

# The P-BLOCK ELEMENTS

1s 2s 2p  
3s 3p 3d  
4s 4p 4d 4f

## GROUP 15 ELEMENTS

Nitrogen (N)	Phosphorus (P)	Arsenic (As)	Antimony (Sb)	Bismuth (Bi)
Non-metals		metalloids		metal

Electronic Configuration :-  $ns^2 np^3$

extra stable electronic configuration due to half filled p-orbital.

### II Atomic and Ionic Radii :-

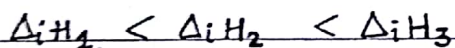
- Down the group, the atomic/ionic radii increases due to increase in the number of inner shells or shielding effect.
- The increase in size from N to P is considerable while from As to Bi, only a small increase is observed due to the presence of completely filled d/f orbitals which are poorly shielding.

### III Ionisation Enthalpy :-

- Down the group, ionisation enthalpy decreases due to gradual increase in atomic size.

**NOTE:-** Because of the extra stable half-filled p orbitals electronic configuration and small size, the <sup>1st</sup> IE of group 15 elements is much greater than that of group 14 elements in the corresponding periods.

The order of successive ionisation enthalpies as expected is



### IV Electronegativity :-

The electronegativity value decreases down the group with increasing atomic size.

### V Occurrence :-

- (i) **NITROGEN** :-
- $N_2$  gas (78% by volume of atmosphere)
  - as sodium nitrate,  $NaNO_3$  (chilesalt petre) & potassium nitrate,  $KNO_3$  (Indian salt petre)

• in the form of proteins in plants & animals.

(ii) PHOSPHORUS : • in minerals of the apatite family  
eg. fluorapatite  $[Ca_5(PO_4)_3 \cdot CaF_2]$

- an essential constituent of animal & plant matter
- present in bones as well as in living cells.

(iii) ARSENIC, ANTIMONY & BISMUTH are found mainly as sulphides.

Ques Nitrogen exists as a diatomic molecule i.e.  $N_2$  while phosphorus exists as tetra-atomic molecule i.e.  $P_4$ . Explain.

Ans It is because phosphorus (P) cannot form p $\pi$ -p $\pi$  multiple bonding because of diffused nature of large 3p-orbital which does not lead to effective overlap.

Nitrogen can form p $\pi$ -p $\pi$  multiple bond because 2p-orbital is smaller in size and can overlap sideways effectively.

Ques Nitrogen is a gas at room temp. while phosphorus is a solid. Explain.

Ans It is because the atomicity increases from diatomic nitrogen ( $N_2$ ) to tetra-atomic phosphorus ( $P_4$ ) which increases the VDW forces largely.

## PHYSICAL PROPERTIES

All the elements of this group are POLYATOMIC.

Dinitrogen is a diatomic gas while all others are solids.

The boiling points increase from top to bottom.

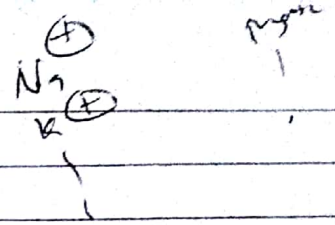
Melting pt. increases upto arsenic & then decreases upto Bismuth.

Metallic character increases down the group.

Why?? due to decrease in IE & increase in atomic size.

Except nitrogen, all the elements show allotropy.

# ~~##~~ CHEMICAL PROPERTIES



## # OXIDATION STATES

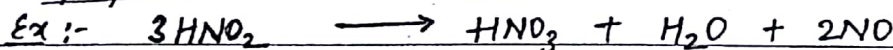
Electronic configuration :  $ns^2 np^3$   
+3  
+5

Examples →  
-3 :  $\overset{\ominus 3}{\text{C}}_3\text{N}_2$  (ionic valency) ;  $\text{NH}_3$  (covalency)  
+3 :  $\overset{\oplus 3}{\text{N}}\text{Cl}_3$ ,  $\overset{\oplus 3}{\text{P}}\text{H}_3$   
+5 :  $\overset{\oplus 5}{\text{P}}\text{Cl}_5$

\* The tendency to exhibit -3 O.S. decreases down the group  
↳ Why?? due to increase in size & metallic character  
(i.e. electronegativity)

\* +3 and +5 are generally the covalency and the tendency to show (+3) O.S. in comparison to (+5) O.S. INCREASES down the group.  
↳ Why??? It is because of inert pair effect i.e. non-participation of s electrons in bond formations as when we go down the group, the bonds formed are weaker & thus, the energy released is not sufficient to cause unpairing of s e.s.

NOTE :- \* In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.



\* Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding

Ques Give reason for the fact that nitrogen shows anomalous behaviour in gp 15. Also give chemical evidence for the same.

Ans Reasons for Anomalous Behaviour :-

- small size
- high ionisation enthalpy
- high electronegativity
- non-availability of d-orbitals.
- unique ability to form p $\pi$ -p $\pi$  multiple bonds.

## CHEMICAL EVIDENCE :-

- Nitrogen is capable of forming p $\pi$ -p $\pi$  multiple bonds with itself & with other elements having small size & high  $\bar{e}$ -negativity (eg. C, O)
- It is capable of showing -3 O.S. as ionic valency

Ex:-  $\text{Ca}_3\text{N}_2$ .

Ques

Ans

Dinitrogen ( $\text{N}_2$ ) is inert at room temp. why??  
It is because of high bond dissociation enthalpy of triple bond in nitrogen molecule.  $\{\text{N}\equiv\text{N} \rightarrow \text{N}_2\}$

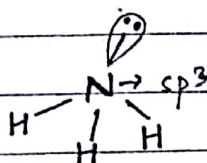
NOTE :-

The single N-N bond is weaker than the single P-P bond because of high inter-electronic repulsion of the non-bonding electrons, owing to the small bond length.

As a result, the catenation tendency is weaker in nitrogen.

## REACTIVITY TOWARDS HYDROGEN

All Grp 15 elements form hydrides of formula  $\text{MH}_3$  which is trigonal pyramidal in shape. Hybridisation of the element is  $sp^3$  with one lone pair of  $\bar{e}$ s present at one of the vertices of tetrahedron.



shape  $\rightarrow$  trigonal pyramidal

geometry  $\rightarrow$  tetrahedron

HYDRIDES :

$\text{NH}_3 \rightarrow$  Ammonia

$\text{P.H}_3 \rightarrow$  Phosphine

$\text{As.H}_3 \rightarrow$  Arsine

$\text{Sb.H}_3 \rightarrow$  Stibine

$\text{Bi.H}_3 \rightarrow$  Bismuthine

(i) Thermal Stability:  $\rightarrow$  {how easily it can be decomposed}

Decreases down the group bcoz of  $\uparrow$ se in size of the element which results in weaker bonds.

(ii)

Reducing characteristic: *Reduce hone ka matlab hai ki kisi jaldi e accept kar leta hai*  
Increases down the group bcoz the thermal stability decreases as the bond length  $\uparrow$ ses down the grp.

NOTE :-

Ammonia is a mild reducing agent &  $\text{BiH}_3$  is the strongest reducing agent amongst all the hydrides.

*Kyunki  $\downarrow$  G weaker bonds*

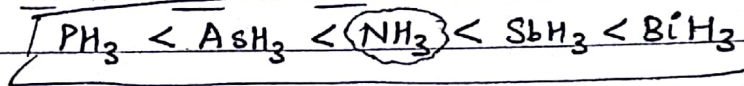
*so bond length  $\uparrow$  so Reducing character  $\uparrow$*

(iii) Boiling Point :-  $\text{NH}_3 \gg [\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3]$   
 (due to hydrogen-bonding) (due to increase in VDW forces)

Boiling pt. ↑ses regularly from  $\text{PH}_3$  to  $\text{BiH}_3$  bcoz of ↑se in VDW forces with ↑se in mass and size.

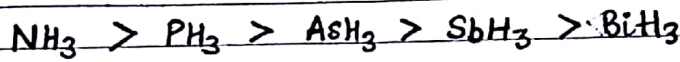
$\text{NH}_3$  in the grp has exceptionally high b.pt. bcoz of its ability to undergo hydrogen-bonding.

Therefore, the correct order is



(iv) Basic character :-

- $\text{NH}_3$  & other hydrides are basic in nature because of presence of lone pair of e<sup>-</sup> over the central atom. (LEWIS BASES)
- The Basic character ↓ses down the group.



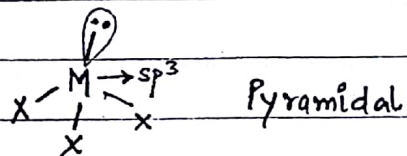
bcoz of ↑se in size of the central atom & thus, reduction in its tendency to give lone pair with ↓se in electron density.

Ques  $\text{PH}_3$  when passed through water forms bubbles while  $\text{NH}_3$  doesnot. why?  
 (means ki  $\text{PH}_3$  is insoluble and  $\text{NH}_3$  is soluble in  $\text{H}_2\text{O}$ )

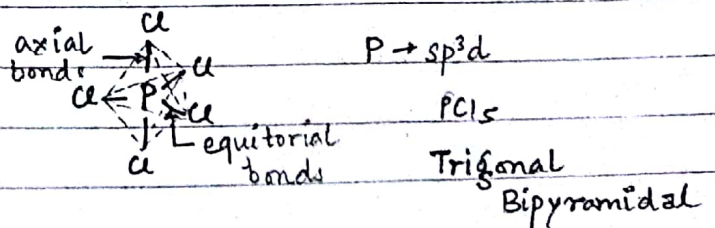
Ans It is because unlike  $\text{PH}_3$ ,  $\text{NH}_3$  is soluble in water as it can form H-bond with  $\text{H}_2\text{O}$  molecules.

## REACTIVITY TOWARDS HALOGENS

- They form TRIHALIDES of the formula  $\text{MX}_3$  with pyramidal shape



- They form PENTAHALIDES of the formula  $\text{MX}_5$  with trigonal bipyramidal shape.



Ques All the bonds in  $PCl_5$  are not equivalent. Why??

Ans It is bcoz along axial lines, there are greater repulsions. Therefore, to minimise repulsions, axial bonds are elongated i.e. longer than equatorial bonds.

Ques Pentahalides are more covalent than trihalides. Explain.

Ans It is bcoz in pentahalides, the oxidation state of the central metal atom is high and thus its charge density and polarising power is also high resulting in greater covalent character.  
(FAZAN RULE)

Ques Bromides are more covalent than chlorides. Why??

Ans size of Bromide > size of chloride.  
(FAZAN RULE) It is bcoz larger the size of the anion, more is its polarisability and hence, greater is the covalent character.

Ques  $BiF_3$  is pre-dominantly ionic. Why?

Ans  $F^-$  → smallest anion, least polarisability  
 $Bi$  → largest cation, least charge density, least polarising power  
⇒ least covalent character  
⇒  $BiF_3$  is pre-dominantly ionic.

Ques  $PCl_5$  exists while  $NCl_5$  doesnot. Why??

Ans It is bcoz unlike P, nitrogen doesnot have vacant d-orbital to which s.e.s can move after getting unpaired.

Ques  $R_3P=O$  exists while  $R_2N=O$  doesnot. Why??

Ans It is because nitrogen doesnot have vacant d-orbitals.  
∴ s.e.s can't get unpaired and nitrogen can't form 5  $\sigma$  bonds.

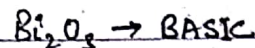
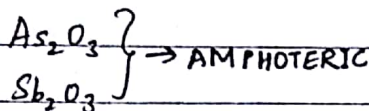
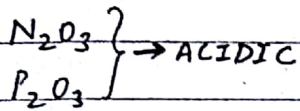
### Try out Yourself

Que. The H-N-H angle value is higher than H-P-H, H-As-H, H-Sb-H angles. Why??

### REACTIVITY TOWARDS OXYGEN

- All these elements form two types of oxides:  $M_2O_3$  &  $M_2O_5$ .
- The oxide in the higher O.S. of the element is more acidic than that of lower O.S.

Their acidic character decreases down the grp.



### REACTIVITY TOWARDS METALS

All these elements react with metals to form their binary compounds exhibiting -3 O.S.

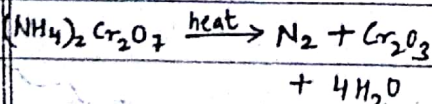
Ex:-  $Ca_3N_2 \rightarrow$  calcium nitride ;  $Ca_3P_2 \rightarrow$  calcium phosphide ;  
 $Na_3As_2 \rightarrow$  sodium arsenide

### DINITROGEN ( $N_2$ )

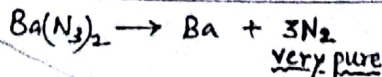
#### PREPARATION

commercially produced by liquefaction and fractional distillation of air.

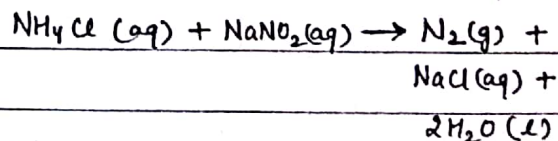
By thermal decomposition of ammonium dichromate



By thermal decomposition of sodium or barium azide.



By treating aq. sol<sup>n</sup> of  $NH_4Cl$  with sodium nitrite.



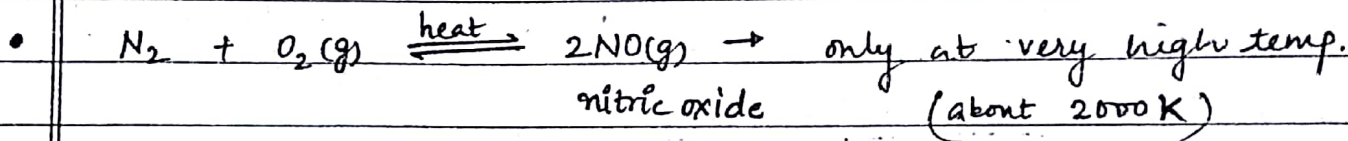
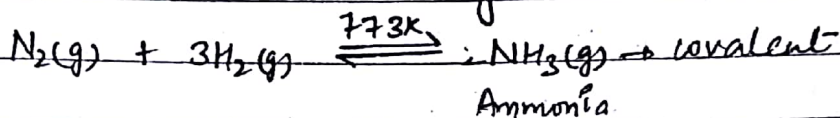
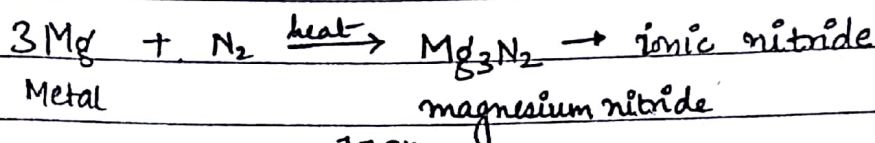
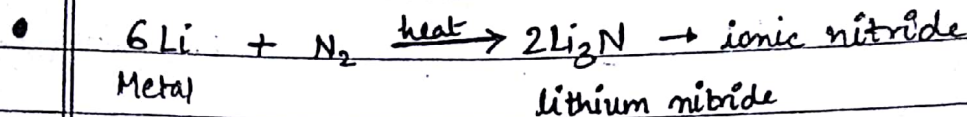
⊙ Small amts of  $NO$  &  $HNO_3$  (impurities) formed & removed by passing the gas through aq.  $H_2SO_4$  containing  $K_2Cr_2O_7$ .

## PROPERTIES

colourless, odourless,  
tasteless and  
non-toxic gas.

is inert at room  
temperature.

has very low solubility  
in water & low  
freezing & boiling pts.



## USES

in the manufacture  
of ammonia &  
other industrial  
chemicals.

liquid dinitrogen is used  
as a refrigerant to  
preserve biological materials,  
food items, etc.

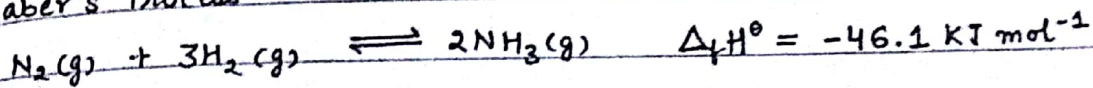
used where  
inert atmosphere  
is required



# AMMONIA

## \* PREPARATION:-

By Haber's Process



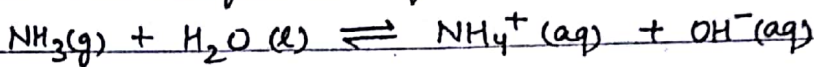
Cond<sup>n</sup> :- pressure about 200 atm

temperature  $\approx 700 \text{ K}$

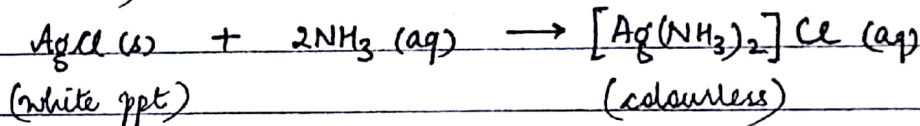
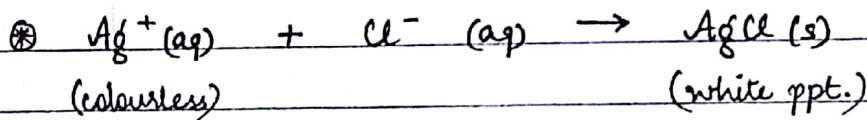
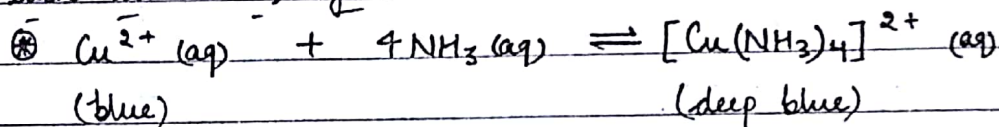
catalyst such as iron oxide with small amts of  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  to increase the rate of attainment of equilibrium.

## \* PROPERTIES:-

- Ammonia gas is highly soluble in water. Its aqueous sol<sup>n</sup> is WEAKLY BASIC due to the formation of  $\text{OH}^-$  ions.



- It donates the electron pair and forms linkages with metal ions & the formation of such complex compounds finds app in detection of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ :



## \* USES

to produce various nitrogenous fertilisers

ex: ammonium nitrate  
ammonium phosphate  
ammonium sulphate  
urea

in the manufacture of some inorganic nitrogen compounds.

(ex:  $\text{HNO}_3$ )

liquid  $\text{NH}_3$  is also used as a refrigerant.

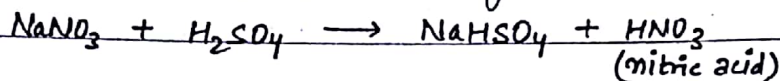
# OXIDES OF NITROGEN

Refer to Table 7.3 : oxides of Nitrogen &  
Table 7.4 : Structures of oxides of Nitrogen  
of NCERT Textbook, Chemistry, Part I

**NITRIC ACID :  $\text{HNO}_3$**  (colourless liquid)

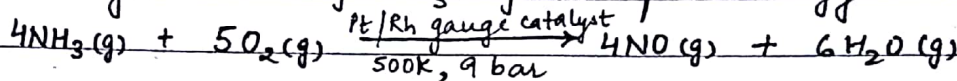
## \* PREPARATION :

- (1) In the laboratory, nitric acid is prepared by heating  $\text{KNO}_3$  or  $\text{NaNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  in a glass retort.

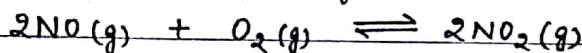


- (2) By Ostwald's Process

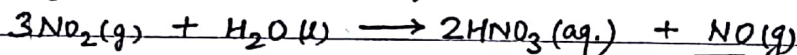
Step 1 : catalytic oxid<sup>n</sup> of  $\text{NH}_3$  by atmospheric oxygen



Step 2 : Nitric oxide ( $\text{NO}$ ) thus formed combines with  $\text{O}_2$  giving  $\text{NO}_2$



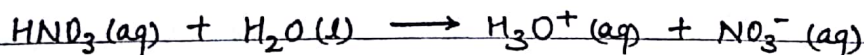
Step 3 : Nitrogen dioxide ( $\text{NO}_2$ ) so formed, dissolves in  $\text{H}_2\text{O}$  to give  $\text{HNO}_3$



\* 98% conc. of  $\text{HNO}_3$  can be achieved  
by dehydration with conc.  $\text{H}_2\text{SO}_4$ . ↳ Recycled

## \* PROPERTIES :

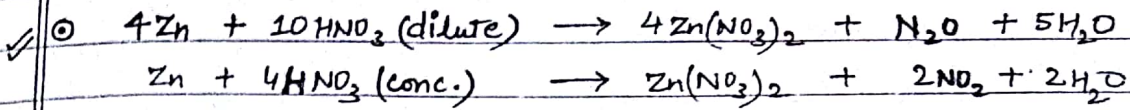
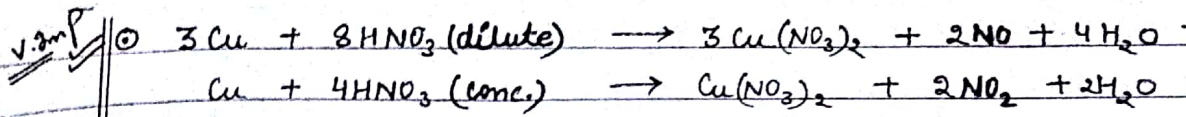
- In aq. sol<sup>n</sup>,  $\text{HNO}_3$  behaves as a strong acid giving hydronium and nitrate ions.



- Conc.  $\text{HNO}_3$  is a strong oxidising agent & attacks most metals except noble metals such as gold and platinum.

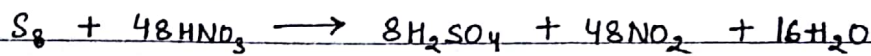
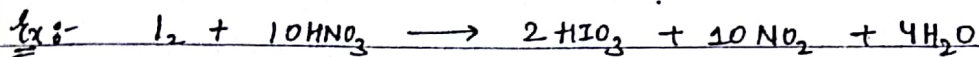
The products of oxid<sup>n</sup> depend upon

- (a) conc. of the acid (b) temperature  
(c) the nature of the material undergoing oxid<sup>n</sup>.

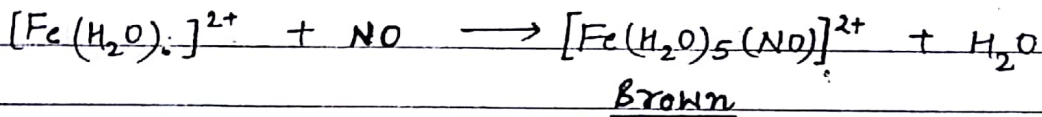
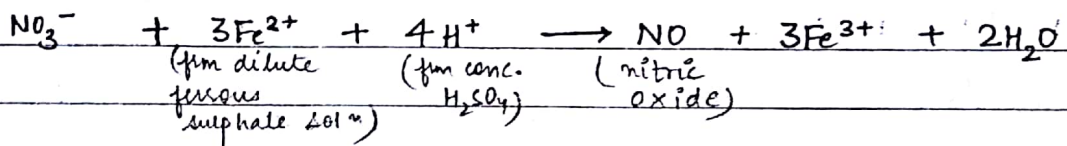


Some metals (eg. Cr, Al) don't dissolve in conc.  $\text{HNO}_3$  becoz of the formation of a passive film of oxide on the surface. (passivation).

Conc.  $\text{HNO}_3$  also oxidises non-metals and their compounds.



\* BROWN RING TEST :- (for nitrate ion)



\*

USES of  $\text{HNO}_3$

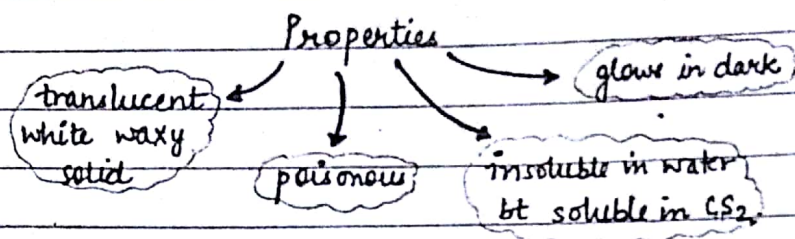
in the manufacture of ammonium nitrate for fertilisers & other nitrate for use in explosives and pyrotechnics.

in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

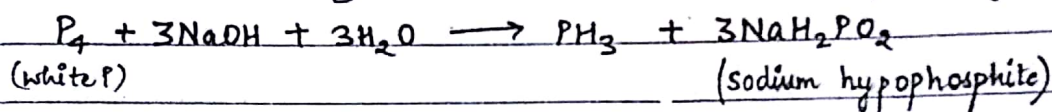
# PHOSPHORUS - ALLOTROPIC FORMS

Allotropic forms of phosphorus are: WHITE, RED & BLACK

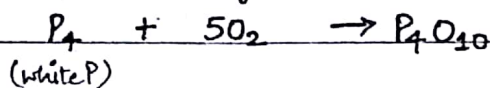
## \* WHITE PHOSPHORUS :



- It dissolves in boiling NaOH sol<sup>n</sup> in an inert atmosphere giving PH<sub>3</sub>.



- It readily catches fire in air to give dense white fumes of P<sub>4</sub>O<sub>10</sub>.



## \* RED PHOSPHORUS :

PREPARATION:  
obtained by heating white P at 573K in an inert atmosphere for several days.

### PROPERTIES.

- possesses iron grey lustre.
- odourless, non-poisonous
- insoluble in H<sub>2</sub>O as well as CS<sub>2</sub>
- doesn't glow in dark.

**BLACK PHOSPHORUS** : obtained by heating red phosphorus under high pressure. It has 2 forms:

α-Black

- formed when red P is heated in a sealed tube at 803 K
- doesnot oxidise in air
- has opaque monoclinic or rhombohedral crystals.

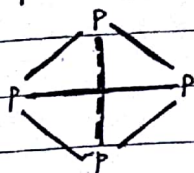
β-black

- prepared by heating white P at 473K under high pressure
- doesnot burn in air upto 673K.

Ques

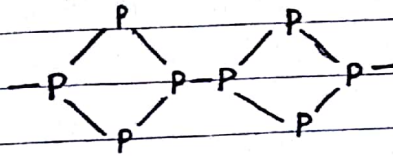
Compare the structure and reactivity of 2 imp. allotropes of P.

Ans



WHITE PHOSPHORUS

discrete P<sub>4</sub> units



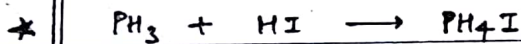
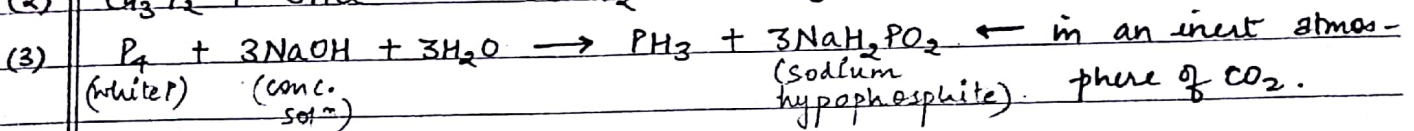
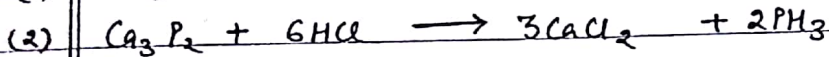
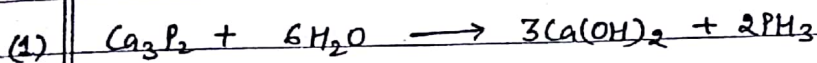
RED PHOSPHORUS

Polymeric Structure of P<sub>4</sub> units

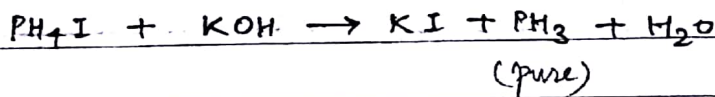
Reactivity :- white P is more reactive than red P bcoz of angular strain in the molecule as the bond angle is very small i.e. 60°.

### PHOSPHINE : PH<sub>3</sub>

#### \* PREPARATION :-



(impure)



\*

#### PROPERTIES

colourless gas with rotten fish smell & is highly poisonous.

weakly basic  
ex:  $PH_3 + HBr \rightarrow PH_4Br$

explodes in contact with traces of oxidising agents like HNO<sub>3</sub>, Cl<sub>2</sub> & Br<sub>2</sub> vapours

slightly soluble in water

\*

#### USES

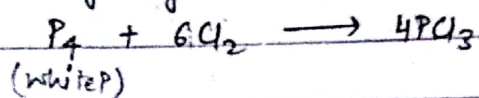
It is used in HOLME'S SIGNALS & in SMOKE SCREENS

# PHOSPHORUS HALIDES

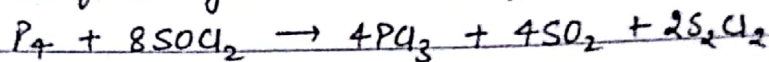
## \* PHOSPHORUS TRICHLORIDE : $PCl_3$

### PREPARATION

(a) By passing dry chlorine over heated white P.

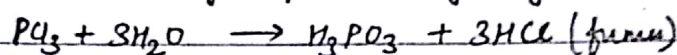


(b) By action of thionyl chloride ( $SOCl_2$ ) on white P

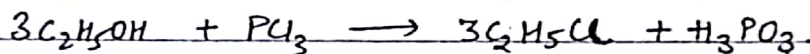
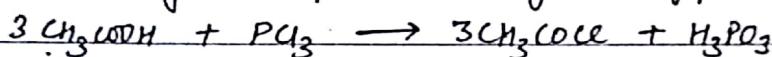


### PROPERTIES

(a) It is a colourless oily liquid & hydrolyses in the presence of moisture.



(b) It reacts with organic compounds containing  $-OH$  grp



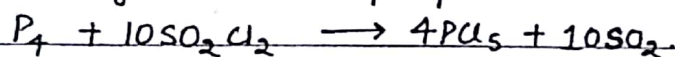
## \* PHOSPHORUS PENTACHLORIDE : $PCl_5$

### PREPARATION

(a) by reaction of white P with excess of dry chlorine

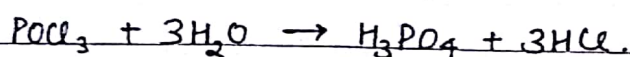
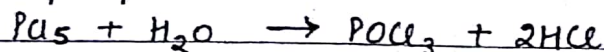


(b) by action of  $SO_2Cl_2$  on phosphorus

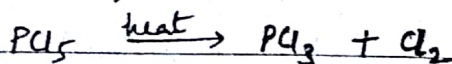


### PROPERTIES :

(a) It is a yellowish white powder & it hydrolyses to  $POCl_3$  & finally gets converted to phosphoric acid.



(b) when heated, it sublimes but decomposes on stronger heating



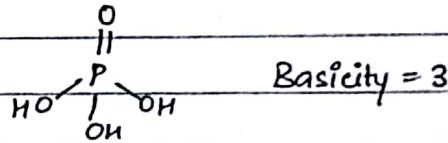
Ques How does  $PCl_5$  exist in solid state?

Ans In the solid state,  $PCl_5$  exists as an ionic solid,  $[PCl_4]^+[PCl_6]^-$  in which the cation,  $[PCl_4]^+$  is tetrahedral & the anion,  $[PCl_6]^-$  is octahedral.

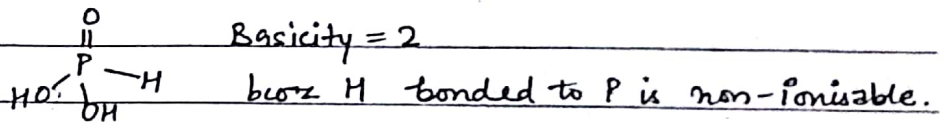
### OXO-ACIDS OF PHOSPHORUS

- \* In all these acids, P atom is tetrahedrally co-ordinated to at least 1 oxygen atom with double bond & at least 1 -OH group.
- \* H bonded to O only is ionisable.

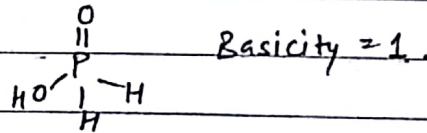
①  $H_3PO_4$  : Phosphoric acid



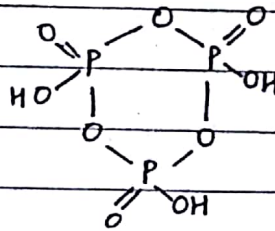
②  $H_3PO_3$  : Phosphorous acid



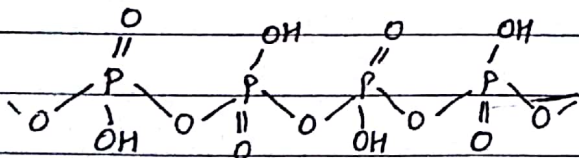
③  $H_3PO_2$  : Hypo-phosphorous acid



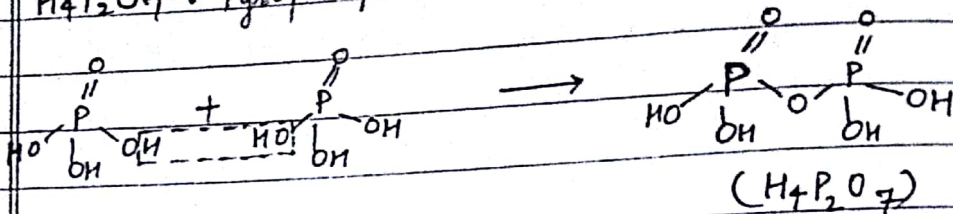
④ Cyclotrimetaphosphoric acid :  $(HPO_3)_3$



⑤ Polymetaphosphoric acid :  $(HPO_3)_n$



⑥  $H_4P_2O_7$  : Pyrophosphoric acid



Ques

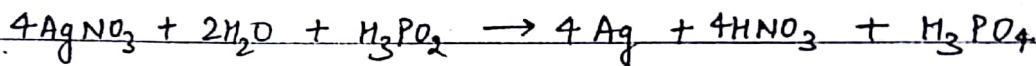
Explain the reducing properties of hypo-phosphorus acid ( $H_3PO_2$ )

Ans

H bonded to P is non-ionisable but imparts reducing characteristics to the acid.

In  $H_3PO_2$ , 2 H are directly bonded to P & hence is reducing in nature.

Ex:-



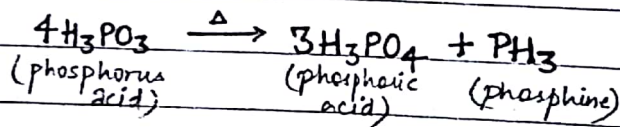
↳  $\text{Ag}^+$  is reduced to Ag.

Ques

What happens when  $H_3PO_3$  is heated??

Ans

Orthophosphorus acid (or phosphorus acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) & phosphine.



(15 Questions)



# GROUP-16 ELEMENTS {Chalcogens}

Atomic No.	Element	Electronic Configuration
8	Oxygen (O)	[He] $2s^2 2p^4$
16	Sulphur (S)	[Ne] $3s^2 3p^4$
34	Selenium (Se)	[Ar] $3d^{10} 4s^2 4p^4$
52	Tellurium (Te)	[Kr] $4d^{10} 5s^2 5p^4$
84	Polonium (Po) → metal ↳ radioactive.	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$

## \* OCCURRENCE :-

**SULPHUR** : as sulphates such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), baryte ( $\text{BaSO}_4$ )  
as sulphides such as galena (PbS), zinc blende (ZnS), etc.

## \* ELECTRONIC CONFIGURATION :-

The elements of grp 16 have 6 e.s in the outermost shell. ( $ns^2 np^4$ )

## \* ATOMIC AND IONIC RADII :-

Down the grp, atomic & ionic radii ↑ due to ↑ in the no. of shells.

## \* IONISATION ENTHALPY (IE) :-

Ionisation Enthalpy ↓ down the group due to ↑ in size.

Ques Elements of Grp 16 generally show lower value of 1st IE compared to the corresponding periods of grp 15. Why??

Ans Due to extra stable half-filled p orbitals electronic configuration of grp 15 elements, larger amt. of energy is reqd. to remove e.s compared to Grp 16 elements.

## \* ELECTRON GAIN ENTHALPY (EGE) :-

EGE becomes less negative down the group. (bcz of ↑ in size)

Bt... EGE of oxygen is LESS than that of sulphur.

Why...?? bcoz the incoming electron faces greater inter-electronic repulsions in the small sized 2p orbital of oxygen atom.

## \* ELECTRONEGATIVITY :-

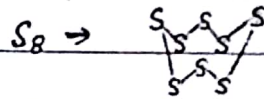
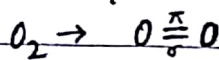
Down the group, electronegativity ↓ as size ↑.

NOTE:- Next to fluorine, OXYGEN has the highest electronegativity value amongst the elements.

⊙ Their MELTING & BOILING pts. ↑ as down the grp.

↳ bcoz VDW forces ↑ as with increase in mass & size.

Ques oxygen exists as diatomic molecule ( $O_2$ ) while sulphur exists as  $S_8$ . Why?



Ques There exists a large difference b/w the melting & Boiling pts. of oxygen & sulphur. Explain.

Ans It can be explained on the basis of their atomicity: oxygen exists as diatomic molecule ( $O_2$ ) whereas sulphur exists as polyatomic molecule ( $S_8$ ).

Ques oxygen exists as gas at room temp. while sulphur as solid. Why?

## CHEMICAL PROPERTIES

### \* OXIDATION STATES :

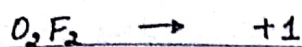
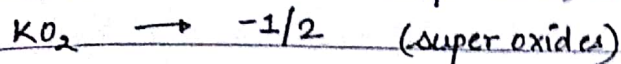
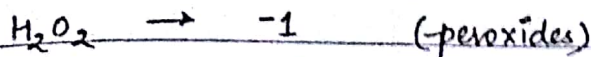
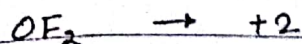
→ The stability of -2 O.S. decreases down the group  
↳ bcoz of decrease in electronegativity.

→ The tendency or stability of +4 O.S. in comparison to +6 O.S. ↑ as down the group due to inert pair effect.

Ques  $SF_6$  exists while  $OF_6$  does not. Why?

Ans This is bcoz oxygen can't show O.S. of +6 as it does not have vacant d-orbitals.

Ques Give an account of all O.S. exhibited by oxygen.



Ques Compound b/w O & F (ex:  $OF_2$ ) is called fluoride while that b/w O & Cl (ex:  $Cl_2O$ ) is called oxide. Why??

Ans  $OF_2$ : Fluorine is more electronegative than oxygen.  
(fluoride) O.S. of oxygen: +2 ; O.S. of fluorine: -1.

$Cl_2O$ : Oxygen is more electronegative than chlorine  
(oxide) O.S. of oxygen: -2 ; O.S. of chlorine: +1.

Ques Give reasons and examples of anomalous behaviour of oxygen.

Ans 1) Small size  $\rightarrow$  can form p $\pi$ -p $\pi$  bond. } can form H-bonding.  
2) High electronegativity  
3) non-availability of vacant d-orbitals.  $\rightarrow$  cannot show O.S. of +4 & +6.

## REACTIVITY TOWARDS HYDROGEN

All the elements of Grp 16 form hydrides of the type  $H_2E$   
(E = O, S, Se, Te, Po)

(a) Thermal stability:

Down the grp, thermal stability  $\downarrow$ ses as the size / bond length  $\uparrow$ ses & hence H-E bond dissociation enthalpy  $\downarrow$ ses.

(b) Reducing character:

- All hydrides except  $H_2O$  possess reducing property.
- Down the grp, reducing character  $\uparrow$ ses as thermal stability  $\downarrow$ ses.

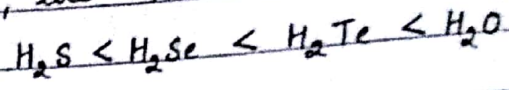
(c) Boiling point:  $H_2O \gg [H_2S < H_2Se < H_2Te]$

exceptionally high  
bpt. becoz of  
H-bonding

$\rightarrow$  becoz of inc. in VDW forces due to  
 $\uparrow$ se in size and mass.

Reducing character  $\rightarrow$  Depends on stg of M-H bond  
 Boiling Point  $\rightarrow$  depends upon v.w forces  $\propto$  M.W & S.A

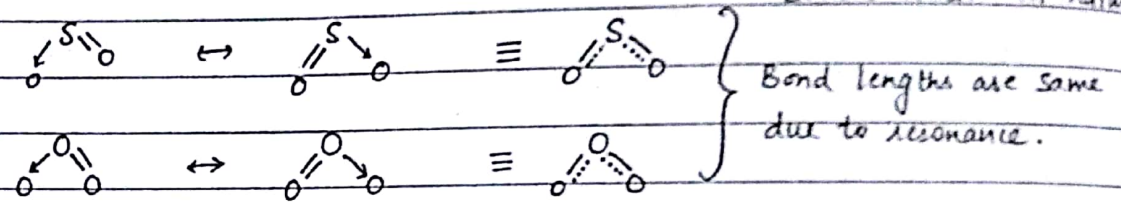
Therefore, the correct order of boiling pt. is:



(d) Acidic strength:  $H_2O < H_2S < H_2Se < H_2Te$   
 Acidic strength  $\uparrow$  down the group as bond length  $\uparrow$ , bond strength  $\downarrow$  which makes the release of  $H^+$  easier.

### REACTIVITY TOWARDS OXYGEN

(1) Group 16 elements form oxides of the formula  $MO_2$  &  $MO_3$   
 Both are acidic in nature



- (2) • The oxides of the formula  $MO_2$  can act as **reducing agents** and  $\therefore$  themselves undergo a change in o.s. from +4 to +6.
- Down the group, reducing property  $\downarrow$  as the stability of +4 o.s.  $\uparrow$  due to inert pair effect.

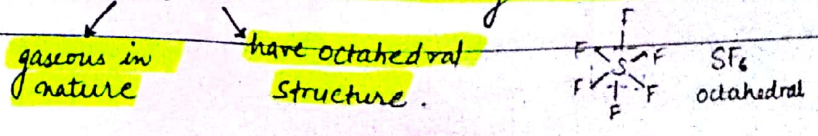
NOTE:  $SO_2$  is **reducing** while  $TeO_2$  is an **oxidising agent**.

(3)  $O_3$  &  $SO_2$  are gases bcoz they exist as discrete molecules while  $SeO_2$  &  $TeO_2$  are solids bcoz they have a **polymeric structure with covalent linkages**.

### REACTIVITY TOWARDS HALOGENS

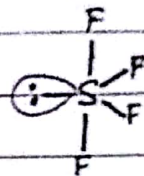
- Group 16 elements form halides of the form  $MX_6$ ,  $MX_4$ ,  $MX_2$ .
- The stability of the halides decreases in the order:  
 $F^- > Cl^- > Br^- > I^-$

Amongst hexahalides, **hexafluorides are the only stable halides**.



Amongst tetrafluorides,  $SF_4 \rightarrow$  gas ;  $SeF_4 \rightarrow$  liquid ;  $TeF_4 \rightarrow$  solid.

$sp^3d$  hybridisation  $\rightarrow$  trigonal bi-pyramidal structure.



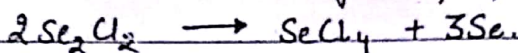
$SF_4 \rightarrow$  see-saw

Dihalides  $\rightarrow sp^3$  hybridisation  $\rightarrow$  tetrahedral structure

$\rightarrow$  All elements except Se form dichlorides & dibromides.

Monohalides  $\rightarrow$  dimeric in nature (Ex:  $S_2F_2$ ,  $S_2Cl_2$ ,  $Se_2Cl_2$ , etc.)

These dimeric halides undergo disproportionation:

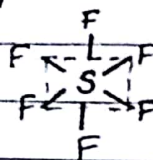


Ques  $^{+6}SF_6$  exists while  $^{+6}S_2Cl_6$  does not. Why??

Ans It is bcoz Cl is not electronegative enough to bring abt such high o.s. of +6 in sulphur. Also, it is difficult for sulphur to accommodate 6 large-sized Cl atoms around itself. [causes steric crowding]

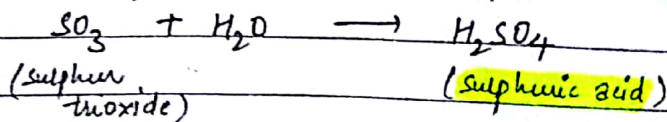
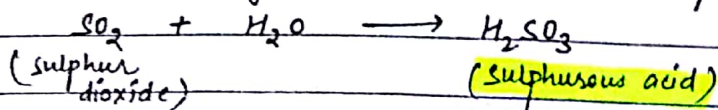
Ques How do you explain the inert nature of  $SF_6$ ?

Ans  $SF_6$  is inert or unreactive bcoz sulphur in  $SF_6$  is sterically protected by six fluorine atoms



Ques Justify that the 2 oxides of sulphur are acidic in nature.

Ans It is because they dissolve in water to produce acids:



Ques Why is  $H_2O$  a liquid &  $H_2S$  a gas??

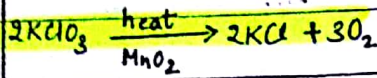
Ans  $H_2O$  : H-bond

$H_2S$  : no H-bond

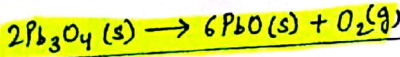
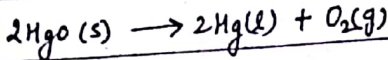
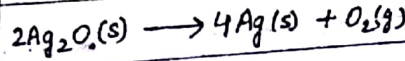
# DIOXYGEN [O<sub>2</sub>]

## PREPARATION

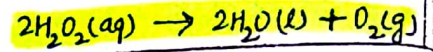
By heating oxygen containing salts such as chlorates, nitrates & permanganates.



By thermal decomposition of the oxides of metals low in the electrochemical series & higher oxides of some metals.



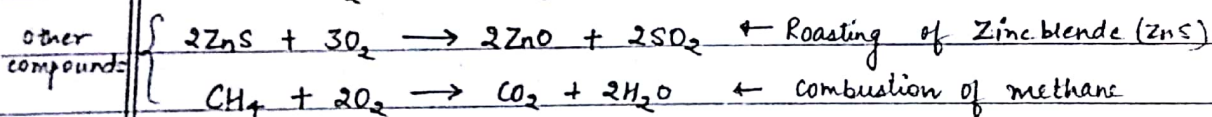
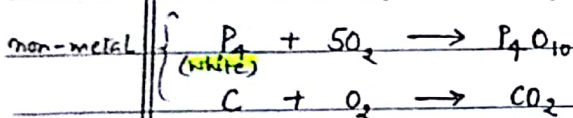
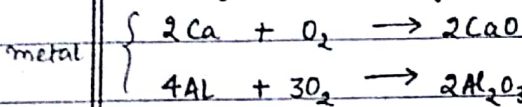
Hydrogen peroxide is readily decomposed into H<sub>2</sub>O & O<sub>2</sub> by catalysts such as finely divided metals and manganese dioxide.



On large scale, dioxygen (O<sub>2</sub>) is obtained from the electrolysis of water. H<sub>2</sub> is released at CATHODE & O<sub>2</sub> at ANODE.

## PROPERTIES

- colourless & odourless gas
- Some of the rxns of O<sub>2</sub> with metals, non-metals & other compds:



## USES

in normal respiration & combustion processes

Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering

used in oxy-acetylene welding, in the manufacture of many metals, particularly steel.

Ques: Dioxygen ( $O_2$ ) is paramagnetic. Explain.

Ans: Dioxygen ( $O_2$ )  $\rightarrow$  even no. of electrons.

It is because of the presence of 2 unpaired e.s in the ANTI-BONDING  $\pi^*$  molecular orbital of  $O_2$ .

Ques: Explain how oxygen acts as a vital support for aquatic & marine life.

Ans: It is because dioxygen ( $O_2$ ) is sufficiently soluble in water.

Ques: Which of the following does not react with  $O_2$  directly: Zn, Ti, Pt, Fe??

Ans: Pt  $\rightarrow$  noble metal

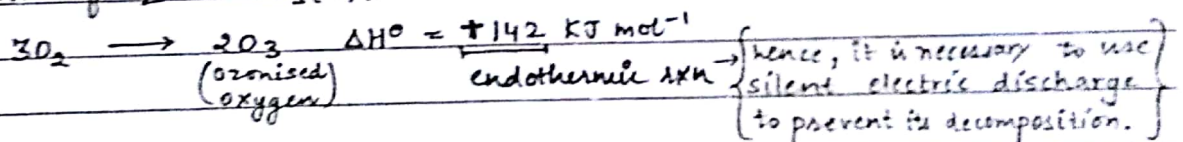
## OZONE $\rightarrow O_3$

① Ozone is an allotropic form of oxygen.

② The ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiation.

### \* PREPARATION :-

When a slow dry stream of  $O_2$  is passed through a SILENT ELECTRICAL DISCHARGE, conversion of  $O_2$  to  $O_3$  (10%) occurs.

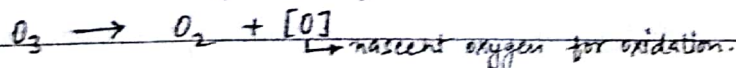


### \* PROPERTIES :-

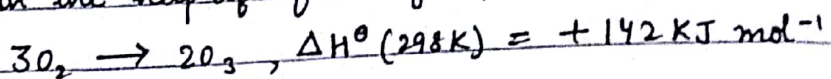
- PALE BLUE GAS ; DARK BLUE LIQUID ; VIOLET - BLACK SOLID.
- has a characteristic smell & is harmless in small concentrations.

Ques: Explain how ozone acts as a powerful oxidising agent.

Ans: It is bcoz it readily decomposes to release nascent oxygen.



Ques Ozone is thermodynamically unstable wrt oxygen. Justify this statement with the help of following eq<sup>n</sup>:



Ans  $2O_3 \rightarrow 3O_2, \Delta H^\circ = -142 \text{ KJ mol}^{-1}$

$\Delta H$  of the rxn is negative i.e.  $\Delta H < 0$

Entropy of the rxn is increasing i.e.  $\Delta S > 0$

We know, gibbs energy change  $\Delta G = \Delta H - T\Delta S$

$$= (-ve) - T(+ve)$$

$$= -ve$$

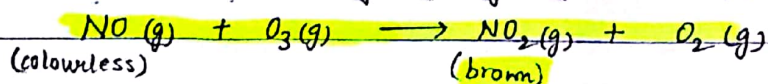
$$\Rightarrow \Delta G < 0$$

$\Rightarrow$  rxn is spontaneous i.e. it has a tendency to move in forward direction.

Hence, ozone is thermodynamically unstable wrt oxygen.

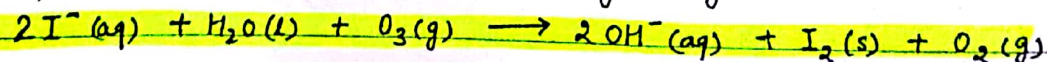
Ques Explain how supersonic jet planes are responsible for the depletion of ozone layer.

Ans It is bcoz the nitrogen oxides emitted from the exhaust systems of these planes combine very rapidly with ozone and hence, deplete it.



Ques How is  $O_3$  estimated quantitatively??

Ans When ozone reacts with an excess of potassium iodide (KI) solution buffered with a borate buffer (pH 9.2) iodine is liberated which can be titrated against a standard sol<sup>n</sup> of sodium thiosulphate. This is a quantitative method for estimating  $O_3$  gas.



\*

#### USES OF OZONE

used as a germicide, disinfectant & for sterilising water.

used for bleaching, oils, ivory, flour, starch, etc.

acts as an oxidising agent in the manufacture of  $KMnO_4$ .



\* SIMPLE OXIDES (at last)

## SULPHUR - ALLOTROPIC FORMS

(1) RHOMBIC SULPHUR ( $\alpha$ -sulphur)  $\leftarrow$  stable form at room temperature. ( $S_8$ )

- Rhombic sulphur crystals are formed on evaporating the sol<sup>n</sup> of roll sulphur in  $CS_2$ .
- yellow in colour
- insoluble in water bt. dissolves to some extent in benzene, alcohol & ether.
- is readily soluble in  $CS_2$

(2) MONOCLINIC SULPHUR ( $\beta$ -sulphur) ( $S_8$ )

Preparation: This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust & the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of  $\beta$ -sulphur are formed.

$\rightarrow$  It is soluble in  $CS_2$ .

\* TRANSITION TEMPERATURE :-

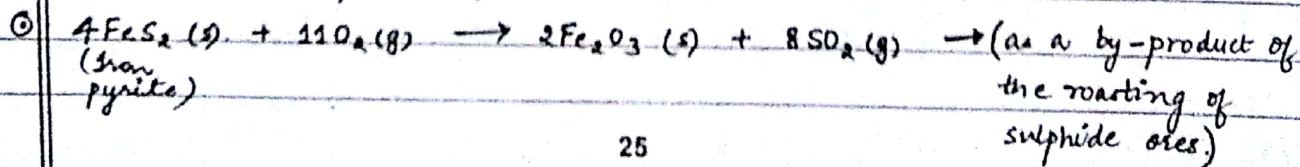
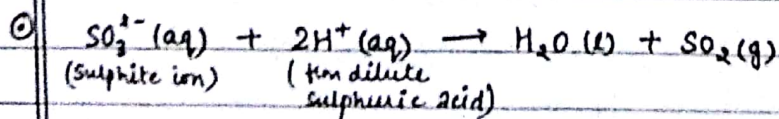
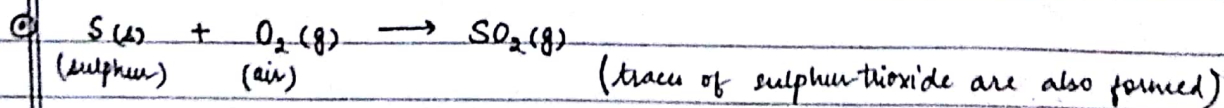
- $\beta$ -sulphur is stable above 369 K & transforms into  $\alpha$ -sulphur below it.
- Conversely,  $\alpha$ -sulphur is stable below 369 K & transforms into  $\beta$ -sulphur above this.
- At 369 K, both the forms are stable. This temp. is called Transition Temperature.

Ques Which form of sulphur shows paramagnetic behaviour?

Ans In vapour state, sulphur partly exists as  $S_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $O_2$  and hence, exhibits paramagnetism.

## SULPHUR DIOXIDE : $SO_2$

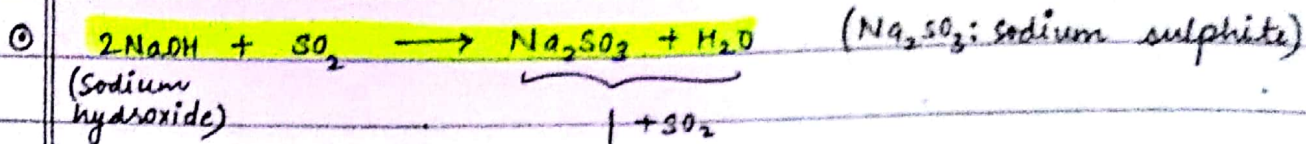
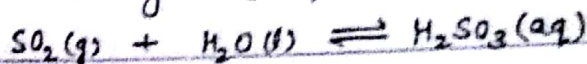
\* PREPARATION :-



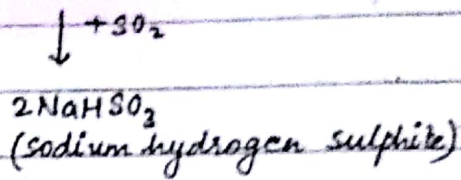
\* PROPERTIES :-

→ It is a colourless gas with pungent smell & is highly soluble in water.

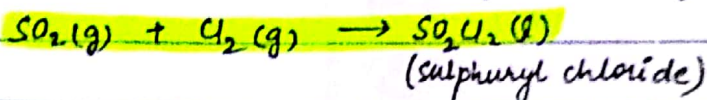
→  $\text{SO}_2$  when passed through  $\text{H}_2\text{O}$  forms a sol<sup>n</sup> of sulphurous acid.



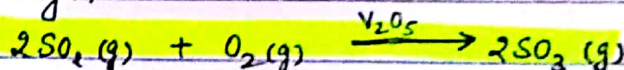
(sodium hydroxide)



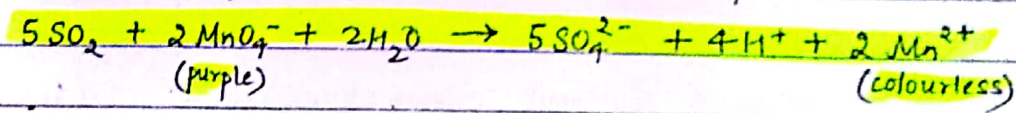
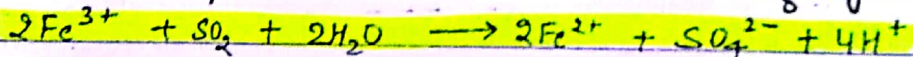
→  $\text{SO}_2$  reacts with chlorine in the presence of charcoal → act as a catalyst



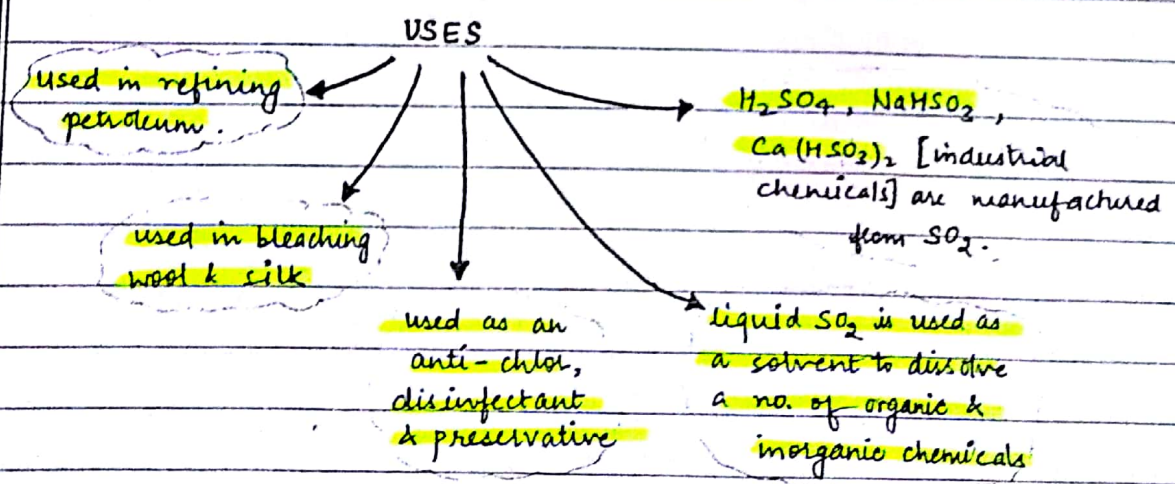
→  $\text{SO}_2$  is oxidised to  $\text{SO}_3$  by oxygen in the presence of vanadium (V) oxide as catalyst.



NOTE:- When moist, sulphur dioxide behaves as a reducing agent.



\* USES



Try out :

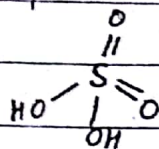
Ques What happens when  $\text{SO}_2$  is passed through an aq. sol<sup>n</sup> of Fe(III) salt?

Ques How is the presence of  $\text{SO}_2$  detected?

Ques Comment on the nature of two S-O bonds ~~are~~ formed in  $\text{SO}_2$  molecule.

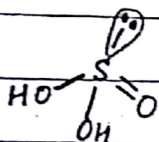
# OXO-ACIDS OF SULPHUR

① Sulphuric Acid:  $H_2SO_4$



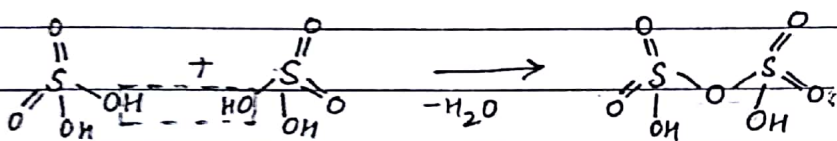
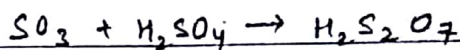
Dibasic Acid

② Sulphurous acid:  $H_2SO_3$

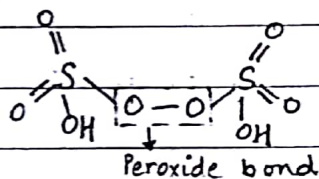


pyramidal structure

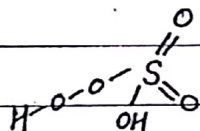
③ Pyrosulphuric Acid:  $H_2S_2O_7$  (oleum)



④ Peroxodisulphuric Acid:  $H_2S_2O_8$



⑤ Peroxomonosulphuric Acid:  $H_2SO_5$

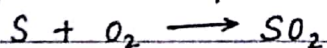


## SULPHURIC ACID: $H_2SO_4$

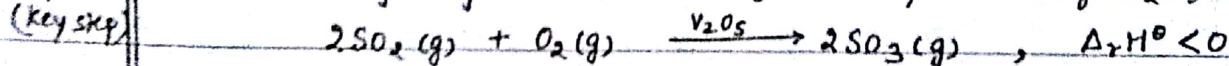
### \* MANUFACTURE

Sulphuric Acid is manufactured by CONTACT PROCESS which involves 3 steps:

Step 1: Burning of sulphur or sulphide ores to generate  $SO_2$ .



Step 2:  $SO_2$  is catalytically oxidised to  $SO_3$  in the presence of  $V_2O_5(s) \rightarrow$  catalyst



- ⊙ The rxn is exothermic, reversible & the forward rxn leads to a decrease in volume.
- ⊙ therefore, low temperature & high pressure are the fav. cond<sup>n</sup> for max. yield.

Step 3 :  $\text{SO}_3$  produced in the above step is absorbed in sulphuric acid to give oleum:



Oleum is then diluted with water to obtain sulphuric acid of desired concentration.

\* The sulphuric acid obtained by contact process is 96-98% pure.

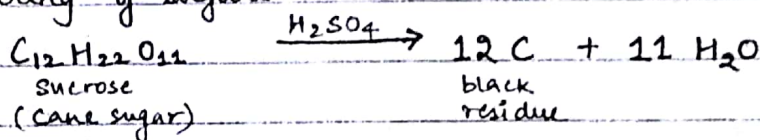
### \* PROPERTIES

- ① is a colourless, dense, oily liquid
- ② dissolves in water with the evolution of a large quantity of heat.

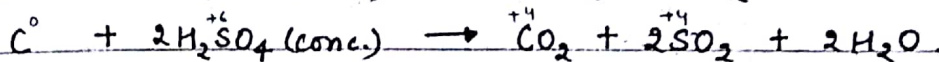
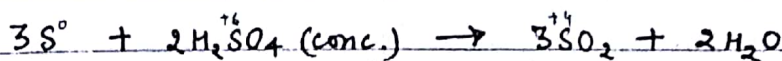
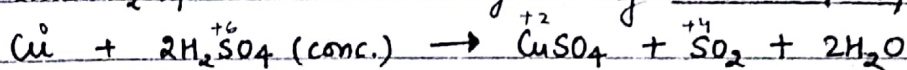
NOTE:- The chemical reactions of  $\text{H}_2\text{SO}_4$  are as a result of following characteristics:

- (a) low volatility
- (b) strong acidic character
- (c) strong affinity for water
- (d) ability to act as an oxidising agent.

③ Conc.  $\text{H}_2\text{SO}_4$  is a very strong DEHYDRATING AGENT and thus, causes charring of sugars

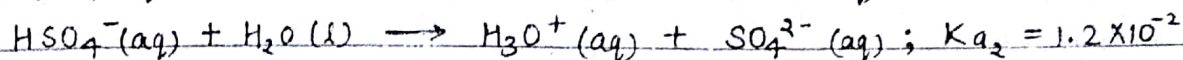
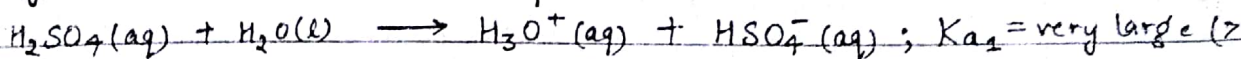


④ Hot conc.  $\text{H}_2\text{SO}_4$  is a moderately strong OXIDISING AGENT.



Ques Why is  $K_{a2} \ll K_{a1}$  for sulphuric acid in water?

Ans



$K_{a2} \ll K_{a1}$  becoz the tendency of bisulphate ion to loose one more  $\text{H}^+$  ion is less.

\* The larger value of  $K_{a1}$  means that  $H_2SO_4$  is largely dissociated into  $H^+$  and  $HSO_4^-$ .

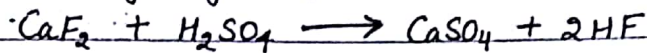
Greater the value of dissociation constant, the stronger is the acid.

Ques

What happens when

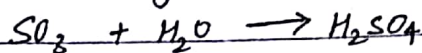
(i) conc.  $H_2SO_4$  is added to calcium fluoride?

It forms hydrogen fluoride



(ii)  $SO_2$  is passed through water?

It dissolves  $SO_2$  to give  $H_2SO_3$



\*

### USES OF $H_2SO_4$

is a very imp. industrial chemical. is used in manufacture of fertilisers.

used in petroleum refining & manufacture of pigments, paints & dyestuff intermediates

used in manufacture of nitro-cellulose products & as a laboratory reagent.

used in detergent industry, metallurgical applications & in storage batteries.

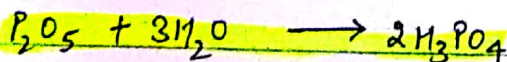
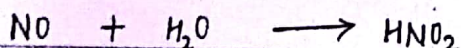
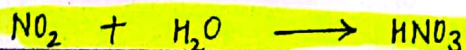
**SIMPLE OXIDES** : A binary compd of oxygen with another element

**ACIDIC OXIDE**

is called OXIDE.

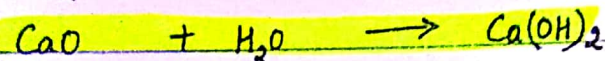
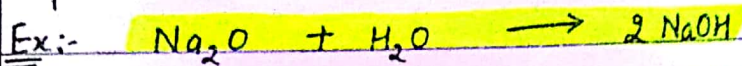
- An oxide that combines with water to give an acid
- Non-metallic oxides are acidic in nature.

Ex:-



## BASIC OXIDE

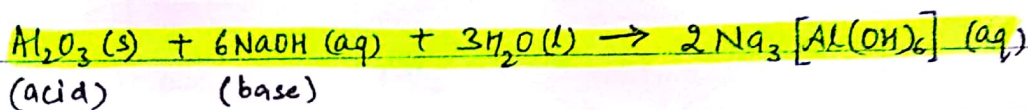
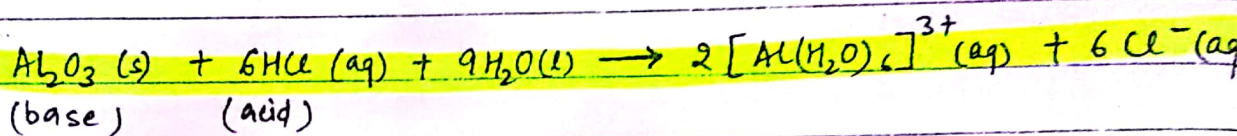
- The oxides which dissolve in water to give alkalis.
- Metallic oxides are basic in nature.



## AMPHOTERIC OXIDES

- The oxides which react with both acids and bases and show both acidic as well as basic characteristics.

Ex:-



## NEUTRAL OXIDE

- Oxides which are neither acidic nor basic.

Ex:- CO, NO and N<sub>2</sub>O.

NOTE:- Oxides of some metals in high oxidation state also have acidic character.

Ex:- Mn<sub>2</sub>O<sub>7</sub>, CrO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>

# GROUP - 17 ELEMENTS

Atomic No.	Element	Electronic Configuration
9	Fluorine (F)	[He] $2s^2 2p^5$
17	Chlorine (Cl)	[Ne] $3s^2 3p^5$
35	Bromine (Br)	[Ar] $3d^{10} 4s^2 4p^5$
53	Iodine (I)	[Kr] $4d^{10} 5s^2 5p^5$
85	Astatine (At) Radioactive	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$

NOTE :- Group 17 elements are collectively known as HALOGENS.

{Halo means salt and Genes means born i.e. salt producers}

The halogens are highly reactive non-metallic elements.

## \* OCCURRENCE :-

→ Fluorine : • as insoluble fluorides ( $\text{CaF}_2 \rightarrow$  fluor spar,  $\text{Na}_3\text{AlF}_6 \rightarrow$  cryolite,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2 \rightarrow$  fluoroapatite)

• small quantities are present in soil, river water plants and bones & teeth of animals.

→ Iodine : • Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine & Chile saltpetre contains upto 0.2% of sodium iodate ( $\text{NaIO}_3$ )

Ques Sea water is the greatest source of some halogens. Comment.

Ans (i) Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium & calcium (mainly NaCl solution).

(ii) The deposits of dried up seas contain these compounds, e.g., NaCl and carnallite  $\rightarrow \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  an ore of Mg.

(iii) Certain forms of marine life contain iodine in their systems.

## \* ELECTRONIC CONFIGURATION :-

All these elements have seven electrons in their outermost shell ( $ns^2 np^5$ )

## \* ATOMIC AND IONIC RADII :-

- The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.
- Atomic & ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

## \* IONISATION ENTHALPY :-

- They have little tendency to lose electron. Thus, they have very high ionisation enthalpy
- Ionisation enthalpy decreases down the group  
↳ Why?? due to increase in atomic size.

## \* ELECTRON GAIN ENTHALPY :-

- Halogens have max. -ve EGE in the corresponding periods.  
↳ Why?? These elements have smallest size in their respective periods and ∴ max. effective nuclear charge. As a result, they readily accept an electron to acquire noble gas configuration. (They have only 1e<sup>-</sup> less than stable noble gas configuration.)  
$$A + e^{-} \rightarrow A^{-}, \Delta H < 0$$

- EGE becomes LESS NEGATIVE down the group. (as size is increasing)  
Bt.....

- ion → EGE of Fluorine (F) is LESS than that of Chlorine (Cl).  
Why?? because the incoming electron faces greater inter-electronic repulsions in the small-sized 2p orbital of fluorine (F).

## \* ELECTRONEGATIVITY :-

- They have VERY HIGH electronegativity due to their small size.
- Down the group, electronegativity ↓ses as size ↑ses.
- ∴ Fluorine is the most electronegative element in the periodic table.



# PHYSICAL PROPERTIES

- (1) Fluorine }  
& Chlorine } → Gases Bromine → liquid Iodine → solid
- (2) Their MELTING and BOILING points increase down the group with atomic number. Bcoz the vanderwaal forces ↑ with ↑ mass.
- (3) All halogens are coloured.  $F_2 \rightarrow$  yellow ;  $Cl_2 \rightarrow$  greenish yellow ;  $Br_2 \rightarrow$  <sup>brown</sup> red  
 $I_2 \rightarrow$  violet

This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours.

- (4) Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform,  $CCl_4$ ,  $CS_2$  and hydrocarbons to give coloured solutions.

- (5) Down the group, from Cl to I, the Bond Dissociation Energy decreases in the order  $(Cl_2 > Br_2 > I_2)$ , bcoz the bond length increases with the increase in the size of the halogen.

Bt... Bond Dissociation Energy of F-F bond is less than Cl-Cl bond.

Why?? bcoz of high electron-electron repulsion among the lone pairs in  $F_2$  molecule where they are much closer to each other than in case of  $Cl_2$ .  
So, the correct order of B.D.E is  $Cl_2 > Br_2 > F_2 > I_2$

# CHEMICAL PROPERTIES

→ All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

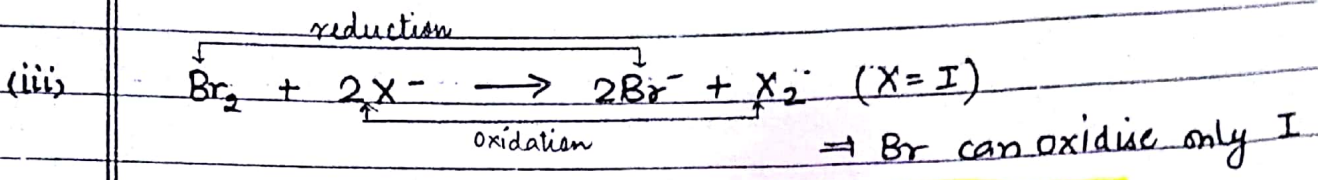
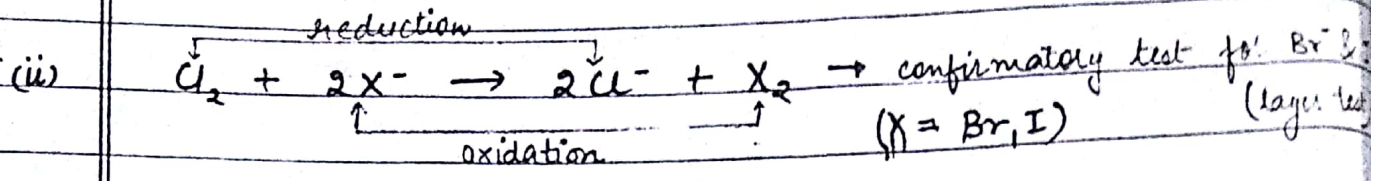
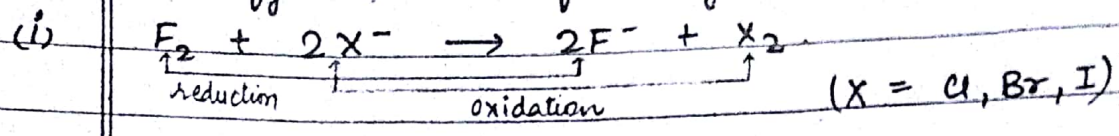
→ The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.

NOTE -  $F_2$  is the strongest oxidising halogen & it oxidises other halide ions in solution or even in the solid phase.

In general, a halogen oxidises halide ions of higher atomic number.

Ques

Identify X in the following rxn from Group 17.



$\therefore$  order of oxidising power:  $F_2 > Cl_2 > Br_2 > I_2$

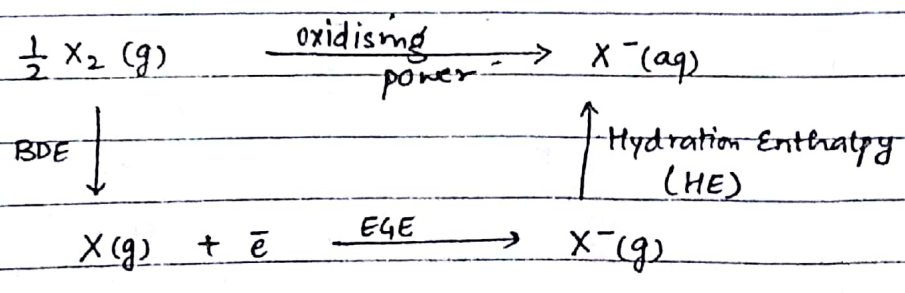
Ques

Considering the parameters such as BDE, EGE, Hydration Enthalpy compare the oxidising power of  $F_2$  and  $Cl_2$ .

Ans

In gas phase,  $E_{GE} \text{ of } F < E_{GE} \text{ of } Cl$ .  
 $E_{GE} \rightarrow$  tendency to gain  $e^-$        $X(g) + e^- \rightarrow X^-(g)$

In aqueous phase, oxidising power of  $F_2 >$  oxidising power of  $Cl_2$   
 oxidising power: red<sup>m</sup>, tendency to gain  $e^-$ .



Energy reqd. must be less

	$F_2$	$Cl_2$
BDE (reqd)	low	high
EGE (released)	low	high
HE (released)	High (due to greater charge density of $F^-$ )	low

Thus, low BDE of  $F_2$  and high HE of  $F^-$  more than compensate low EGE of F.

Therefore, oxidising power of  $F_2 >$  oxidising power of  $Cl_2$

measured in aqueous phase even though  $E_{\text{aq}}^{\circ}$  of  $F < E_{\text{aq}}^{\circ}$  of  $Cl$  measured in gaseous phase.

Ques The max O.S. for any element is exhibited in its oxides and fluorides. Why?  
Ans Bcoz F and O are the most electronegative element of the periodic table and  $\therefore$  are able to bring abt max O.S. of an element.

Ques F exhibits only -1 O.S. while other elements also exhibit +1, +3, +5 and +7 O.S.!! Why??

Ans

F $\rightarrow$ HF	;	UF <sub>3</sub>	;	IF <sub>7</sub>	} Being the most electro-negative element, fluorine cannot exhibit any +ve oxidation state.
O.S. of F $\rightarrow$ -1		-1		-1	
Cl $\rightarrow$ ClF <sub>3</sub>		O.S. of Cl $\rightarrow$ +3			
Br $\rightarrow$ BrF <sub>3</sub> (+3)	;	BrF <sub>5</sub> (+5)			
I $\rightarrow$ IF <sub>5</sub> (+5)	;	IF <sub>7</sub> (+7)			

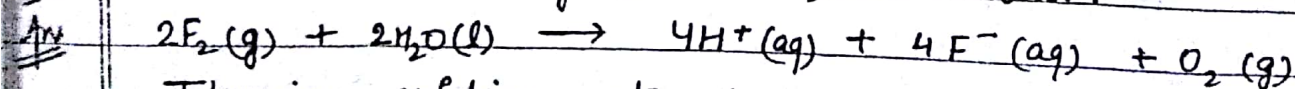
The F atom has no d-orbitals in its valence shell &  $\therefore$  cannot expand its octet. Whereas other halogens have vacant d-orbitals due to which they can expand their octets to show higher O.S. of +3, +5, +7.

### ANOMALOUS BEHAVIOUR OF FLUORINE

\* Reasons :- very small size, highest electronegativity, low F-F BDE, and non-availability of d-orbitals in valence shell.

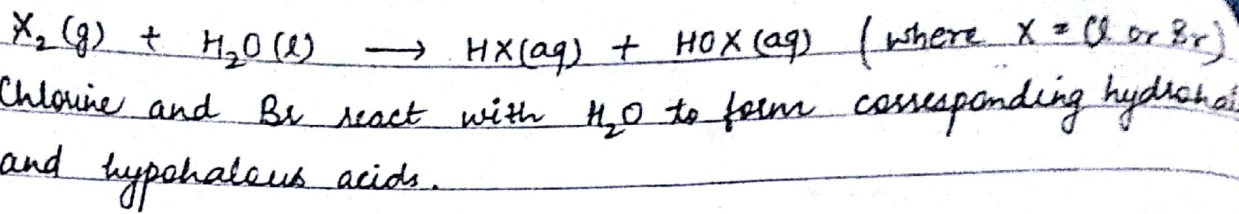
- \* Examples :- (a) It doesnot show higher O.S. like +3, +5, +7.  
(b) It forms only 1 oxo-acid while other halogens form a number of oxoacids.  
(c) It is capable of forming H-bonding due to which HF is a liquid while other halides are gases.

Ques Write the reactions of F<sub>2</sub> and Cl<sub>2</sub> with water.



Fluorine oxidises water to oxygen.

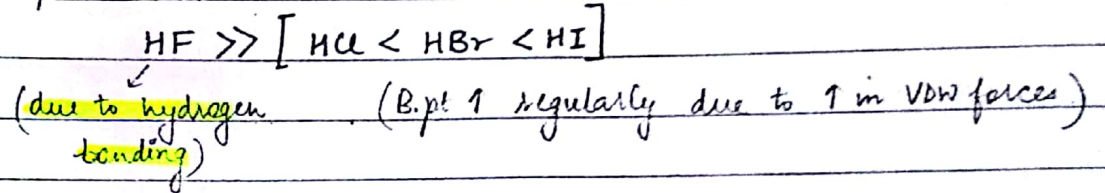
And



### REACTIVITY OF HALOGENS TOWARDS HYDROGEN

All halogens react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine.

#### (i) BOILING POINT :-



∴ The correct order is  $HCl < HBr < HI < HF$ .

but remember that reactivity ↓

#### (ii) Stability :- $HF > HCl > HBr > HI$      $F^- > Cl^- > Br^- > I^-$

Down the Group, Bond length ↑ and Bond strength ↓.

#### (iii) Acid Strength :- $HF < HCl < HBr < HI$

∵ Bond length ↑ down the group which makes the release of  $H^+$  easier.

### REACTIVITY OF HALOGENS TOWARDS METALS

→ Halogens react with metals to form metal halides like  $NaCl, MgBr_2$

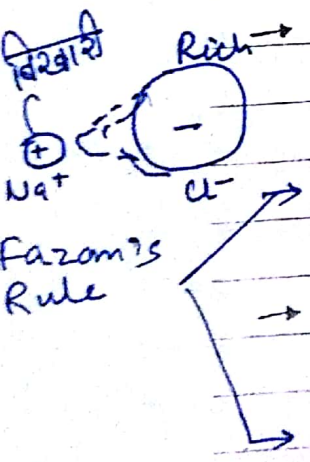
→ The ionic character of the halides decreases in the order  $MF > MCl > MBr > MI$  (M → monovalent metal)

Acc. to Fajan's rule, larger the size of anion, greater is its polarisability. i.e.  $e^-$  density will be shifted towards cation, hence, more covalent.

→ If a metal exhibits more than one O.S., the halides in higher O.S. will be more covalent than the one in lower O.S.

Acc. to Fajan's rule, greater the charge on cation, greater is the covalent character.

ex:-  $SnCl_4$  is more covalent than  $SnCl_2$ ;  $PbCl_4$  than  $PbCl_2$ .



## REACTIVITY OF HALOGENS TOWARDS OXYGEN

(i) Fluorine :- forms two oxides ( $OF_2$ ) and  $O_2F_2$ .

only thermally stable at 298K

\* Both are strong fluorinating agents.

\* These are essentially OXYGEN FLUORIDES beoz fluorine is more electronegative than oxygen.

\*  $O_2F_2$  oxides plutonium to  $PuF_6$ .

(ii) Chlorine :- Chlorine oxides  $Cl_2O$ ,  $ClO_2$ ,  $Cl_2O_6$  &  $Cl_2O_7$

are highly reactive oxidising agents

tend to explode

\* NOTE :-  $ClO_2$  is used as a BLEACHING AGENT for paper pulp & textiles and in water treatment.

(iii) Bromine :- Bromine oxides :  $Br_2O$ ,  $BrO_2$ ,  $BrO_3$

least stable halogen oxides.

exist only at low temp.

are very powerful oxidising agents

(iv) Iodine :- Iodine oxides ;  $I_2O_4$ ,  $I_2O_5$ ,  $I_2O_7$

are insoluble solids

decompose on heating

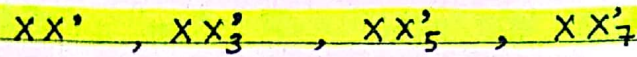
\* NOTE :-  $I_2O_5$  → very good oxidising agent.

→ is used in the estimation of carbon monoxide.

NOTE → The higher oxides of halogens tend to be more stable than the lower ones.

# REACTIVITY OF HALOGENS TOWARDS OTHER HALOGENS

Halogens combine amongst themselves to form a number of compounds known as INTERHALOGENS of the type



where  $X \rightarrow$  larger size halogen

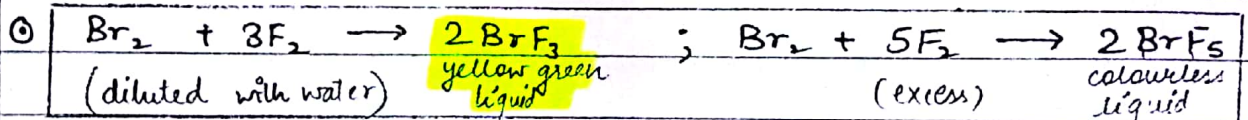
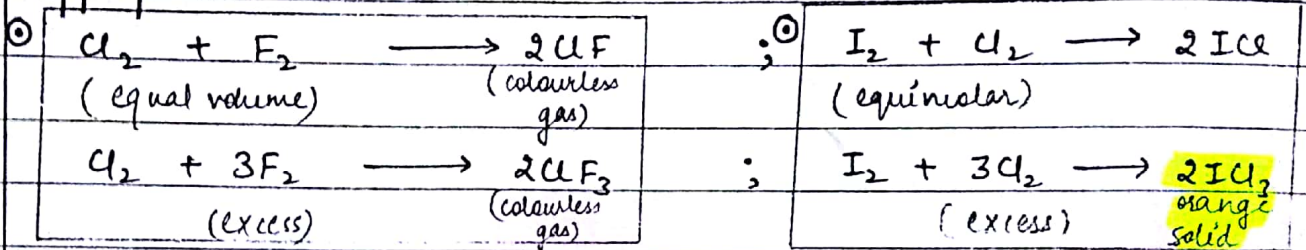
$X' \rightarrow$  smaller size halogen

&  $X$  is more electropositive than  $X'$ .

## INTERHALOGEN COMPOUNDS :-

### \* PREPARATION :-

They are formed by direct combination of halogens under appropriate conditions.



### \* PROPERTIES :-

are volatile solids or liquids at 298K except  $\text{ClF}$  which is a gas.

covalent molecules

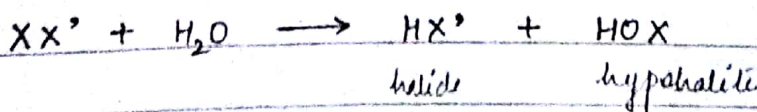
diamagnetic in nature

→ Interhalogen compounds are more reactive than halogens (except fluorine)

Imp → Why?? Bcoz...  $X-X'$  bond in interhalogens is weaker than  $X-X$  bond in halogens except  $F-F$  bond. That's why they are stronger  $\delta$  O.A than halogens except  $\text{F}_2$ .

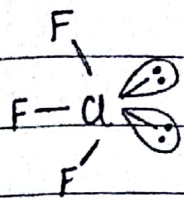
→ All these undergo hydrolysis.

Ex:-

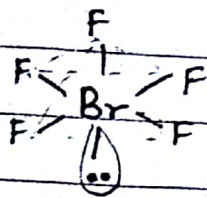


(NOTE:- Halide ion is derived from the smaller halogen.)

\* STRUCTURE :-



$ClF_3 \rightarrow$  T-shape



$BrF_5 \rightarrow$  square pyramidal

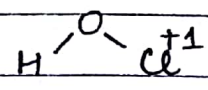


$IF_7 \rightarrow$  pentagonal bipyramidal

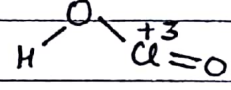
OXOACIDS OF HALOGENS

$\rightarrow$  Due to high electronegativity & small size, fluorine (F) forms only 1 oxoacid, HOF known as fluoric(I) acid or hypofluorous acid.

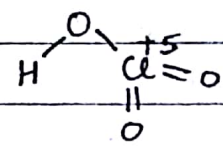
OXOACIDS OF CHLORINE (hoip)



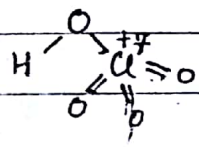
$HOCl \rightarrow$  hypochlorous acid



$HClO_2 \rightarrow$  chlorous acid



$HClO_3 \rightarrow$  chloric acid



$HClO_4 \rightarrow$  Perchloric acid

Ques Arrange the following acids in order of their acid strength

(i)  $HOCl, HClO, HClO_2, HClO_4$

Ans  $HOCl < HClO_2 < HClO_3 < HClO_4$

stability of conjugate base :  $^-OCl < ^-ClO_2 < ^-ClO_3 < ^-ClO_4$   $\rightarrow$  -ve charge is dispersed by four oxygen atoms

\* STABLE THE CONJUGATE BASE, STRONGER IS THE ACID.

(ii)  $HOF, HOCl, HOBr, HOI$

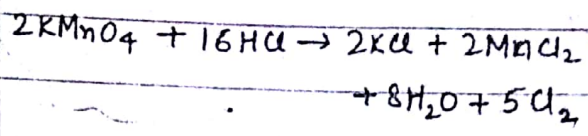
Ans  $HOF > HOCl > HOBr > HOI$

It can be explained on the basis of the fact that F is the most  $\bar{e}$ -ve halogen &  $\therefore$  will polarise the -O-H bond to the max, making HOF the strongest acid.

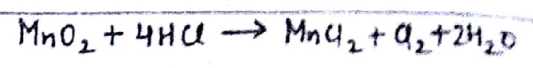
# CHLORINE → named on the account of its colour. (chloros = greenish yellow)

## (A) PREPARATION

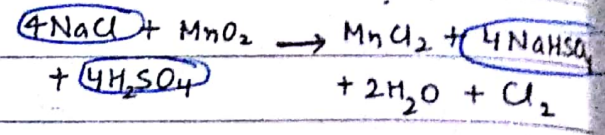
By action of HCl on  $KMnO_4$



By heating  $MnO_2$  with conc. HCl



However, .. a mixture of NaCl & conc.  $H_2SO_4$  is used in place of HCl.

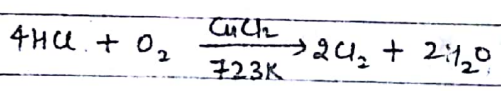


## (B)

### MANUFACTURE OF CHLORINE

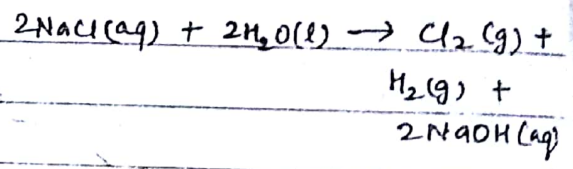
#### Deacon's Process

By oxid<sup>n</sup> of HCl gas by atmospheric oxygen in the presence of  $CuCl_2$  (catalyst) at 723K



#### Electrolytic Process

Chlorine is obtained by the electrolysis of brine sol<sup>n</sup>.  $Cl_2$  is liberated at anode.



## (C)

### PROPERTIES

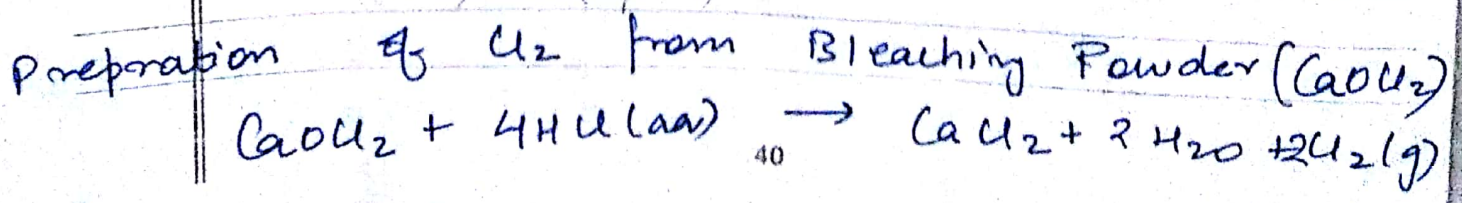
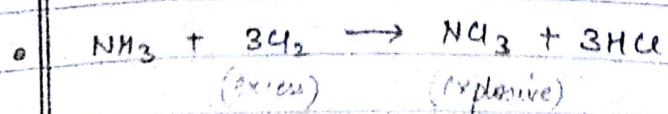
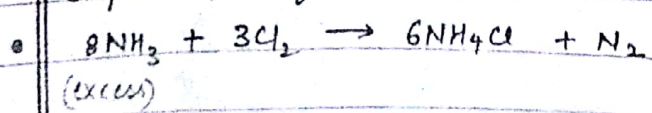
greenish yellow gas with pungent & suffocating odour

can be liquefied easily into greenish yellow liquid which boils at 239K.

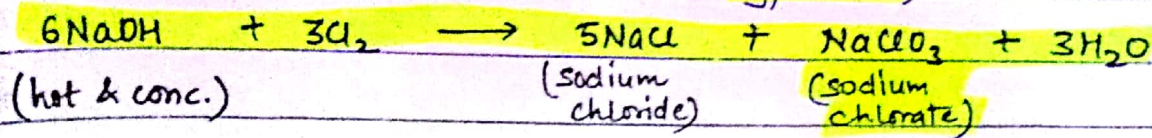
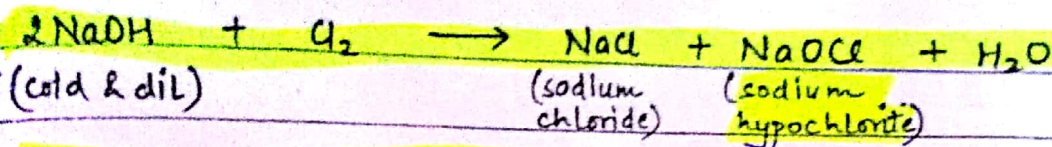
about 2-5 times heavier than air

soluble in water

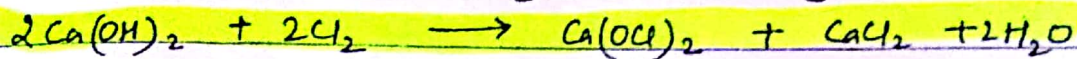
→ With Excess ammonia, chlorine gives nitrogen & ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.







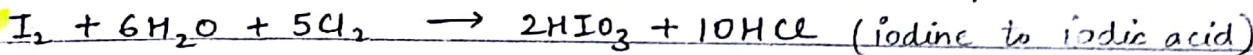
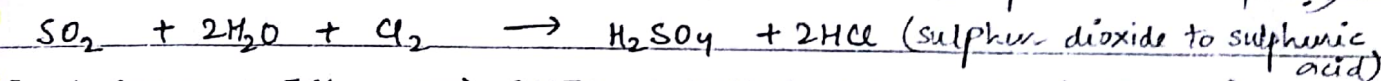
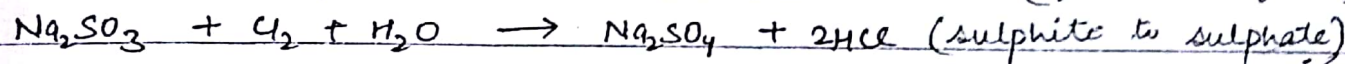
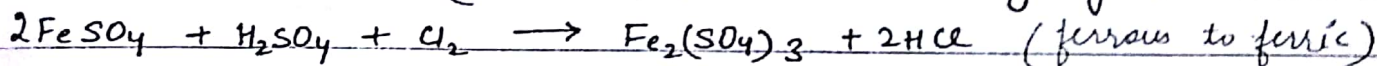
With dry slaked lime, it gives Bleaching Powder



\* Chlorine water on standing loses its YELLOW COLOUR due to the formation of HCl and HOCl.

HOCl so formed gives nascent oxygen which is responsible for oxidising & bleaching properties of chlorine.

(i) Oxidation-reactions (Chlorine ( $\text{Cl}_2$ ) as an oxidising agent)



(ii) Chlorine is a powerful bleaching agent



coloured substance + O → colourless substance.

It bleaches vegetable or organic matter in the presence of moisture.

Bleaching effect of chlorine is permanent.

(D)

### USES OF CHLORINE

for bleaching woodpulp, cotton and textiles

in the extraction of gold and platinum

in the manufacture of dyes, drugs & organic compds such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , DDT

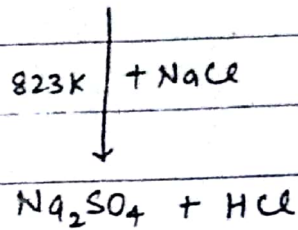
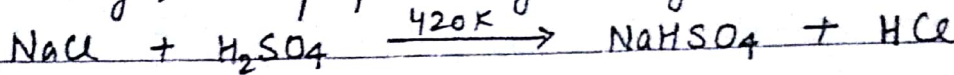
in preparation of poisonous gases such as  
 phosgene:  $\text{COCl}_2$   
 tear gas:  $\text{CCl}_3\text{NO}_2$   
 mustard gas:  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$

in sterilising drinking water

# HYDROGEN CHLORIDE

## (A) PREPARATION :

In laboratory, it is prepared by heating NaCl with conc.  $H_2SO_4$ .



## (B) PROPERTIES

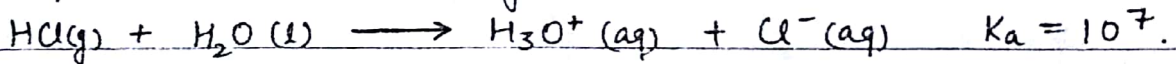
colourless and pungent smelling gas

extremely soluble in water

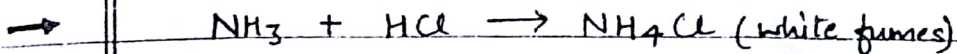
easily liquified to a colourless liquid

freezes to a white crystalline solid

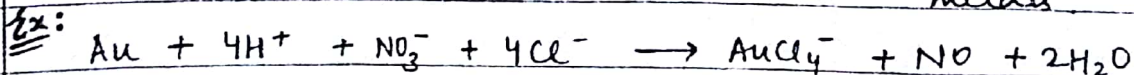
→ Its aqueous sol<sup>n</sup> is called hydrochloric acid. It ionises as:



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



→ Aqua-regia (conc. HCl : conc.  $HNO_3$ )  $\rightarrow$  for dissolving noble metals  
3 : 1



## (C) USES OF HYDROGEN CHLORIDE

1) in the manufacture of chlorine,  $NH_4Cl$  and glucose

2) for extracting glue from bones and purifying bone black

3) in medicine and as a laboratory reagent.

# GROUP-18 ELEMENTS

Atomic No.	Element	Electronic Configuration
2	Helium (He)	$1s^2$
10	Neon (Ne)	$[\text{He}] 2s^2 2p^6$
18	Argon (Ar)	$[\text{Ne}] 3s^2 3p^6$
36	Krypton (Kr)	$[\text{Ar}] 3d^{10} 4s^2 4p^6$
54	Xenon (Xe)	$[\text{Kr}] 4d^{10} 5s^2 5p^6$
86	Radon (Rn) ↓ Radioactive	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^6$

## \* OCCURRENCE :-

- All noble gases except RADON occur in the atmosphere.
- Helium (He) and sometimes Neon (Ne) are found in minerals of RADIOACTIVE ORIGIN e.g. pitchblende, monazite, cleveite.
- The main commercial source of Helium (He) is natural gas.

NOTE → The elements present in Group 18 have their valence shell orbitals completely filled and therefore, react with a few elements only under certain conditions.

They are almost unreactive i.e. they have extremely high I.E. and large +ve value of EGE.

Therefore, they are known as noble gases.

## \* ELECTRONIC CONFIGURATION :-

All noble gases have general electronic configuration  $ns^2 np^6$  except HELIUM which has  $1s^2$ .

## \* IONISATION ENTHALPY :-

Due to stable electronic configuration, these gases exhibit very high Ionisation Enthalpy.

It decreases down the group with increase in atomic size.

## \* ATOMIC RADII :-

Atomic radii increase down the group with increase in atomic number.

## \* ELECTRON GAIN ENTHALPY (EGE) :-

Since noble gases have stable electronic configurations, they have no tendency to accept the electron & therefore, have large +ve values of EGE.

## PHYSICAL PROPERTIES

- All noble gases are MONOATOMIC, COLOURLESS, ODOURLESS and TASTELESS.
- They are SPARINGLY SOLUBLE in WATER.
- They have LOW MELTING & BOILING POINTS.

Why??

bcoz of weak dispersion forces between the atoms or weak vander waal forces.

### POINT TO REMEMBER

So,

\* Helium has the lowest Boiling Point.

Boiling point increases down the group with ↑ in VDW forces.

↓  
increases with increase in mass

Ques

Explain how Neil Bartlett synthesized the first noble gas compound?

Ans

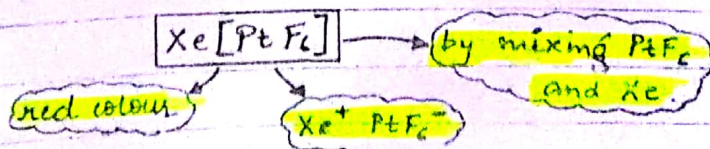
N. Bartlett based on his synthesis on the existence of compound

$O_2[PtF_6]$  in which oxygen exists as  $O_2^+$ .

Red colour

He, then realised that the energy required to convert Xe to  $Xe^+$  was of the same order as required to convert  $O_2$  to  $O_2^+$ .

So, the first noble gas compound synthesized was  $Xe[PtF_6]$ .



# CHEMICAL PROPERTIES

noble gases are least reactive

or chemically inert

completely filled  
electronic configuration  
in their valence shell

high ionisation  
enthalpy

large +ve values  
of EGE

Ques Noble gases are known to form compounds only with oxygen and fluorine. Why??

Ans Because oxygen and fluorine are the most electronegative elements of the periodic table and are able to bring about the oxidation of noble gases.

Ques Amongst noble gases, only Kr and Xe are known to form compounds. Why??

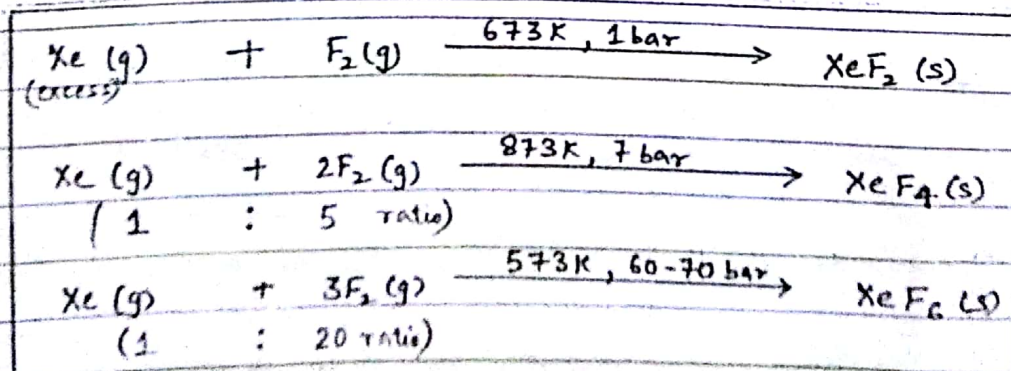
Ans Because in group 18, they have comparatively lesser IE as they lie at the end of the group.

NOTE :- For Krypton  $\rightarrow$  Only difluoride ( $\text{KrF}_2$ ) has been studied in detail.

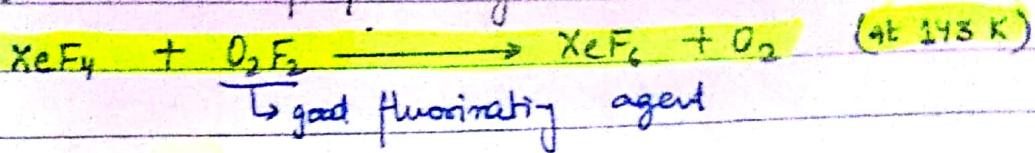
## XENON - FLUORINE COMPOUNDS

(a) PREPARATION:-

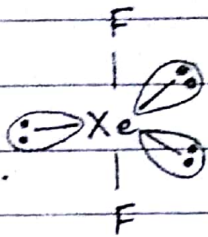
Xenon forms three binary fluorides,  $\text{XeF}_2$ ,  $\text{XeF}_4$  &  $\text{XeF}_6$  by the direct reaction of elements under appropriate experimental conditions.



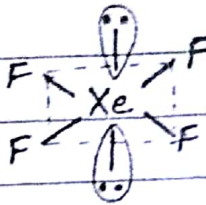
NOTE:-  $\text{XeF}_6$  can also be prepared by :



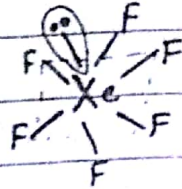
(b) STRUCTURES:-



$\text{XeF}_2 \rightarrow$  linear

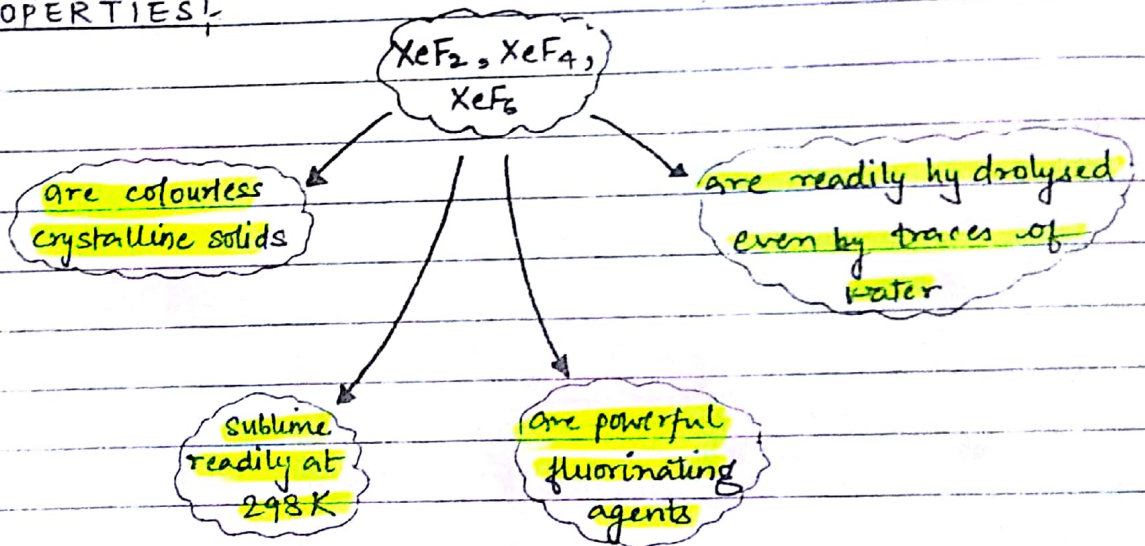


$\text{XeF}_4 \rightarrow$  square planar

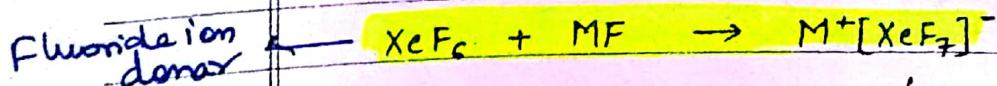
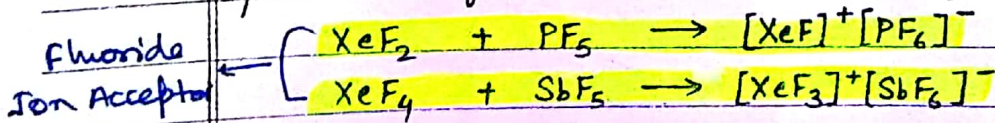


$\text{XeF}_6 \rightarrow$  distorted octahedral

(c) PROPERTIES:-

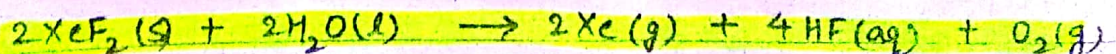


NOTE:- (1) Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



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

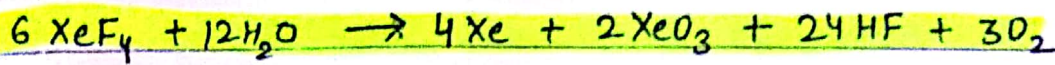
(2) Hydrolysis of  $\text{XeF}_2$  give the following products :-



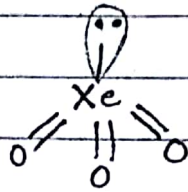
# XENON - OXYGEN COMPOUNDS

## (a) PREPARATION:-

Hydrolysis of  $\text{XeF}_4$  and  $\text{XeF}_6$  with water gives  $\text{XeO}_3$ .



## (b) STRUCTURE :-



$\text{XeO}_3 \rightarrow$  Pyramidal

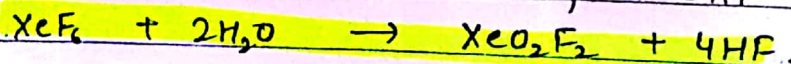
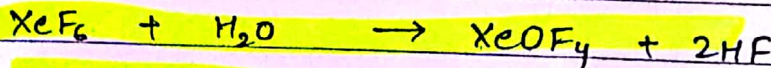
colourless  
explosive solid

(c) PROPERTY

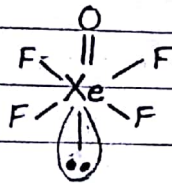
## OXY-FLUORIDES OF XENON

### (a) PREPARATION:-

Partial hydrolysis of  $\text{XeF}_6$  gives oxyfluorides,  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$ .



### (b) STRUCTURE :-



$\text{XeOF}_4 \rightarrow$  square pyramidal

colourless volatile  
liquid

(c) PROPERTY

Ques Does the hydrolysis of  $\text{XeF}_6$  lead to a redox reaction ??

Ans No, the products of hydrolysis are  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$  where the oxidation states of all the elements remain the same as it was in the reacting state.

## USES OF NOBLE - GASES

### HELIUM :-

- It is a non-inflammable and light gas. Hence, it is used filling balloons for meteorological observations.
- It is also used in gas-cooled nuclear reactors.

Ques Why is helium used in diving apparatus??

Ans Helium is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

### NEON :-

- It is used in discharge tubes & fluorescent bulbs for adv. display purposes.
- used in botanical gardens & in green houses.

### ARGON :-

- used mainly to provide inert atmosphere in high temp. metallurgical processes.
- used for filling electric bulbs.
- used in the laboratory for handling substances that are air-sensitive.

### XENON & KRYPTON :-

- used in light bulbs designed for special purposes.