due to

- i) completely filled  $ns^2 np^6$  electronic configuration except He
- ii) High IE and more +ve electron gain enthalpy



Discovery: Neil Bartlett, 1962 prepared  $O_2^+ PtF_6^-$  (red compound) & then prepared  $Xe^+ PtF_6^-$  (Red colour comp) by mixing  $PtF_6$  and xenon.

After this discovery a no. of Xe compounds mainly with most EN elements like F and O, have synthesized.

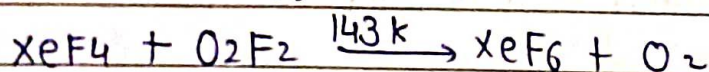
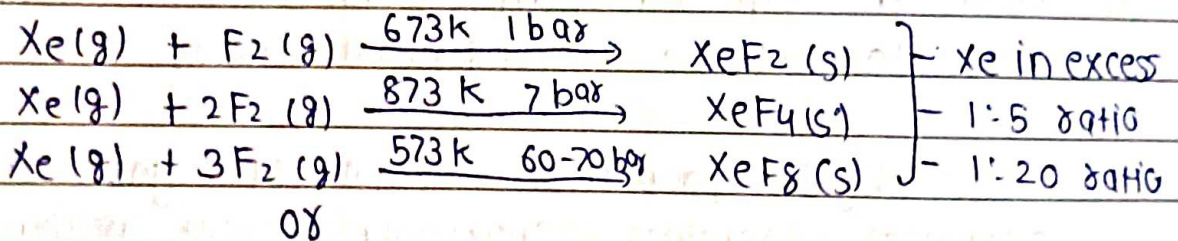
Compounds of Kr are fewer, only difluoride ( $KrF_2$ ) has been studied in detail.

Compounds of radon have not been isolated but only identified (Ex-  $RnF_2$ ) by radiotracers technique.

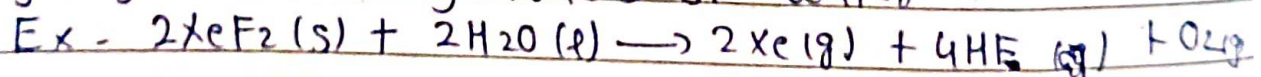
No blue compounds of Ar, Ne, or He are yet known.

### Xenon-fluorine compounds

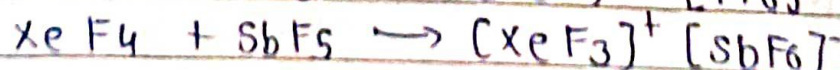
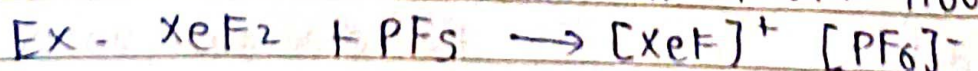
Xe form 3 binary fluorides  $XeF_2$ ,  $XeF_4$ ,  $XeF_6$



Properties: Colourless, crystalline solids, sublime readily at 298 K, powerful fluorinating agents, readily hydrolysed even by traces of water.



Xenon fluoride ion acceptors to form cationic species and fluoride ion donors in form fluoroanions.

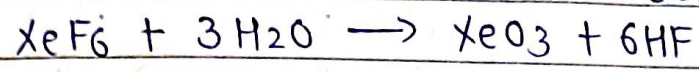
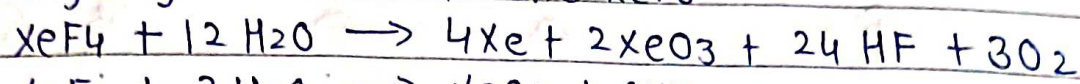


where (M = Na, K, Rb, or Cs)

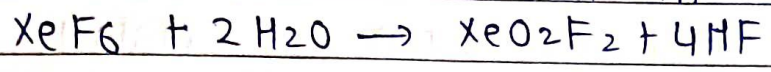
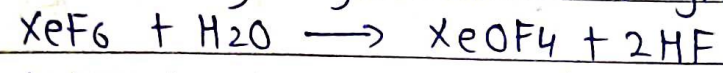


Xenon - Oxygen compounds -  $XeO_3$  &  $XeOF_4$ ,  $XeO_2F_2$

i) Hydrolysis of  $XeF_4$  and  $XeF_6$



ii) Partial hydrolysis of  $XeF_6$  gives oxyfluorides



Properties -  $XeO_3$  - colourless explosive solid

$XeOF_4$  - colourless volatile liquid

Uses -

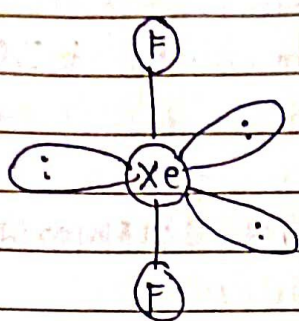
Helium - It is a non-inflammable & light gas. It is used in filling balloons, gas-cooled nuclear reactors. Liquid He is used as cryogenic agent for, used to produce and sustain powerful superconducting magnets which is essential part of modern NMR Spectrometers & Magnetic Resonance Imaging (MRI) system. It is used as diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon - Used in discharge tubes & fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

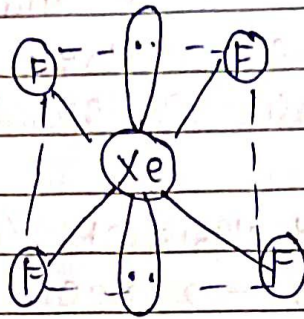
Argon - It is used to provide inert atmosphere in high temp & for filling electric bulbs, used in laboratory for handling air sensitive.



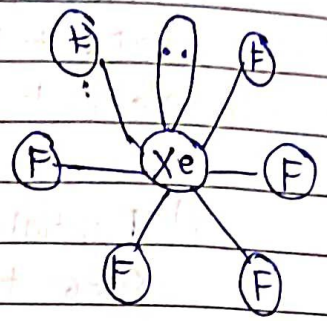
Xe & krypton - No significant uses. They are used in light bulbs synthesized designed for special purposes



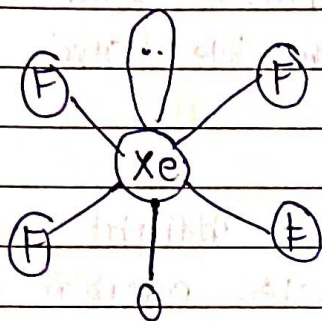
linear  $\text{XeF}_2$



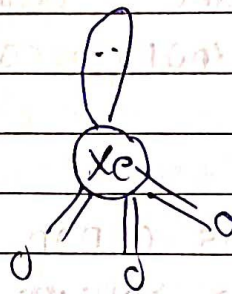
sq. planar  
 $\text{XeF}_4$



distorted octahedral  
 $\text{XeF}_6$



sq. pyramidal  
 $\text{XeOF}_4$



pyramidal  
 $\text{XeO}_3$