

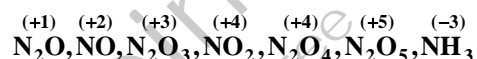
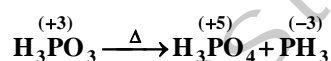
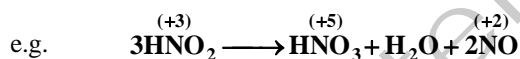
p-Block Elements XII

[www.einsteinclasses.com](http://www.einsteinclasses.com)  
Free Quality Education

## p-BLOCK ELEMENTS (XIIth)

### C1A Group 15 (General properties of Group 15)

- I. Atomic radius :** increases down the group because of increase of number of shells. From As to Bi only a small increase in radius is observed because of the presence of inner d and f-orbital which having poor shielding effect and hence effective nucleus charge increases.
- II. Ionisation enthalpy :** (a) IE decreases down the group because of increase of atomic size  
First ionisation energy of group 15 elements higher than group-14 and group-16 because of stable config. half filled orbitals i.e., stable config.
- III. Electronegativity :** decreases down the group because of increase of atomic size.
- IV. Metallic Character :** increases down the group because of increase of atomic size and decrease of IE.
- V. Melting Point :** increases from N to As but decreases from As to Bi. Lower m.p. of Sb and Bi are due to their tendency to form 3-covalent bonds instead of 5 due to inert pair effect.
- VI. Allotropy :** All elements show except nitrogen. Allotropic forms (white, red and black) As and Sb forms two (white and grey).
- VII. Catenation :** Tendency for catenation increases from N to P. N has some extent to show catenation because of triple bond.
- VIII. Oxidation State : -3, +3, +5**
- (i) The tendency to show -3 o.s. decreases down the group due to decrease in EN, which is due to increase in atomic size, therefore increase in metallic character.
- (ii) The stability of +5 o.s. decreases whereas +3 o.s. increases down the group due to inert pair effect. Thus the electrons present in the 's' subshell do not participate in bond formation and only the p-electrons participate.
- (iii)  $\text{Bi}^{3+}$  is more stable than  $\text{Bi}^{5+}$  due to inert pair effect i.e., why  $\text{Bi}^{5+}$  is a good oxidising agent. The only well characterised  $\text{Bi}^{5+}$  is  $\text{BiF}_5$ .
- (iv) Nitrogen shows o.s. from -3 to +5.  
-3 o.s. acts as reducing agent while +5 o.s. acts as oxidising agent while +1 to +4 shows disproportionation in acid solution.



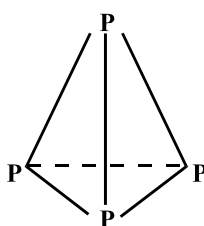
- (v) The nitrogen can show maximum covalency upto 4 not more than 4 because of absence of d-orbitals. While rest elements can show higher covalency due to presence of vacant d-orbitals e.g.  $\text{PF}_6^-$ .
- (vi) Nitrogen does not show pentavalent because of absence of d-orbitals.

### C1B Anomalous behaviour of Nitrogen :

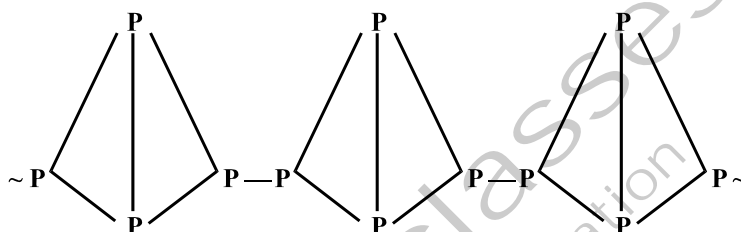
Reasons : (a) small size (b) high EN, IE (c) absence of d-orbitals and hence cannot expand its covalency more than 4. (d) has tendency to form  $p\pi-p\pi$  multiple bonds with itself and other elements having small size and high EN like carbon and oxygen.

### C1C Allotropy of Phosphorous :

Phosphorous exists in 3 main allotropic forms : (1) white phosphorous (2) red phosphorous (3) black phosphorous.

**(1) White Phosphorous :**

- (i) It is formed by condensation from the gaseous or liquid states.
- (ii) It is a waxy solid which is insoluble in water but highly soluble in  $\text{CS}_2$  and benzene.
- (iii) It is highly reactive and spontaneously indigestive and hence it is stored under water.
- (iv) It glows in dark and this property gives the element its name PHOSPHOROUS (green for “light bringing”)
- (v) It consists of discrete  $\text{P}_4$  molecules in which the four phosphorous atoms are at the corners of a tetrahedron and each phosphorous atoms is covalently linked to the other 3 phosphorous atoms.
- (vi) It is highly toxic.

**(2) Red Phosphorous :**

- (i) When white phosphorous is heated to 570 K in an inert atmosphere for several days it gets converted into red phosphorous.
- (ii) It has higher m.p. (870 K) and greater density ( $\sim 2.16 \text{ gcm}^{-3}$ ) than white phosphorous.
- (iii) It is very less reactive than white phosphorous
- (iv) It is safer and easier to handle
- (v) It is essentially non-toxic
- (vi) It is amorphous and has a polymeric structure

**(3) Black Phosphorous :**

- (i) It is obtained by heating white phosphorous at 470 K and under high pressure. A series of phase of black phosphorous are formed. One of these phases consists of an extended layer structure in which each P is bound to three neighbours by single bonds.
- (ii) Thermodynamically it is most stable form of phosphorous. It is least reactive and crystalline in nature.

**C1D Comparison of nitrogen with phosphorus**

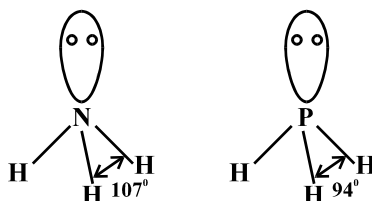
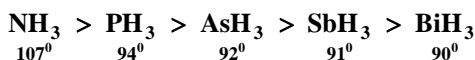
- (i) N-N bond is weaker than P-P bond due to high interelectronic repulsion of the non-bonding electrons.
- (ii) Nitrogen cannot form  $d\pi-d\pi$  and  $d\pi-p\pi$  bonds only form  $p\pi-p\pi$  due to absence of d-orbitals. Others can form  $d\pi-p\pi$  bond e.g.  $\text{R}_3\text{P}=\text{O}$  and  $d\pi-d\pi$  bond with transition element when their compounds act as ligands e.g.  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{As}(\text{C}_6\text{H}_5)_3$ .

**C1E Compounds : (1) Hydrides :  $(\text{MH}_3)$  ( $\text{sp}^3$  hybridisation)**

- (i) **Thermal Stability :** Moving down in the group it decreases because increase of size of central atom (M) and hence increase of M-H bond length and hence decrease of bond strength and bond dissociation energy.  
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
- (ii) **Reducing Character :** Except  $\text{NH}_3$  all hydrides are strong (good) reducing agent and hence react with metal ions ( $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ) to give phosphides, arsenides or antimonides.

**Order of Reducing Character :**  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$  because of increase of atomic size and hence increase of M - H bond length, decrease of bond dissociation energy thus bond weakens from  $\text{NH}_3$  to  $\text{BiH}_3$ . Bi-H bond can be easily broken.

(iii) **Bond Angle :**



EN of N is highest  $\therefore$  lone pairs will be towards nitrogen, so there is high  $e^-$  density around the N-atom and hence more repulsion between bond pairs  $\therefore$  bond angle increases.

As EN  $\downarrow$ ,  $e^-$  density also decreases down the group  $\therefore$  repulsive interaction between bond pair electrons also decreases and bond angle decreases.

(iv) **Boiling Point :**  $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$

$\text{NH}_3$  : exception high boiling point because of intermolecular H-bond.

$\text{PH}_3$  to  $\text{BiH}_3$  B.P. increases because of increase of atomic size and hence increase of vanderwall's interaction.

(v) **Basicity :** group-15 hydrides are lewis base because of presence of lone pairs of electrons on the central atom and hence has tendency to donate a pair of  $e^-$ . Order of basicity is  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$  i.e., basicity decreases down the group because nitrogen atom has the smallest size among the hydrides  $\therefore$  the lone pair  $e^-$ s is concentrated on a small region so  $e^-$  density per unit volume is more. As we move down the group the size of central atom keeps on increases  $\therefore$  then the  $e^-$  is distributed over large volume as a result  $e^-$  density decreases. Thus the  $e^-$  donar capacity i.e. basic strength decreases.

2. **Halides of Group 15 :** (a)  $\text{MX}_3$  (b)  $\text{MX}_5$

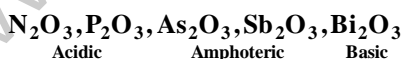
Trihalides ( $\text{MX}_3$ ) :  $sp^3$  hybridised, covalent except  $\text{BiF}_3$  which is ionic in nature.

Pentahalides ( $\text{MX}_5$ ) :  $sp^3d$  (Trigonal bipyramidal in shape)

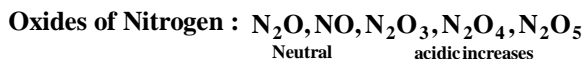
- Nitrogen does not form pentahalides because of absence of d-orbitals.
- They are lewis acids because of presence of vacant d-orbitals accept a pair of  $e^-$ . i.e.,  $\text{PCl}_5 + \text{Cl}^- \rightarrow [\text{PCl}_6]^-$
- $\text{PCl}_5$  is covalent in gaseous and liquid phase as it has a trigonal bipyramidal geometry while in solid state it is ionic as it exist as  $[\text{PCl}_4]^+ [\text{PCl}_6]^-$  i.e., tetrahedral cation and octahedral anion.
- In  $\text{PCl}_5$ , 3 P-Cl bonds are equatorial & 2 P-Cl bonds are axial. Axial bonds are longer due to greater repulsion from equatorial bonds and hence bond length are not equivalent and bonds become weaker and hence easily dissociated into  $\text{PCl}_3$  and  $\text{Cl}_2$  so  $\text{PCl}_5$  is quite reactive.
- $\text{PCl}_3$  fumes in moist air because of production of HCl with water  $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$

3. **Oxides of Group 15 :**

- All group-15 elements form tri-oxides and pentoxides. Pentoxides are more acidic than trioxides.
- Acidic character decreases down the group and basic character increases.

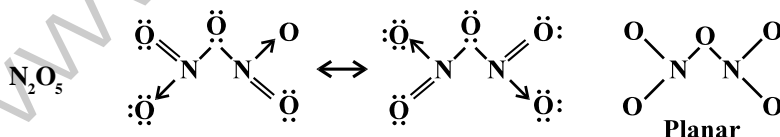
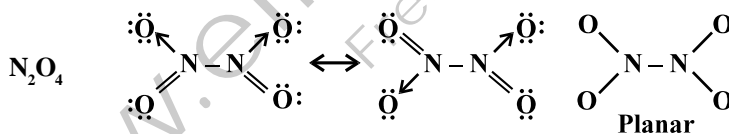
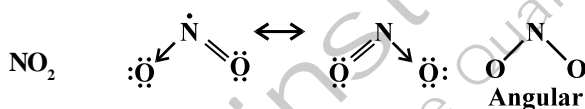
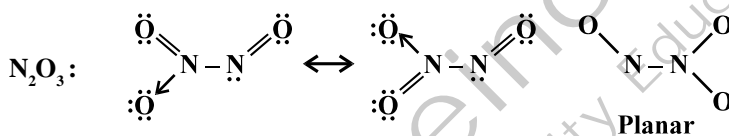
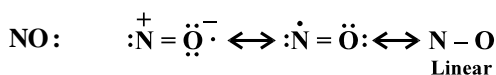
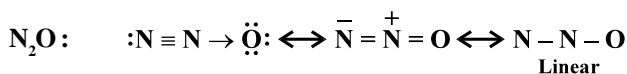


**Reason :** because the size of N is very small. It has a strong positive field in a very small area  $\therefore$  it attracts the  $e^-$ s of water's O-H bond to itself and releases  $\text{H}^+$  ions easily.

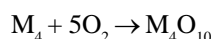
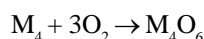


**Oxides of Nitrogen :**

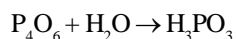
Name	Formula o.s.	Common Methods of Preparation	Physical Appearance and Chemical Nature
1. Nitrogen (I) oxide	N <sub>2</sub> O	+1 $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	colourless, neutral gas
2. Nitrogen (II) oxide (nitrogen monoxide)	NO	+2 $\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + \text{H}_2\text{O} + 2\text{NO}$	colourless, neutral gas
3. Nitrogen (III) oxide	N <sub>2</sub> O <sub>3</sub>	+3 $2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{k}} 2\text{N}_2\text{O}_3$	blue solid, acidic
4. Nitrogen (IV) oxide	NO <sub>2</sub>	+4 $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 4\text{NO}_2 + 2\text{PbO}$	Brown gas, acidic
5. Nitrogen (IV) oxide	N <sub>2</sub> O <sub>4</sub>	+4 $2\text{NO}_2 \xrightleftharpoons[\text{heat}]{\text{cool}} \text{N}_2\text{O}_4$	colourless, solid, acidic
6. Nitrogen (V) oxide	N <sub>2</sub> O <sub>5</sub>	+5 $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow \text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless, solid, acidic

**Structure of oxides of nitrogen :**

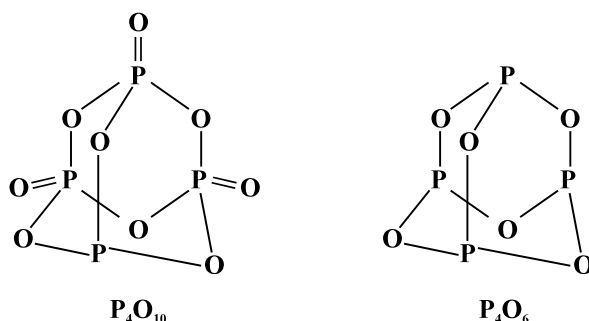
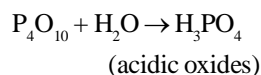
**Oxides of Phosphorous :** (P<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>) but exist as a dimer form. P to Bi oxides exist as the dimer form because of reluctance of pπ - pπ multiple bonds leads to cage like structure i.e, M<sub>4</sub>O<sub>6</sub> and M<sub>4</sub>O<sub>10</sub>



Bi<sub>4</sub>O<sub>10</sub> is unstable

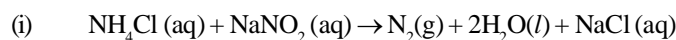


(acidic oxides)

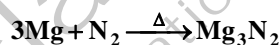
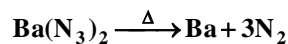
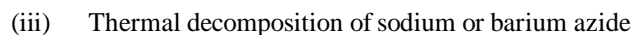
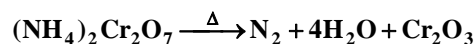
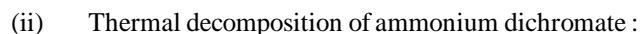


#### 4. Preparation of $\text{N}_2$ (Dinitrogen) :

##### Preparation

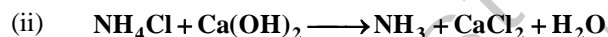
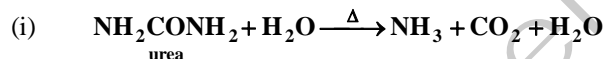


small amount of impurities like NO and  $\text{HNO}_3$  are removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.



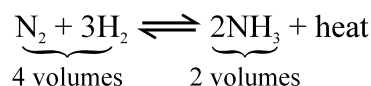
#### 5. $\text{NH}_3$ (Ammonia) :

##### Preparation



(iii) **Haber-Bosch process**

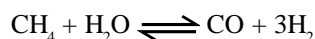
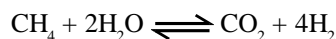
The most important commercial process is the Haber - Bosch process. Fritz Haber discovered how to make  $\text{N}_2$  and  $\text{H}_2$  combine directly in the laboratory. He was awarded the Nobel Prize for Chemistry in 1918. Carl Bosch was a chemical engineer who developed the plant to make ammonia using this reaction on an industrial scale. He too was awarded the Nobel Prize for Chemistry in 1931 for his work on high pressure reactions.



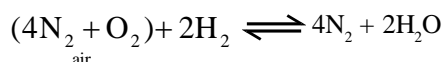
The reaction is reversible, and Le Chatelier's principle suggests that a high pressure and low temperature are required to drive the reaction to the right, and thus form  $\text{NH}_3$ . A low temperature gives a higher percentage conversion to  $\text{NH}_3$ , but the reaction is slow in reaching equilibrium, and a catalyst is required. In practice the conditions used are 200 atmospheres pressure, a temperature of 380 - 450°C and a catalyst of promoted iron. It is more economic to use a higher temperature, so that equilibrium will be reached much faster, even though this gives a lower percentage conversion. At a temperature of about 400°C a 15% conversion is obtained with a single pass over the catalyst. The gas mixture is cooled to condense liquid  $\text{NH}_3$ , and the unchanged mixture of  $\text{N}_2$  and  $\text{H}_2$  gases is recycled. The plant is made of steel alloyed with Ni and Cr.

The catalyst is made by fusing  $\text{Fe}_3\text{O}_4$  with  $\text{KOH}$  and a refractory material such as  $\text{MgO}$ ,  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ . This is broken into small lumps and put into the ammonia convertor, where the  $\text{Fe}_3\text{O}_4$  is reduced to give small crystals of iron in a refractory matrix. This is the active catalyst.

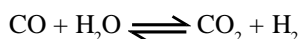
The actual plant is more complicated than this one-stage reaction implies, since the  $\text{N}_2$  and  $\text{H}_2$  must be made before they can be converted to  $\text{NH}_3$ . The cost of  $\text{H}_2$  is of great importance for the economy of the process. Originally the  $\text{H}_2$  required was produced by electrolysis of water. This was expensive, and a cheaper method using coke and water was then used (water gas, producer gas). Nowadays the  $\text{H}_2$  is produced from hydrocarbons, either naphtha or  $\text{CH}_4$ , by reacting with steam at  $750^\circ\text{C}$  with a  $\text{Ni}$  catalyst. All traces of  $\text{S}$  must be removed since these poison the catalyst.



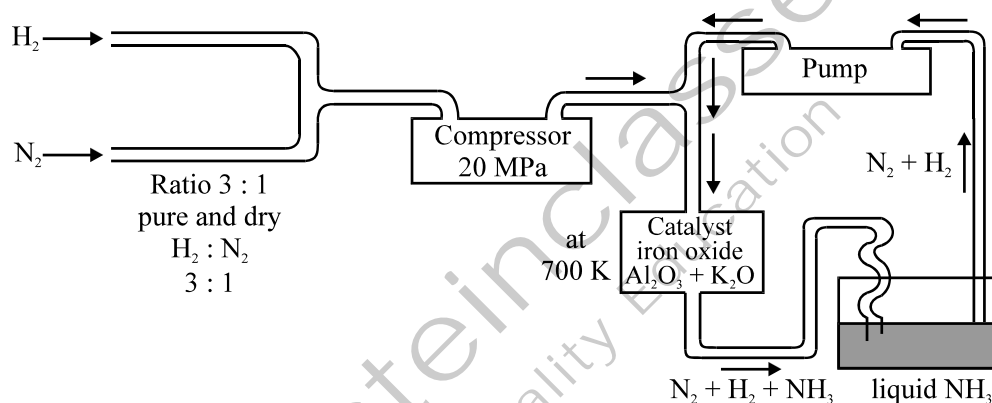
Some air is added. The  $\text{O}_2$  burns with some of the  $\text{H}_2$ , thus leaving  $\text{N}_2$  to give the required reaction ratio  $\text{N}_2$  :  $\text{H}_2$  of 1 : 3.



$\text{CO}$  must also be removed as it too poisons the catalyst.



Finally the  $\text{CO}_2$  is removed in a scrubber by means of a concentrated solution of  $\text{K}_2\text{CO}_3$ , or ethanolamine.



Ammonia is used as a fertilizer. Other uses include the following :

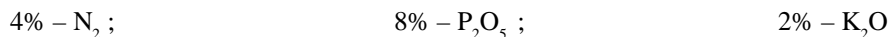
1. Making  $\text{HNO}_3$ , which can be used to make  $\text{NH}_4\text{NO}_3$  (fertilizer), or explosive such as nitroglycerine, nitrocellulose and TNT.  $\text{HNO}_3$  can be used for many other purposes.
2. Making caprolactam, which on polymerization forms nylon-6 (see hydroxylamine).
3. Making hexamethylenediamine which is used in making nylon-6-6, polyurethanes and polyamides.
4. Making hydrazine and hydroxylamine.
5. Liquid  $\text{NH}_3$  is often used as a cheaper and more convenient way of transporting  $\text{H}_2$  than cylinders of compressed  $\text{H}_2$  gas. The  $\text{H}_2$  is obtained from  $\text{NH}_3$  by heating over a catalyst of finely divided  $\text{Ni}$  or  $\text{Fe}$ .
6. Ammonia has been used as the cooling liquid in refrigerators. It has a very high heat of vaporization, and convenient boiling and freezing points. With the environmental concern over using Freons in refrigerators, this use of  $\text{NH}_3$  could increase.

#### Fertilizers

- Nitrogen, phosphorous and potassium are three most essential plant nutrients consumed by them. Fertility of soil is maintained by using these nutrients in the form of fertilisers.
- Fertiliser used should :
  - be water soluble — not disturb alkaline nature (pH)
  - be stable.

- $\text{NH}_2\text{CONH}_2$  (urea)  
 $\text{NH}_4\text{NO}_3$  (ammonium nitrate)  
 $(\text{NH}_4)_2\text{SO}_4$  (ammonium sulphate)  
 $\text{NH}_4\text{H}_2\text{PO}_4$  (mono ammonium hydrogen phosphate)

These are either used on their own or in conjugation with other chemicals, often to make **NPK** fertilisers. These are designed to release nitrogen (N), phosphorus (P) and potassium (K) into the soil. If the NPK fertiliser is marked 4-8-2, it means it has :



### Urea

Urea is widely used as a nitrogenous fertilizer. It is very soluble, and hence quick acting, but it is easily washed away. It has a very high nitrogen content (46%). It is manufactured from  $\text{NH}_3$ , and the reaction proceeds in two stages.

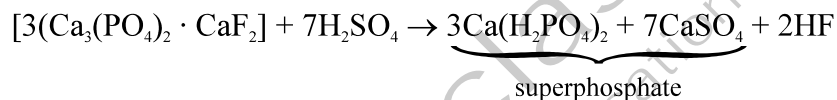


In the soil, urea slowly hydrolyses to ammonium carbonate.



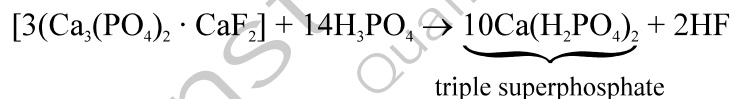
### Phosphate Fertilizers

Phosphate rocks such as fluoroapatite [ $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ] are very insoluble, and thus are of no use to plants. Superphosphate is made by treating phosphate rock with concentrated  $\text{H}_2\text{SO}_4$ . The acid salt  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is more soluble, and over a period of weeks the superphosphate will dissolve in the soil water.

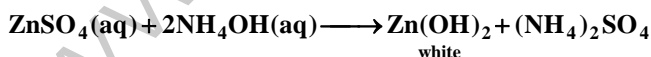
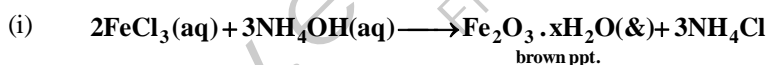


The  $\text{CaSO}_4$  is an insoluble waste product, and is of no value of plants, but is not removed from the product sold.

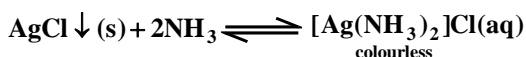
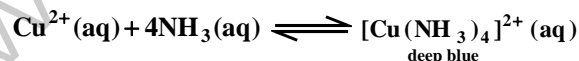
'Triple superphosphate' is made in a similar way, using  $\text{H}_3\text{PO}_4$  to avoid the formation of the waste product  $\text{CaSO}_4$ .



### Properties of ammonia :



(ii)  $\text{NH}_3$  is a weak base. It has a lone pair of  $e^-$ .



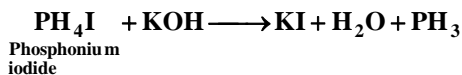
Ammonia is a good complexing agent because of presence of lone pair of electron it act as a legand and forms complexes

**$\text{PH}_3$  (Phosphine) :** because of presence of lone pair, and it acts as ligand and forms complexes.



**6. PH<sub>3</sub> (Phosphine) : Preparation**

- (i)  $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$   
 $\text{Ca}_3\text{P}_2 + 6\text{HCl} \rightarrow 3\text{CaCl}_2 + 2\text{PH}_3$
- (ii)  $\text{P}_4 (\text{white}) + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$
- (iii) **Lab preparation :**

**Properties :**

- (i) Weak base :  $\text{PH}_3 + \text{HBr}$  or  $\text{HI} \rightarrow \text{PH}_4\text{Br}$
- (ii)  $3\text{CuSO}_4 + 3\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$
- (iii)  $3\text{HgCl}_2 + 2\text{PH}_3 \rightarrow \text{Hg}_3\text{P}_2 + 6\text{HCl}$

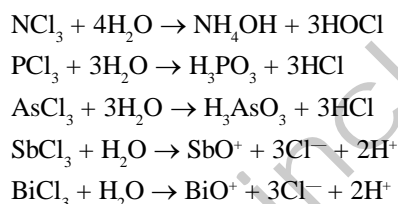
**Uses :** used in Huleme's signals and smoke screens.

**7. Halides of Group 15 PCl<sub>3</sub> (Phosphorous trichloride)****Trihalides**

All the possible trihalides of N, P, As, Sb and Bi are known. The nitrogen compounds are the least stable. Though NF<sub>3</sub> is stable, NCl<sub>3</sub> is explosive.

The trihalides are predominantly covalent and, like NH<sub>3</sub>, have a tetrahedral structure with one position occupied by a lone pair. The exceptions are BiF<sub>3</sub> which is ionic and the other halides of Bi and SbF<sub>3</sub> which are intermediate in character.

The trihalides typically hydrolyse readily with water, but the products vary depending on the element :



They also react with NH<sub>3</sub>.



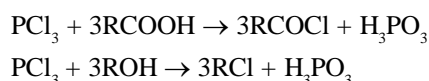
NF<sub>3</sub> behaves differently from the others. It is unreactive, rather like CF<sub>4</sub>, and does not hydrolyse with water, dilute acids or alkali. It does react if sparked with water vapour.

NF<sub>3</sub> has little tendency to act as a donor molecule. The molecule is tetrahedral with one position occupied by a lone pair, and the bond angle F—N—F is 102°30'. However, the dipole moment is very low (0.23 Debye units) compared with 1.47D for NH<sub>3</sub>. The highly electronegative F atoms attract electrons, and these moments partly cancel the moment from the lone pair, and this reduces both the dipole moment and its donor power.

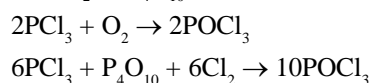
PCl<sub>3</sub> is the most important trihalide, and 250000 tonnes/year are produced commercially from the elements. Some PCl<sub>3</sub> is used to make PCl<sub>5</sub>.



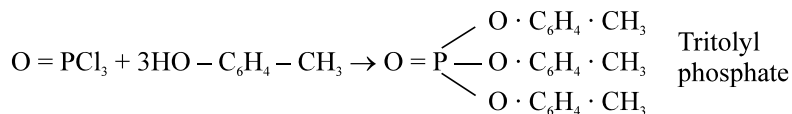
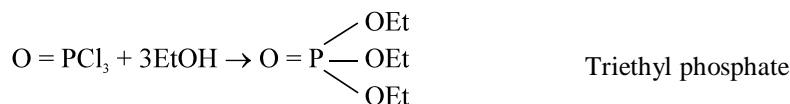
PCl<sub>3</sub> is widely used in organic chemistry to convert carboxylic acids to acid chlorides, and alcohols to alkyl halides.



PCl<sub>3</sub> can be oxidized by O<sub>2</sub> or P<sub>4</sub>O<sub>10</sub> to give phosphorus oxochloride POCl<sub>3</sub>.

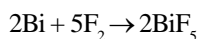
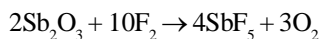
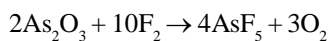
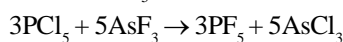
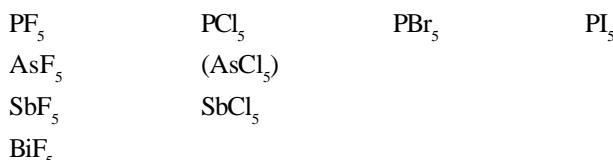


POCl<sub>3</sub> is used in large amounts in the manufacture of trialkyl and triaryl phosphates (RO)<sub>3</sub>PO.



### Pentahalides

Nitrogen is unable to form pentahalides because the second shell contains a maximum of eight electrons, i.e. four bonds. The subsequent elements have suitable d orbitals, and form the following pentahalides :



These molecules have a trigonal bipyramid shape in the gas phase, as expected from the VSEPR theory for five pairs of electrons.

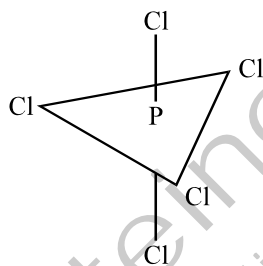
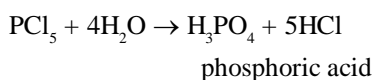


Figure : Structure of gaseous phosphorus pentachloride.

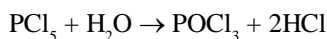
The trigonal bipyramid is not a regular structure. Electron diffraction on  $\text{PF}_5$  gas shows that some bond angles are  $90^\circ$  and others are  $120^\circ$ , and the axial P — F bond lengths are  $1.58 \text{ \AA}$  whilst the equatorial P — F lengths are  $1.53 \text{ \AA}$ . The axial and equatorial F atoms are thought to interchange their positions in less time than that needed to take the NMR. The interchange of axial and equatorial positions is called '**pseudorotation**'.

$\text{PF}_5$  remains covalent and keeps this structure in the solid state. However,  $\text{PCl}_5$  is close to the ionic-covalent borderline, and it is covalent in the gas and liquid states, but is ionic in the solid state.  $\text{PCl}_5$  solid exists as  $[\text{PCl}_4]^+$  and  $[\text{PCl}_6]^-$ : the ions have tetrahedral and octahedral structures respectively. In the solid,  $\text{PBr}_5$  exists as  $[\text{PBr}_4]^+\text{Br}^-$ , and  $\text{PI}_5$  appears to be  $[\text{PI}_4]^+$  and  $\text{I}^-$  in solution.

$\text{PCl}_5$  is the most important pentahalide, and it is made by passing  $\text{Cl}_2$  into a solution of  $\text{PCl}_3$  in  $\text{CCl}_4$ . Complete hydrolysis of the pentahalides yields the appropriate -ic acid. Thus  $\text{PCl}_5$  reacts violently with water :



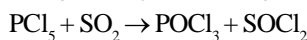
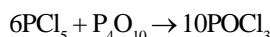
If equimolar amounts are used, the reaction is more gentle and yields phosphorus oxochloride  $\text{POCl}_3$ .



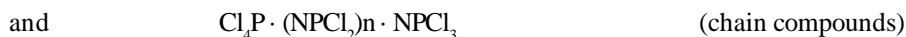
$\text{PCl}_5$  is used in organic chemistry to convert carboxylic acids to acid chlorides, and alcohols to alkyl halides.



It reacts with  $\text{P}_4\text{O}_{10}$ , forming  $\text{POCl}_3$ , and with  $\text{SO}_2$ , forming thionyl chloride  $\text{SOCl}_2$ .



$\text{PCl}_5$  also reacts with  $\text{NH}_4\text{Cl}$ , forming a variety of phosphonitrilic chloride polymers.



## 8. Oxoacids of Nitrogen and Phosphorous

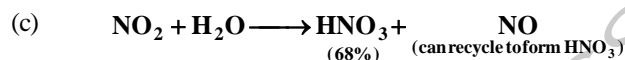
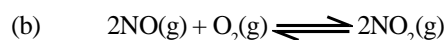
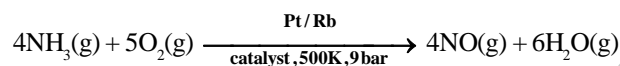
1. Nitrogen oxacids are  $\text{HNO}_2$ ,  $\text{HNO}_3$

### 2. Preparation of $\text{HNO}_3$



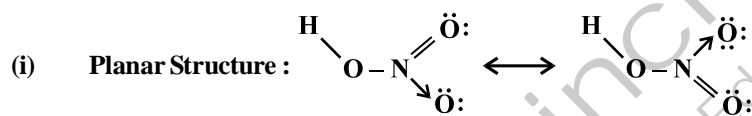
(ii) **Ostwald's process**

(a) catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen :

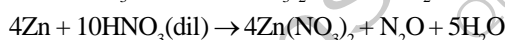
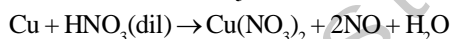


(d) Further concentration upto 98% is done by dehydration with concentrated  $\text{H}_2\text{SO}_4$ .

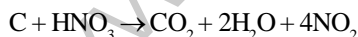
### Properties :



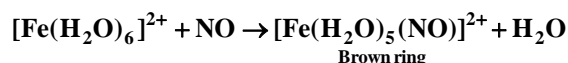
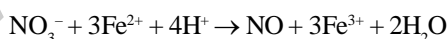
(iii) **Concentration  $\text{HNO}_3$  is a strong oxidising agent :**



**with non-metals : (conc.  $\text{HNO}_3$ )**



(iv) **Brown ring test :**

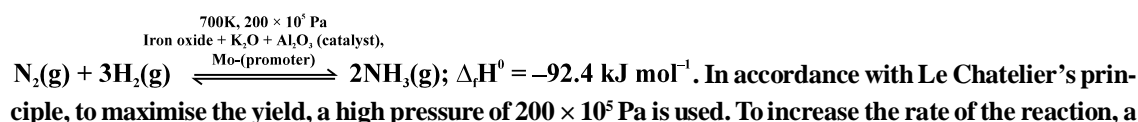


### Practice Problems :

1. How is  $\text{N}_2$  differ from rest of elements ?
2. Nitrogen is inert while other (e.g. phosphorous) are rightly reactive in elemental state.
3. Why are pentahalides more covalent than trihalides ?

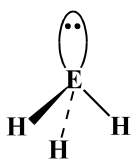
4. Why is  $\text{BiH}_3$  the strongest reducing agent amongst all the hydrides of Group 15 elements ?
5. Why is  $\text{N}_2$  less reactive at room temperature ?
6. Mention the conditions required to maximise the yield of ammonia.
7. How does ammonia react with a solution of  $\text{Cu}^{2+}$  ?
8. What is the covalence of nitrogen in  $\text{N}_2\text{O}_5$  ?
9. Bond angle in  $\text{PH}_4^+$  is higher than that in  $\text{PH}_3$ . Why ?
10. What happens when white phosphorus is heated with concentrated  $\text{NaOH}$  solution in an inert atmosphere of  $\text{CO}_2$  ?
11. What happens when  $\text{PCl}_5$  is heated ?
12. Write a balanced equation for the hydrolytic reaction of  $\text{PCl}_5$  in heavy water.
13. What happens when  $\text{H}_3\text{PO}_3$  is heated ?
14. Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.
15. Why does the reactivity of nitrogen differ from phosphorus ?
16. Discuss the trends in chemical reactivity of Group 15 elements.
17. Why does  $\text{NH}_3$  form hydrogen bond but  $\text{PH}_3$  does not ?
18. How is nitrogen prepared in the laboratory ? Write the chemical equations of the reactions involved.
19. How is ammonia manufactured industrially ?
20. Illustrate how copper metal can give different products on reaction with  $\text{HNO}_3$ .
21. Give the resonating structures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$ .
22. The HNH angle value is higher than HPH, HAsH and HSbH angles. Why ?
23. Why does  $\text{R}_3\text{P}=\text{O}$  exist but  $\text{R}_3\text{N}=\text{O}$  does not (R = alkyl group) ?  
[Due to the absence of d-orbitals, nitrogen cannot form  $\text{p}\pi\text{-d}\pi$  multiple bonds.]
24. Explain, why  $\text{NH}_3$  is basic while  $\text{BiH}_3$  is only feebly basic.
25. Nitrogen exists as diatomic molecule and phosphorus as  $\text{P}_4$ . Why ?
26. Write main differences between the properties of white phosphorus and red phosphorus.
27. Why does nitrogen show catenation properties less than phosphorus ?
28. Give the disproportionation reaction of  $\text{H}_3\text{PO}_3$ .
29. Can  $\text{PCl}_5$  act as an oxidising as well as a reducing agent ? Justify.
30. What are the oxidation states of phosphorus in the following :  
(i)  $\text{H}_3\text{PO}_3$       (ii)  $\text{PCl}_3$       (iii)  $\text{Ca}_3\text{P}_2$       (iv)  $\text{Na}_3\text{PO}_4$   
(v)  $\text{POF}_3$

[Answers (1) (i)  $\text{N}_2$  is gas while other elements (e.g.  $\text{P}_4$ ....) solid (ii) Nitrogen is diatomic while other elements polyatomic ( $\text{P}_4$ ) (2) because of small size and high EN nitrogen has tendency to form  $\text{p}\pi\text{-p}\pi$  multiple bond and form triple bond due to which bond dissociation energy is very high whereas others are more reactive due to presence of single bond p-p and exist as tetrahedral form ( $\text{P}_4$ ) in which four p-atoms is bonded by three p-atoms by single p-p bonds and therefore exist as solid (4) As we move down the Group 15, the size of the element increases and, therefore, the length of the bond with hydrogen increases and its strength decreases. In other words, as we move down the Group, the bond with hydrogen can break more easily to evolve  $\text{H}_2$  gas which acts as the reducing agent. Thus, Bi — H bond is the weakest amongst the hydrides of elements of Group 15, and hence,  $\text{BiH}_3$  is the strongest reducing agent. (5) Due to the presence of a triple bond between the two nitrogen atoms, the bond dissociation energy of  $\text{N}_2$  ( $941.4 \text{ kJ mol}^{-1}$ ) is very high. Therefore,  $\text{N}_2$  is less reactive at room temperature. However, nitrogen reacts with metals at higher temperature to form nitrides. (6) Ammonia is prepared by the Haber's process. Optimum conditions for the manufacture of ammonia are as under :





(E stands for element of Group 15),  $\sigma$ -bonds while the fourth contains the, lone pair of electrons as shown



. Since the lone pair-bond pair repulsions are stronger than the bond pair-bond pair repul-

sions, therefore, the bond angle decreases from  $109^{\circ}28'$  to  $107.8^{\circ}$  in  $\text{NH}_3$ . As we move from N to P to As to Sb, the atomic size goes on increasing. As a result, bond pairs of electrons, lie away and away from the central atom. In other words, force of repulsion between the adjacent bond pair goes on decreasing and, consequently, the bond angles keep on decreasing from  $\text{NH}_3$  to  $\text{SbH}_3$ . In other words, HNH bond angle is maximum ( $107.8^{\circ}$ ) followed by HPH ( $93.6^{\circ}$ ), followed by HAsH ( $91.8^{\circ}$ ) and HSbH ( $91.3^{\circ}$ ). (27) The property of catenation depends upon the strength of the element-element bond. Weaker the bond, smaller is the possibility of catenation. Since the N — N ( $159 \text{ kJ mol}^{-1}$ ) bond strength is much weaker than P — P ( $213 \text{ kJ mol}^{-1}$ ) bond strength, therefore, nitrogen shows less catenation properties than phosphorus. (29) Phosphorus has maximum oxidation state of +5 in  $\text{PCl}_5$ . It cannot increase its oxidation state further and therefore,  $\text{PCl}_5$  cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, therefore,  $\text{PCl}_5$  acts as an oxidising agent.]

## C2A Group-16 (Chalcogens) ( $ns^2np^4$ )

### General Properties

- IE, EN, Electron Gain Enthalpy ( $\Delta H_{\text{eg}}$ ) decreases down the group because of increase of atomic size. Exception : O has less negative  $\Delta H_{\text{eg}}$  than S because of small size of O.
- Metallic character increases from O to Po because of increase of atomic size and decrease of IE.
- Non-metallic character decreases due to decrease in EN.
- Melting point & Boiling point : Increased down the group because of increase of atomic number. Oxygen has much lower m.p. and b.p. than S because oxygen exist as diatomic ( $\text{O}_2$ ) form while S is octaatomic ( $\text{S}_8$ )
- Oxidation state :
  - oxygen shows -2; except in  $\text{OF}_2$ ,  $\text{O}_2\text{F}_2$ ,  $\text{KO}_2$ ,  $\text{H}_2\text{O}_2$  (peroxide-1)
  - S shows -2, +4, +6; Se, Te show +4, +6 with F and oxygen.
  - stability of -2 o.s. decreases down the group because increase in atomic size and decrease in EN.
  - The stability of +6 o.s. decreases and +4 o.s. increases due to inert pair effect.

Oxygen does not shows +4 and +6 o.s. while sulphur shows because of absence of d-orbital to oxygen and presence of vacant d-orbitals to S.

- Multiple bonds : formation tendency decreases down the group because of increase of atomic size they become unstable.

## C2B Compounds of Group - 16

- Hydrides :**  $\text{H}_2\text{O}$  liquid ( $sp^3$  bent shape) (because of H-bond)  
 $\text{H}_2\text{S}$  (gas),  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$ ,  $\text{H}_2\text{PO}$

- Bond angle :**  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$   
 $104.5^{\circ} \quad 92^{\circ} \quad 91^{\circ} \quad 90^{\circ}$

$\text{H}_2\text{O}$  bond angle is higher because O has the highest EN  $\therefore$  lone pair will be towards O and hence bond pairs will move away while going down in the group EN decrease and atomic size increases due to which bond pair-bond pair. repulsion decreases.

- Boiling point :**  $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$   
 higher intermolecular H-bond      increase in vanderwaal 's forces
- Acidic character :**  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$  (weak diprotic acid)  
 neutral      increase in acidic character

**Reasons :** As the size of the central atom increases in the order  $O < S < Se < Te$ , the distance between the central atom and hydrogen also increases. As a result the bond length increases the bond dissociation energy decreases and bond cleavage become more and more easy. Therefore, the acidic strength of the hydrides increases down the group.

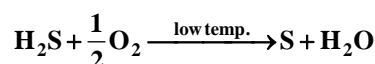
(iv) **Thermal Stability :**  $H_2O > H_2S > H_2Se > H_2Te > H_2PO$

**Reason :** On going down the group, the size of the central atom increases and thereby its tendency to form stable covalent bond with hydrogen decreases as a result the M-H bond strength decreases and thermal stability decreases.

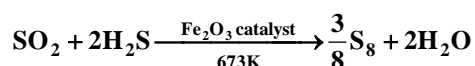
(v) **Reducing Character :**  $H_2O < H_2S < H_2Te < H_2PO$  due to decrease in thermal stability.

## 2. Preparation of Sulphur and its properties

(a) Hydrogen sulphide is oxidized to sulphur by passing oxygen at low temperature



(b)  $H_2S + \frac{3}{2}O_2 \longrightarrow SO_2 + H_2O$



### Uses of Sulphur and other Elements :

- (i) S : used as a manufacture of  $H_2SO_4$  & other industrially compounds.
- (ii) Se as photoconductor in photocopying (xerox) machines.
- (iii) major use is as a decolouriser of glass.

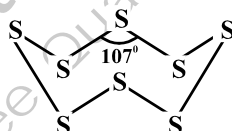
**Te :** Alloy, **Po :** Radioactive (highly toxic)

### Allotropy of S and Se :

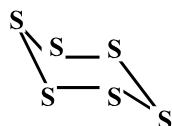
S exists 3 main allotropic forms

- (i) Rhombic (orthorhombic)  $\alpha$  : yellow, stable at room temperature
- (ii) Monoclinic  $\beta$  : which is formed by heating rhombic sulphur to about 368 K.

Both  $\alpha$ ,  $\beta$  are soluble in  $CS_2$ , exist as  $S_8$  molecules with puckered ring structures and has a crown shape.



- (iii) Plastic Sulphur : It is amorphous form of sulphur when molten sulphur heated to about 625 K is poured into cold water, a soft rubber like mass is obtained called plastic sulphur. It is soft and elastic in beginning but hardens on standing and gradually changes to rhombic sulphur. It is also regarded as supercooled liquid.
- (iv) Cyclo- $S_6$  : chair form
- (v) Catena-Sn : chain polymer
- (vi)  $S_2$  is paramagnetic



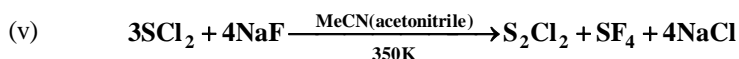
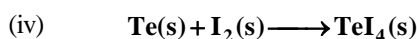
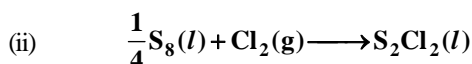
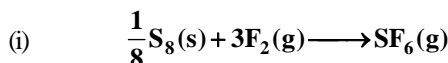
S in vapour state exhibit paramagnetic behaviour because in vapour state S partly exists as  $S_2$  molecule and  $S_2$  molecule like  $O_2$  has 2 unpaired electrons in the antibonding  $\pi^*$  orbital and hence exhibit paramagnetism.

3. Halides of Group 16 :  $EX_2, EX_4, EX_6$ 

S	Se, Te
$S_2X_2$ (X = F, Cl, Br, I)	$Se_2Cl_2, Se_2Br_2$
$SX_2$ (X = F or Cl)	$SeCl_2, TeCl_2, SeBr_2, TeBr_2$
$SF_4$	$SeX_4, TeX_4$ (X = F, Cl, Br), $TeI_4$
$SF_6$	$SeF_6, TeF_6$

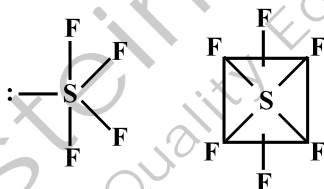
The stability of the halides decreases in the following order because of bond length increases  $F^- > Cl^- > Br^- > I^-$ . The highest O.S. is in the fluorides only with iodine only  $TeI_4$  is known.

**Preparation :** Chalcogens halides prepared by direct combination.



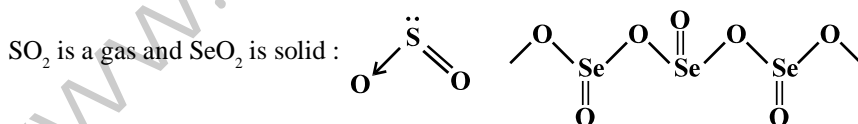
$SF_4$  undergoes hydrolysis while  $SF_6$  not because  $SF_6$  is inert in nature. Its inertness is due to the presence of sterically protected sulphur atom which does not allow thermodynamically favourable reactions like hydrolysis while  $SF_4$  and  $SeF_4$  are less sterically hindered and undergo hydrolysis readily.

Because of its inertness and good dielectric properties  $SF_6$  is used as a gaseous insulator in high voltage generator. Both  $SF_4$  and  $SF_6$  are used as a fluorinating agents for conversion of  $-COOH$  into  $CF_3$  and  $C=O, P=O$  groups into  $CF_2, PF_2$  groups.



$SeCl_4, SeBr_4, TeCl_4, TeBr_4, TeI_4$  exist as tetramers. While  $TeF_4 \rightarrow$  polymeric structure.

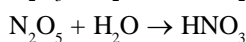
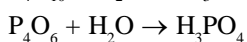
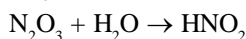
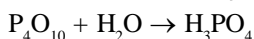
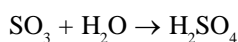
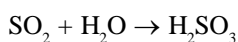
+6 O.S. stability decreases down the group and +4 O.S. increases because of inert pair effect

4. Oxides :  $EO_2, EO_3$  ( $SO_2, SO_3, SeO_2, SeO_3$ )

- $SeO_2$  is solid because it has a chain polymeric structure whereas  $SO_2$  forms discrete units.
- Reducing power of dioxides decreases down the group.
- $SO_3$  gas while  $SeO_3, TeO_3$  solids.
- Dioxides and trioxides both are acidic in nature

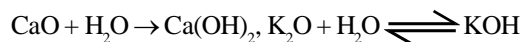
## 5. Oxides are of four types :

- Acidic :** Oxides that combine with water to give acid. They are non-metallic oxides e.g.  $SO_2, NO_2$  etc.

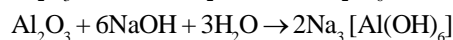
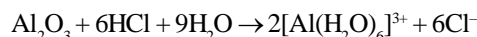




- (ii) **Basic oxides** : Metallic oxides and form bases when dissolved in water  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$



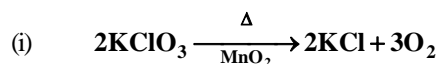
- (iii) **Amphoteric Oxides** : Reacts with acids as well as base



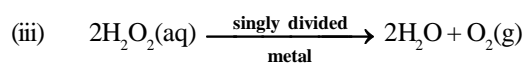
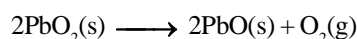
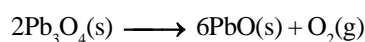
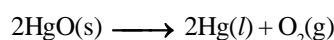
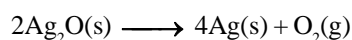
- (iv) **Neutral oxides** :  $\text{CO}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ .

## 6. Oxygen ( $\text{O}_2$ )

### Preparation :

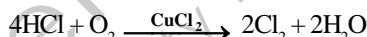
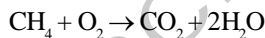
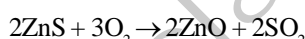
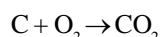
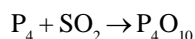
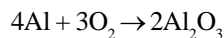
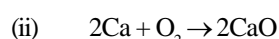


- (ii) By thermal decomposition of oxides :



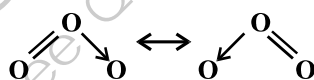
### Properties :

- (i) Paramagnetic nature

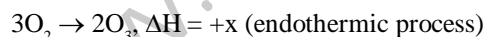


## 7. Ozone ( $\text{O}_3$ ) :

Very reactive

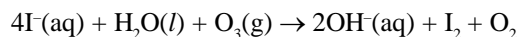
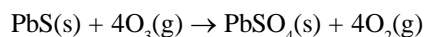


**Preparation** : When a slow dry steam of oxygen is passed through a silent electrical discharge, oxygen gets converted to ozone. This is called ozonised oxygen (10%).



### Properties :

- (i) Pale blue gas, dark blue liquid, violet black solid.
- (ii) Its decomposition to oxygen liberate heat and increase entropy  $\therefore \Delta G$  has a large negative value  $\therefore$  ozone is thermodynamically unstable. Also high concentrations of ozone can be dangerously explosive.
- (iii) It is a powerful oxidising agent because it liberates atoms of nascent oxygen  $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$

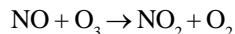


Estimation of Ozone is done by reacting ozone with KI solution buffered with a barate buffer (pH 9.2)  $\text{I}_2$  is liberated which can be liberated against a standard solution of sodium thiosulphate

- (iv) Depletion of ozone layer : Is caused by

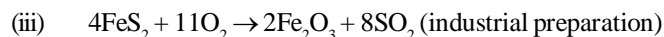
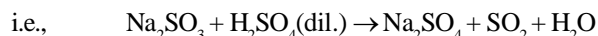
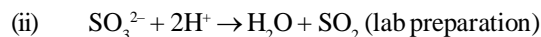
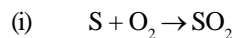
(a) use of freons i.e., CFC's used in aerosol sprays and refrigerants.

(b) Nitrogen oxides emitted from the exhaust system of supersonic jet aeroplanes

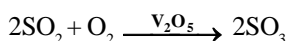
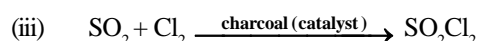
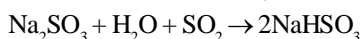
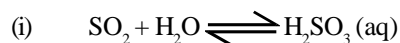


### 8. SO<sub>2</sub> (Sulphur dioxide) :

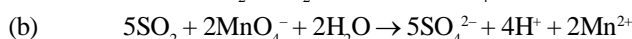
#### Preparation :



#### Properties :

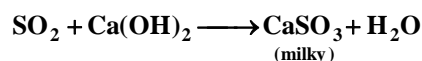


(iv) Reducing agent :

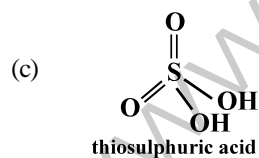
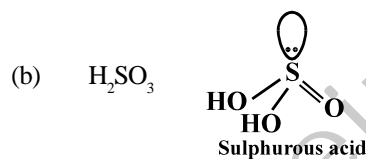
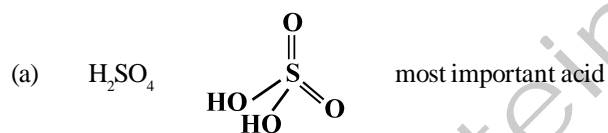


(KMnO<sub>4</sub> colour decolourize)

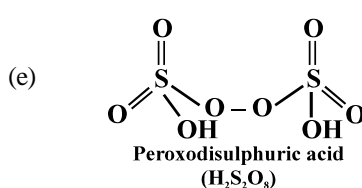
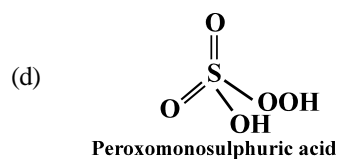
(v) SO<sub>2</sub> can be detected by passing through the lime water

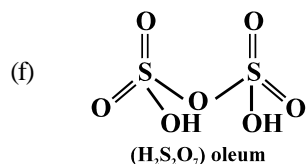


### 9. Oxoacids of sulphur :



H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> are unstable and cannot be insoluble. They are only known in aqueous solutions or in the form of their salts.





### 10. H<sub>2</sub>SO<sub>4</sub> manufacture by contact process

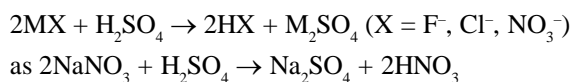
There are three stages :

- (i)  $S + O_2 \rightarrow SO_2$   
 $FeS + O_2 \rightarrow SO_2 + Fe_2O_3$
- (ii)  $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3; \Delta H = -196.6 \text{ kJ/mol}$
- (iii)  $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$   
 (SO<sub>3</sub> absorbed by H<sub>2</sub>SO<sub>4</sub> to form oleum)  
 $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$  (96-98%)

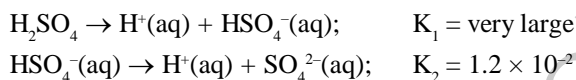
#### Properties of H<sub>2</sub>SO<sub>4</sub> :

The concentration H<sub>2</sub>SO<sub>4</sub> acid must be added slowly into water with constant stirring during the manufacture of dil. H<sub>2</sub>SO<sub>4</sub> from conc. as there is evolution of large quantity of heat (exo.)

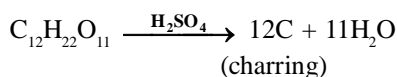
- (i) **Low Volatility** : because of low volatility can be used to manufacture more volatile acids from their corresponding salts



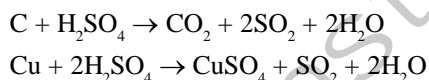
- (ii) **Strong acidic character** :



- (iii) **Strong affinity for water (dehydrating agent) :**



- (iv) **Strong oxidizing agent** : reduce itself to SO<sub>2</sub>. It oxidizes both metals and non-metals.



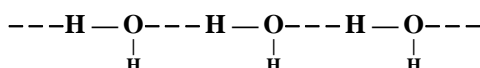
#### Practice Problems :

- List the important sources of sulphur.
- Write the order of thermal stability of the hydrides of Group 16 elements.
- Why is H<sub>2</sub>O a liquid and H<sub>2</sub>S a gas ?
- Which of the following does not react with oxygen directly ? Zn, Ti, Pt, Fe
- Complete the following reactions :
  - $C_2H_4 + O_2 \rightarrow$
  - $4Al + 3O_2 \rightarrow$
- Why does O<sub>3</sub> act as a powerful oxidising agent ?
- How is O<sub>3</sub> estimated quantitatively ?
- What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt ?
- Comment on the nature of two S – O bonds formed in SO<sub>2</sub> molecule. Are the two S – O bonds in this molecule equal ?
- How is the presence of SO<sub>2</sub> detected ?
- Mention three areas in which H<sub>2</sub>SO<sub>4</sub> plays an important role.
- Write the conditions to maximise the yield of H<sub>2</sub>SO<sub>4</sub> by Contact process.

13. Why is  $K_{a_2} \ll K_{a_1}$  for  $H_2SO_4$  in water ?
14. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation, state and hydride formation.
15. Knowing the electron gain enthalpy values of  $O \rightarrow O^-$  and  $O \rightarrow O^{2-}$  as  $-141$  and  $702 \text{ kJ mol}^{-1}$  respectively, how can you account for the formation of a large number of oxides having  $O^{2-}$  species and not  $O^-$  ?
16. Which aerosols deplete ozone ?
17. Describe the manufacture of  $H_2SO_4$  by contact process.
18. How is  $SO_2$  an air pollutant ?
19. Write balanced equations for the following :
- (i) NaCl is heated with sulphuric acid in presence of  $MnO_2$ .
- (ii) Chlorine gas is passed into a solution of NaI in water.

[Answers : (1) Sulphur occurs in the earth's crust in the combined state primary in form of sulphates and sulphides. As sulphates : Gypsum,  $CaSO_4 \cdot 2H_2O$ ; Epsom salt,  $MgSO_4 \cdot 7H_2O$ ; Baryte,  $BaSO_4$ , etc. As sulphides : Galena,  $PbS$ ; Zinc blende,  $ZnS$ ; Copper pyrites,  $CuFeS_2$ ; Iron pyrites,  $FeS_2$ , etc. Traces of sulphur occur as  $H_2S$  and in organic matter such as eggs, proteins, garlic, onion, mustard hair and wool. (2) As the size of the element increases down the group, the E — H (E stands for element of Group 16) bond dissociation energy decreases and hence E — H bond breaks more easily. Thus, the thermal stability of the hydrides of Group 16 elements decreases down the Group :

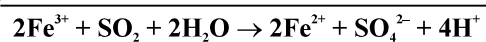
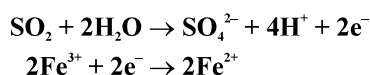
$H_2O > H_2S > H_2Se > H_2Te > H_2Po$ . (3) Due to greater electronegativity of O than S,  $H_2O$  undergoes extensive intermolecular H-bonding. As a result,  $H_2O$  exists as an associated,  $H_2O$  is a liquid at room temperature.



. In contrast,  $H_2S$  does not undergo H-bonding as the electronegativity difference between H and S is not appreciable. It exists as discrete molecules which are held together by weak van der Waals' forces of attraction. To break these forces of attraction, only a small amount of energy is required. Therefore,  $H_2S$  is a gas at room temperature. (4) Platinum is a noble metal. Its ionisation enthalpy is very large. Therefore, it does not react with oxygen directly. In contrast, Zn, Ti and Fe are active metals and hence, directly react with oxygen to form their respective oxides.  $Zn + O_2 \rightarrow ZnO_2$ ,  $Ti + O_2 \rightarrow TiO_2$ ,  $4Fe + 3O_2 \rightarrow 2Fe_2O_3$  (5) (i)  $C_2H_4$  undergoes combustion to form  $CO_2$  and  $H_2O$ .  $C_2H_4 + 3O_2 \xrightarrow{\text{Heat}} 2CO_2 + 2H_2O$ . (ii) Al combines with  $O_2$  to form alumina.  $4Al + 3O_2 \xrightarrow{\text{Heat}} 2Al_2O_3$  (6)  $O_3$  is an endothermic compound i.e., it possesses greater internal energy than oxygen. On heating, it readily decomposes to give dioxygen and nascent oxygen.  $O_3 \xrightarrow{\text{Heat}} O_2 + O$  (nascent oxygen). (7) When  $O_3$  is treated with excess of KI solution buffered with borate buffer (pH 9.2),  $I_2$  is liberated quantitatively, according to the following equation :

$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$ . The  $I_2$  thus liberated is titrated against a standard solution of sodium thiosulphate using starch as an indicator.

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$  (8)  $SO_2$  acts as a reducing agent and reduces an aqueous solution of Fe(III) salt to Fe(II) salt, given by the following equation :



(9) In the structure of  $SO_2$ , S is  $sp^2$ -hybridised. Two of the three  $sp^2$ -orbitals form two  $\sigma$ -bonds while the third contains the lone pair of electrons (10)  $SO_2$  is a pungent smelling gas. Following two sets tests can be performed to detect  $SO_2$ . (i)  $SO_2$  turns the pink violet colour of  $KMnO_4$  solution to colourless due to reduction of  $MnO_4^-$  to  $Mn^{2+}$  ions.

$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$  (ii)  $SO_2$  turns acidified  $K_2Cr_2O_7$  solution (pink violet) (colourless)

green due to reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$  ions.  $\text{Cr}_2\text{O}_7^{2-} + 3\text{SO}_2 + 2\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + \text{H}_2\text{O}$  (11)

(orange)  (green)

(i) It is used as an electrolyte in storage batteries. (ii) It is used in petroleum refining, detergent industry and in the manufacture of paints, pigments and dyes. (iii)  $\text{H}_2\text{SO}_4$  is used in the manufacture of fertilizers such as ammonium sulphate, calcium superphosphate. (12) The main step in the preparation of  $\text{H}_2\text{SO}_4$  is the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .

$\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}); \Delta_f H^\circ = -196.6 \text{ kJ mol}^{-1}$ . The reaction is exothermic and reversible. The forward reaction proceeds with decrease in volume. Therefore, in accordance with Le Chatelier's principle, to maximise the yield of  $\text{SO}_3$ , a low temperature (720 K), a high pressure (2 bar) are required.  $\text{V}_2\text{O}_5$  is used as a catalyst. (13) This is because the negatively charged  $\text{HSO}_4^-$  ion has much less tendency to donate a proton to  $\text{H}_2\text{O}$  as compared to neutral  $\text{H}_2\text{SO}_4$ . (15) Consider the reaction of a divalent metal (M) with oxygen. The formation of  $\text{M}_2\text{O}$  and  $\text{MO}$  involves the following steps :

$\text{M}(\text{g}) \xrightarrow{\Delta_f H_1} \text{M}^+(\text{g}) \xrightarrow{\Delta_f H_2} \text{M}^{2+}(\text{g})$ .  $\Delta_f H_1$  and  $\Delta_f H_2$  are first and second ionisation enthalpies of the metal M.  $\text{O}(\text{g}) \xrightarrow{\Delta_{eg} H_1} \text{O}^-(\text{g}) \xrightarrow{\Delta_{eg} H_2} \text{O}^{2-}(\text{g})$ .  $\Delta_{eg} H_1$  and  $\Delta_{eg} H_2$  are first and second electron

gain enthalpies.  $2\text{M}^+(\text{g}) + \text{O}^-(\text{g}) \xrightarrow{\text{Lattice energy}} \text{M}_2\text{O}(\text{s})$ ,  $\text{M}^{2+}(\text{g}) + \text{O}_2^-(\text{g}) \xrightarrow{\text{Lattice energy}} \text{MO}(\text{s})$ .

Although  $\Delta_f H_2$  is much more than  $\Delta_f H_1$  and  $\Delta_{eg} H_2$  is much higher than  $\Delta_{eg} H_1$ , yet the lattice energy of formation of  $\text{MO}(\text{s})$  due to higher charges is much more than that of  $\text{M}_2\text{O}(\text{s})$ . In other words, formation  $\text{MO}(\text{s})$  is energetically more favourable than  $\text{M}_2\text{O}(\text{s})$ . It is due to this reason that oxygen forms preferably oxides having the  $\text{O}^{2-}$  species and not  $\text{O}^-$ . (16) Aerosols such as chlorofluorocarbons (CFC's), for example, freon ( $\text{CCl}_2\text{F}_2$ ) depletes the  $\text{O}_3$  layer by supplying Cl free radicals which convert  $\text{O}_3$  to

$\text{O}_2$  in the following sequence of reactions :  $\text{Cl}_2\text{CF}_2(\text{g}) \xrightarrow{h\nu} \bullet\text{Cl}(\text{g}) + \bullet\text{CClF}_2(\text{g})$ ,  
Freon

$\bullet\text{Cl}(\text{g}) + \text{O}_3(\text{g}) \longrightarrow \text{ClO}\bullet(\text{g}) + \text{O}_2(\text{g})$ ,

$\text{ClO}\bullet(\text{g}) \longrightarrow \text{Cl}\bullet(\text{g}) + \bullet\text{O}(\text{g})$ ,  $\text{ClO}\bullet(\text{g}) + \bullet\text{O}(\text{g}) \longrightarrow \bullet\text{Cl}(\text{g}) + \text{O}_2(\text{g})$  (18) (i)  $\text{SO}_2$  is strongly irritating to the respiratory tract.  $\text{SO}_2$  at a concentration of 5 ppm causes throat and eye irritation causing cough, tears and redness in eyes. It causes breathlessness and affects larynx, i.e., voice box. (ii) Even at low concentration, it has a damaging effect on the plants. If exposed for a long time, it slows down the formation of chlorophyll resulting in injury to the leaves including loss of green colour. This is called chlorosis. (iii)  $\text{SO}_2$  dissolves in rainwater and produces acid rain which damages building materials especially marble ( $\text{CaCO}_3$ ).  $\text{CaCO}_3 + \text{H}_2\text{SO}_3 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} + \text{CO}_2$ . (iv) It corrodes metals particularly iron and steel. It also deteriorates fabrics, leather, paper, etc., and effects the colour of paints.]

### C3A Group 17 (Halogen family) (Salt producing)

#### General properties

$ns^2p^5$

F – $[\text{He}]2s^22p^5$	$\text{F}_2(\text{g})$ Pale yellow
Cl – $[\text{Ne}]3s^23p^5$	$\text{Cl}_2(\text{g})$ greenish yellow
Br – $[\text{Ar}]3d^{10}4s^24p^5$	$\text{Br}_2(\text{l})$ reddish brown
I – $[\text{Kr}]4f^{14}5s^25p^5$	$\text{I}_2(\text{s})$ violet vapours

At → Radioactive element

**Physical State :** Diatomic  $\text{F}_2$ ,  $\text{Cl}_2$  are gases,  $\text{Br}_2$  is liquid and  $\text{I}_2$  is solid because of increase of atomic size and increase of vander waal's interaction.

**Colour :** The colour of the halogen is due to absorption of visible light molecules resulting in the excitation of outer electron to higher energy levels. F has smaller size so high excitation energy light (violet light) is required to excite the  $e^-$  and shows reflected complementary pale yellow light while I due to large size low excitation energy yellow light absorbs and ∴ appears violet black. In between the colour of Cl is yellowish-green and Br is reddish brown i.e., in the group the size increases low excitation energy is required and hence dark colour. Thus the colour deepens down the group.

**Bond dissociation energy :**  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

$\text{F}_2$  bond dissociation energy is smaller than  $\text{Cl}_2$  because of large electronic repulsions of lone pair - lone pair e<sup>-</sup>s and i.e. due to small size of F ∴ e<sup>-</sup>s are much closer to each other. B.D.E. decrease from  $\text{Br}_2$  to  $\text{I}_2$  due to large bond length.

**Atomic Size :** Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.

**Electron gain enthalpy :** Halogens have maximum EGE because they have one electron less than stable noble gas configuration i.e. they have strong tendency to accept the electron.

EGE ↓ down the group because of increase of atomic size

**F :**  $\Delta H_{\text{eg}}$  is lower than Cl because of small size e<sup>-</sup> - e<sup>-</sup> repulsion occurs in 2p-compact subshell and the added e<sup>-</sup> does not feel much attraction resulting in low value of  $\Delta H_{\text{eg}}$ .

**EN :** Halogens are highly EN and EN decreases down the group because of decrease of effective nuclear charge.

**Melting and Boiling Point :** Increases downing the group because of ↑ of atomic size and hence ↑ of van der Waals' interaction.

<b>Oxidation State :</b> F	-1
Cl	-1, +1, +3, +5, +7
Br	-1, +1, +3, +5, +7
I	-1, +1, +3, +5, +7

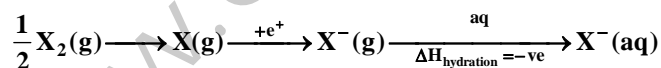
- F only shows -1 o.s. not positive o.s. because F is most EN.
- F not shows higher o.s. because of absence of d-orbitals.
- 1 o.s. is common for all elements because of high EN.
- Cl to Br all show +1 to +7 o.s. because of vacant d-orbitals.

**C3B Nature of bonds with other elements :** Halogens combine with metal to form predominantly ionic halides. This halides ionic character decreased down the group while covalent character increases because of decrease of EN and increase of halogen size and hence polarizability increases and covalent character increases. e.g.

- Increasing order of ionic character of metal halide :  $\text{M} - \text{I} < \text{M} - \text{Br} < \text{M} - \text{Cl} < \text{M} - \text{F}$  (M = Na, K etc.)
- $\text{AlF}_3$  is ionic while  $\text{AlCl}_3$ ,  $\text{AlBr}_3$  are covalent.
- Higher o.s. of metal and non-metals halides are covalent but polar and this polarity ↓ down the group.

**Oxidising Power :** Halogens act as strong oxidising agent because of high electron affinity that they have strong tendency to accept the e<sup>-</sup>s. The O.A. tendency decreases down the group from F to I. i.e.,  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .

$\text{F}_2$  is a better oxidising agent than  $\text{Cl}_2$  although its electron affinity is less than that of  $\text{Cl}_2$  because of high reduction electrode potential value of  $\text{F}_2$  and  $\text{Cl}_2$ .



$$; \frac{1}{2} \Delta H_{\text{dissociation}} = +ve$$

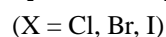
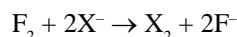
$$\Delta H_{\text{gain enthalpy}} = -ve$$

$$E_0 = \frac{1}{2} \Delta H_{\text{dissociation}} + \Delta H_{\text{gain enthalpy}} + \Delta H_{\text{hydration}}$$

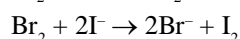
$\text{F}_2 \rightarrow$  B.D.E. ( $\frac{1}{2} \Delta H_{\text{dissociation}}$ ) is less than of  $\text{Cl}_2$

$\text{F}_2 \rightarrow \Delta H_{\text{eg}}$

$F_2 \rightarrow \Delta H_{\text{hydration}}$  is higher than  $Cl_2$  due to small size and high charge density of  $F^-$  ion. Thus the net energy released for  $\frac{1}{2} F_2(g) \rightarrow F^-(aq)$  is  $-752$  kJ whereas  $\frac{1}{2} Cl_2(g) \rightarrow Cl^-(aq)$  is  $-708$  kJ which accounts for higher oxidising power of  $F_2$ .



**Reactivity :** All the halogens are very reactive but  $F_2$  is most reactive because of high Electronegativity decreases moving down in the group, the reactivity decreases because decrease of EN.  $F_2 > Cl_2 > Br_2 > I_2$  (reactivity order)



**Hydrides :**  $H - F, H - Cl, H - Br, H - I$

**Thermal Stability :**  $H - F > H - Cl > H - Br > H - I$

**Reducing Character :**  $H - F < H - Cl < H - Br < H - I$

**Acid Strength :**  $HF < HCl < HBr < HI$

because of increase of X size and increases M – H bond length and decrease of B.D.E. and hence easily gives  $H^+$  ion.

**B.P. :**  $HF > HI > HBr > HCl$  [ $HF$  : intermolecular H-bond,  $HI > HBr > HCl$  : Vander waal's forces]

**% ionic character :**  $HF > HCl > HBr > HI$

**Dipole moment :**  $HF > HCl > HBr > HI$  [ $HF$  : electronegative]

**Oxides :** Halogens form many oxides with oxygen but most of them are unstable.

- (i)  $F_2$  forms two oxides  $OF_2$  and  $O_2F_2$  in which  $OF_2$  is thermally stable at room temperature. These are called oxygen fluorides because of the higher electronegativity of F then oxygen. Both are strong fluorinating agents.
- (ii)  $Cl, Br, I$  form oxides of o.s. from +1 to +7. The kinetics and thermodynamic stability oxides formed by halogen order is  $I > Br > Cl$ . The higher oxides are more stable than lower.
- (iii)  $Cl$  oxides :  $Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7$
- (iv)  $Br$  oxides :  $Br_2O, BrO_2, BrO_3$  least stable halogen oxides and exist only at low temperature and powerful oxidising agent.
- (v)  $I$  oxides :  $I_2O_4, I_2O_5, I_2O_7$  are insoluble solid and decompose on heating.  $I_2O_5$  is a very good oxidising agents and used for estimation of  $CO$ .

**Reactivity with Metals :** Halogens react with metals to form metal halides  $Mg + Br_2 \rightarrow MgBr_2$

**Ionic Character :**  $MF > MCl > MBr > MI$

**Covalent Character :** Halides in higher oxidation state will be more covalent than lower o.s.

e.g.,  $SnCl_4, PbCl_4, SbCl_5, UF_6$  more covalent than  $SnCl_2, PbCl_2, SbCl_3, UF_4$ .

**Halides :** Interhalogens compounds : Binary compounds of two different halogen of general formula  $XX'n$  are called interhalogen compounds (where  $n = 1, 3, 5, 7$ )

– The larger halogen atom is the central atom. All are covalent

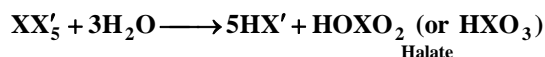
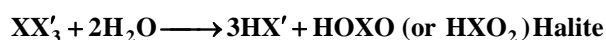
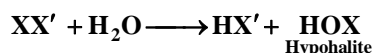
– Interhalogens compounds are more reactive than halogens because  $X - X'$  is more polar bond and weaker than  $X - X$  bonds.

$\mathbf{XX}'(\text{sp}^3)$	$\mathbf{XX}_3(\text{sp}^3\text{d})$	$\mathbf{XX}_5(\text{sp}^3\text{d}^2)$	$\mathbf{XX}'_7(\text{sp}^3\text{d}^3)$
ClF, BrF, ClF <sub>3</sub> , BrF <sub>3</sub>	BrF <sub>3</sub> , ClF <sub>5</sub>	IF <sub>7</sub>	
IF, BrCl, ICl	IF <sub>3</sub> , ICl <sub>3</sub>	IF <sub>5</sub>	
<b>Shape :</b> Linear	T-shape	Square pyramidal	Pentagonal bipyramidal

X = large size and more electropositive halogen

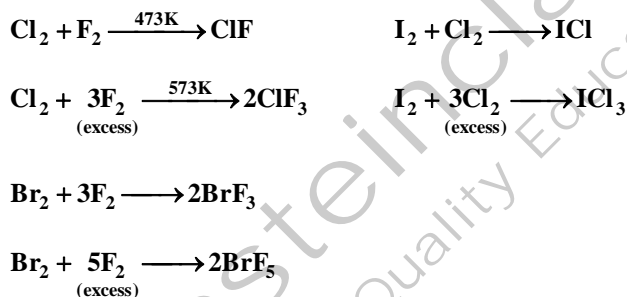
X' = smaller size and more electronegative halogen.

- I only shows higher halogens fluorides i.e. IF<sub>7</sub>. All are covalent, diamagnetic in nature. They are volatile solids or liquids except ClF which is gas. Melting point higher than halogens.
- All these undergoes hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (XX'), halite (XX<sub>3</sub>'), halate (XX<sub>5</sub>') and perhalate (XX<sub>7</sub>').



**Shapes :** on the basis of VSEPR theory

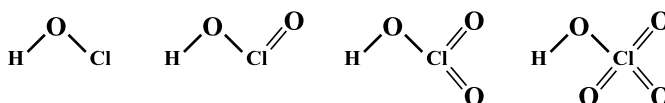
**Preparation of bond interhalogens compounds** can be prepared by the direct combination of halogen



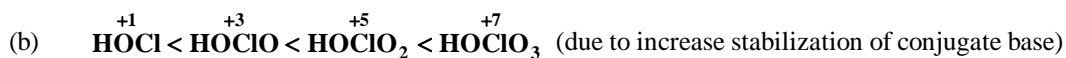
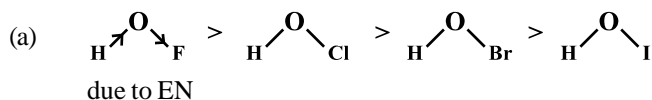
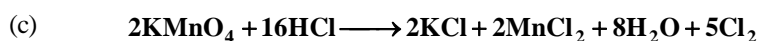
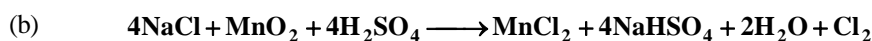
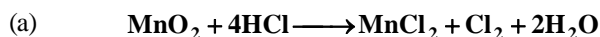
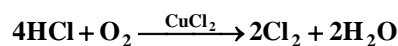
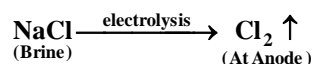
**Oxoacids :**

Due to high EN and small size, F forms only one oxoacids i.e. HOF.

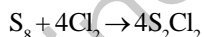
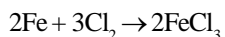
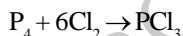
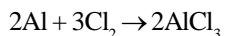
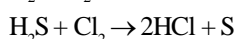
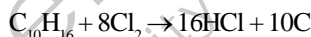
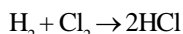
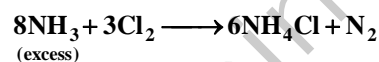
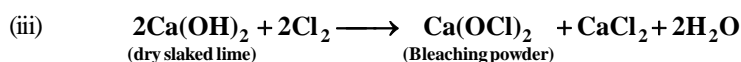
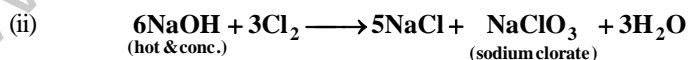
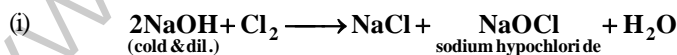
<b>Halic (I) acid</b> (Hypohalous acid)	<b>HOF</b>	<b>HOCl</b> (Hypochlorous acid)	<b>HOBr</b>	<b>HOI</b>
Halic (III) acid (Halous acid)	–	HOCIO (Chlorous acid)	–	–
Halic (V) acid (Halic acid)	–	HOCIO <sub>2</sub> (Chloric acid)	HOBrO <sub>2</sub>	HOIO <sub>2</sub>
Halic (VII) acid (Perhalic acid)	–	HOCIO <sub>3</sub> (Perchloric acid)	HOBrO <sub>3</sub>	HOIO <sub>3</sub>



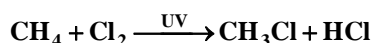


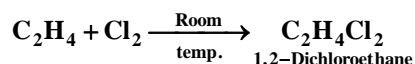
**Acidic Strength Order :****Chlorine (Cl<sub>2</sub>) :****Preparation :****(1) Lab preparation :****(2) Deacon's Process :****(3) Electrolytic Process :****Properties :**

It is a greenish yellow gas with pungent and suffocating odour.

**(a) Reaction with metals and non-metals :** to form chlorides**(b) Reacts with hydrogen :****(c) Reaction with Ammonia :****(d) Reaction with alkali :**

The composition of bleaching powder is  $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$

**(iv) with hydrocarbons :**



(v) with water :



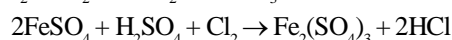
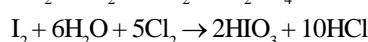
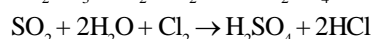
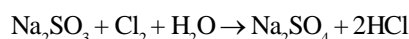
due to nascent oxygen it is responsible for oxidising and bleaching properties of chlorine.

$\text{Cl}_2$  is a powerful bleaching agent; bleaching action is due to oxidation.

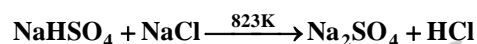
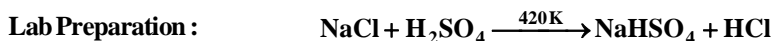
Coloured substance + O → Colourless substance

Bleaching effect of  $\text{Cl}_2$  is permanent.

**Oxidising Agent :**



**HCl (Hydrogen Chloride)**



HCl gas can be dried by passing through concentrated  $\text{H}_2\text{SO}_4$ .

**Properties :**

- (i) It is colourless, pungent smelling gas and easily liquified to colourless liquid and extremely soluble in water and ionizes as  $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$  [ $K_a = 10^7$ ]
- (ii) It's aqueous solution is called hydrochloric acid. High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid.
- (iii)  $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$  (white fumes)
- (iv) Aqua regia → 3 parts of HCl + 1 part of  $\text{HNO}_3$  and used for dissolving noble metals like Au, Pt.  
 $\text{Au} + 4\text{H}^+ + \text{NO}_3^- + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + \text{NO} + 2\text{H}_2\text{O}$   
 $3\text{Pt} + 16\text{H}^+ + 4\text{NO}_3^- + 18\text{Cl}^- \rightarrow 3\text{PtCl}_6^{2-} + 4\text{NO} + 8\text{H}_2\text{O}$
- (v)  $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$   
 $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$   
 $\text{Na}_2\text{SO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2$
- (vi)  $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$

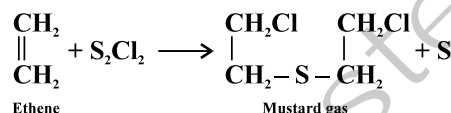
**Practice Problems :**

1. Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of  $\text{F}_2$  and  $\text{Cl}_2$ .
2. Give two examples to show the anomalous behaviour of fluorine.
3. Sea is the greatest source of some halogens. Comment.
4. Give the reason for bleaching action of  $\text{Cl}_2$ .
5. Name two poisonous gases which can be prepared from chloride gas.
6. Why is ICl more reactive than  $\text{I}_2$  ?
7. Why are halogens strong oxidising agents ?
8. Explain why fluorine forms only one oxoacid, HOF.
9. Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.
10. Write two uses of  $\text{ClO}_2$ .

11. Why are halogens coloured ?
12. Write the reactions of  $F_2$  and  $Cl_2$  with water.
13. How can you prepare  $Cl_2$  from  $HCl$  and  $HCl$  from  $Cl_2$  ? Write reactions only.
14. With what neutral molecule is  $ClO^-$  isoelectronic ? Is that molecule a Lewis base ?
15. Arrange the following in the order of property indicated for each set :
  - (i)  $F_2, Cl_2, Br_2, I_2$ , – increasing bond dissociation enthalpy.
  - (ii)  $HF, HCl, HBr, HI$  – increasing acid strength.
  - (iii)  $NH_3, PH_3, AsH_3, SbH_3, BiH_3$  – increasing base strength.
16. Give the formula and describe the structure of a noble gas species which is isostructural with :
  - (i)  $ICl_4^-$
  - (ii)  $IBr_2^-$
  - (iii)  $BrO_3^-$

[Answers : (2) (i) Fluorine exhibits only  $-1$  oxidation state whereas other halogens exhibit  $+1, +3, +5$  and  $+7$  oxidation states also. The m.p and b.p of hydrogen halides follow the order :  $HF > HCl < HBr < HI$ . (ii) The anomalous behaviour of fluorine is due to its (i) small size, (ii) highest electronegativity. (3) Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but the main constituents is sodium chloride (2.5% by mass). Dried up sea beds contain sodium chloride and carnallite,  $KCl.MgCl_2.6H_2O$ . Certain seaweeds contain up to 0.5% of iodine as sodium iodide and chile saltpetre ( $NaNO_3$ ) contains up to 0.2% of sodium iodate. Thus, sea is the greatest source of halogens. (4) In presence of moisture or in aqueous solution,  $Cl_2$  liberates nascent oxygen.  $Cl_2 + H_2O \longrightarrow 2HCl + \underset{\text{Nascent oxygen}}{[O]}$ . This nascent oxygen brings about the oxidation of

coloured substances present in vegetable and organic matter to convert them to colourless substances. Coloured substance + O  $\rightarrow$  Colourless substance. Thus, the bleaching action of  $Cl_2$  is due to oxidation. (5) Two poisonous gases which can be prepared from  $Cl_2$  are : (i) Phosgene (ii) Mustard gas. These are prepared as follows : (i)  $CO + Cl_2 \xrightarrow{\text{hvcharcol}} COCl_2$  (ii)  $Cl_2$  is passed through boiling S, when  $S_2Cl_2$  is formed. This on reaction with ethene gives mustard gas.



than  $I-I$  bond. A bond between two different atoms is always weaker than that between identical atoms. Consequently,  $ICl$  breaks easily to form halogen atoms which readily bring about the reactions. (7) Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.  $X + e^- \rightarrow X^-$ . In other words, halogens act as strong oxidising agents. (8) This is due to limitation of having only one oxidation state that it forms only one oxo acid. Chlorine, bromine and iodine form four series of oxoacids of the general formula  $HOX, HOXO, HOXO_2$  and  $HOXO_3$  in which the oxidation states of halogen ( $X = Cl, Br$  or  $I$ ) is  $+1, +3, +5$  and  $+7$ , respectively. However, due to high electronegativity and small size, fluorine forms only  $HOF$  with oxidation state  $+1$ . (9) Although  $O$  and  $Cl$  have about the same electronegativity, yet their atomic size (covalent radii) are much different with radius of oxygen being 66 pm and that of chlorine being 99 pm. As a result, electron density per unit volume on oxygen atom is much higher than that on chlorine atom. Therefore, oxygen forms hydrogen bonds while chlorine does not even though both have approximate, the same electronegativity. (10) (i) It is an excellent bleaching agent. Its bleaching power is about 30 times higher than that of  $Cl_2$ . It is used for bleaching flour to make white bread. (ii)  $ClO_2$  is a powerful oxidising agent and chlorinating agent. Large quantities of  $ClO_2$  are used for bleaching wood pulp and cellulose and for purifying drinking water. (14)  $ClO^-$  has  $17 + 8 + 1 = 26$  electrons. A neutral molecule with 26 electrons is  $OF_2$  ( $8 + 2 \times 9 = 26$  electrons).  $OF_2$  is a Lewis base due to the presence of two lone pairs of electrons.]

## C4 Group - 18 (Noble Gases)

**He, Ne, Ar, Kr, Xe, Rn** (Radioactive)  
 $1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10} 4s^2 4p^6, 4d^{10} 5s^2 5p^6, 4f^{14} 5d^{10} 6s^2 6p^6$

He, Ne, Ar → no compound known

Kr → only few compounds known (KrF<sub>2</sub>)

Xe → many compounds

Rn → identical but not isolated

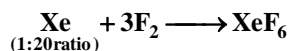
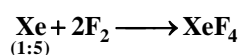
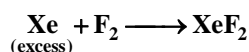
The elements of group 18 known as noble gases because their valence shell orbitals completely filled and ∴ react with a few elements only under certain conditions. Therefore they are known as noble gases.

- (i) **General Electronic Configuration** :  $ns^2 np^6$  except He =  $1s^2$
- (ii) **I.E.** : (a) Due to stable (fully filled) configuration the I.E. very high. (b) down the group I.E. decreases because of increase of atomic size.
- (iii) **Atomic radii** : down the group increases because ↑ in atomic number of shells.
- (iv) **E.G.E.** : They have large positive EGE values because of stable electronic configuration, they have no tendency to accept the electron.
- (v) **m.p. and b.p.** : low because of weak dispersion forces.

B.P. are low of noble gases because noble gases being monoatomic have no inter atomic forces except weak dispersion forces and hence can be liquified at very low temp. and have low B.P.

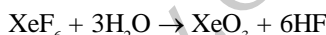
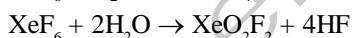
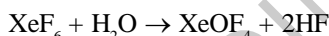
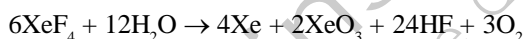
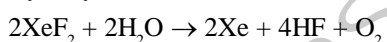
Ist compound of noble gas is Xe<sup>+</sup> [PtF<sub>6</sub>]<sup>-</sup> be neil Bartlett.

**Xenon-fluorine compounds :**

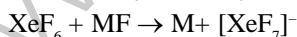
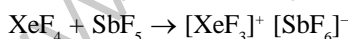


**Properties :**

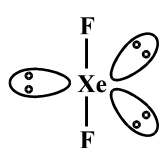
- (i) Xe-Fluorine are powerful fluorinating agent.
- (ii) Hydrolysis :



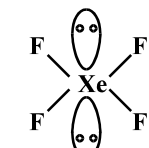
**Complete Hydrolysis :**



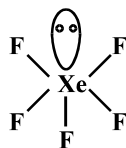
**Structure of Fluorides :**



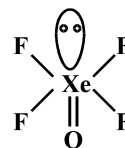
(Linear)  
(XeF<sub>2</sub>)



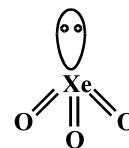
(Square planar)  
(XeF<sub>4</sub>)



(Distorted Octahedral)  
(XeF<sub>6</sub>)



(Square Pyramidal)  
(XeOF<sub>4</sub>)



(Pyramidal)  
(XeO<sub>3</sub>)

**Practice Problems :**

- Why is helium used in diving apparatus ?
- Balance the following equation :  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + \text{HF}$ .
- Why has it been difficult to study the chemistry of radon ?
- What inspired N. Bartlett for carrying out reaction between Xe and  $\text{PtF}_6$  ?
- How are xenon fluorides  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  obtained ?
- How are  $\text{XeO}_3$  and  $\text{XeOF}_4$  prepared ?
- Which one of the following does not exist ?
  - $\text{XeOF}_4$
  - $\text{NeF}_2$
  - $\text{XeF}_4$
  - $\text{XeF}_6$

[Answers : (1) Because of its low solubility (as compared to  $\text{N}_2$ ) in blood, a mixture of oxygen and helium is used in diving kit used by deep sea divers. (2)  $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$  (3) This is because radon is a radioactive element with a short life of 3.82 days. This makes the study of chemistry of radon difficult. (4) Neil Bartlett observed that  $\text{PtF}_6$  reacts with  $\text{O}_2$  to yield an ionic solid,  $\text{O}_2^+$ ,  $\text{PtF}_6^-$ .  $\text{O}_2(\text{g}) + \text{PtF}_6(\text{g}) \rightarrow \text{O}_2^+[\text{PtF}_6]^-$ . In this reaction,  $\text{O}_2$  gets oxidised to  $\text{O}_2^+$  by  $\text{PtF}_6$ . He thought since the first ionisation enthalpy of Xe is lower than that of  $\text{O}_2$ , Xe should be oxidised to  $\text{Xe}^+$  by  $\text{PtF}_6$ . This inspired Bartlett to carry out the reaction between Xe and  $\text{PtF}_6$ . When Xe and  $\text{PtF}_6$  were mixed, actually a rapid reaction took place and a red solid with a formula,  $\text{Xe}^+[\text{PtF}_6]^-$  was obtained.

$\text{Xe} + \text{PtF}_6 \xrightarrow{278\text{K}} \text{Xe}^+[\text{PtF}_6]^-$  (7) The ionisation enthalpy of Ne is much higher than that of Xe. As a result,  $\text{F}_2$  can oxidise Xe to  $\text{Xe}^{2+}$  but cannot oxidise Ne to  $\text{Ne}^{2+}$ . Thus,  $\text{NeF}_2$  does not exist. In contrast, all the xenon fluorides ( $\text{XeF}_4$  and  $\text{XeF}_6$ ) and xenon oxyfluoride ( $\text{XeOF}_4$ ) do exist. This is because ionisation enthalpy of Xe is not very high. It is compensated by electron gain enthalpy of F.]