



## LESSON AT A GLANCE

- **p-block elements:** The elements of groups 13 to 18 are known as p-block elements. These elements have 3, 4, 5, 6, 7 and 8 electron in their outer shell respectively. Their general electronic configuration is  $ns^2np^{1-6}$
- **Group 15 elements:** Consist of five elements namely; N, P, As, Sb and Bi. Their general electronic configuration is  $ns^2np^3$ .
- Dinitrogen forms oxides in various oxidation states such as  $N_2O$ , NO,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$  and  $N_2O_5$ . These oxides have resonating structures and multiple bonds.
- **Ammonia** prepared by Haber's process.
- $HNO_3$ —powerful oxidising agent.
- **Maximum Oxidation State:** +6.
- **Dioxygen:** Prepared by heating  $KClO_3$  in presence of  $MnO_2$ .
- $O_3$ : Allotropic form of oxygen.
- Group 17 elements consist of F, Cl, Br, I and At. They are extremely reactive elements.
- Group 17 elements are found in combined state only. Common oxidation state -1. Highest oxidation state can be +7. They form oxides, hydrogen halides, inter halogen compounds and oxoacids.
- Group 18 elements consist of noble gases—He, Ne, Ar, Kr, Xe, Rn. Electronic configuration  $ns^2np^6$ . He (Helium) has electronic configuration— $1s^2$ .
- All gases except Rn occur in atmosphere.
- **Group 15:** The elements of nitrogen family are nitrogen (N), Phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi).

- **Nitrogen:** The first member of this group, *i.e.* nitrogen occurs as a diatomic gas  $N_2$ . It makes about 78 % by volume of the atmosphere. It mainly occurs as nitrates, *i.e.*  $NaNO_3$  (Chile saltpetre) and  $KNO_3$  (Indian saltpetre). Nitrogen is essential component of proteins, amino acids and nucleic acids.
- **Phosphorus:** Phosphorus is the second member of the nitrogen family, *i.e.*, elements the group 15 of the periodic table.
- **Arsenic, Antimony and Bismuth:** *Arsenic* mainly occurs as sulphides, symbol *As*. A metalloid element of group V of the periodic table.

Ores are roasted in air to form arsenic oxide and then reduces by hydrogen or carbon to metallic arsenic.

*Antimony* is an element belonging to group VA of the periodic table. It has several allotropes. Symbol is *Sb*. The main source is stibnite ( $Sb_2S_3$ ).

Bismuth is a white crystalline metal with a pinkish tinge belonging to group V of the periodic table. Symbol is *Bi*. The most important ores are bismuthinite ( $Bi_2S_3$ ) and bismite ( $Bi_2O_3$ ).

- **Electronic Configuration:** The general shell electronic configuration of the elements of group 15 is  $ns^2np^3$

where  $n = 2$  to  $6$

The *S* orbital is completely filled and the *P* orbitals are half filled.

- **Electronegativity:** Group 15 elements are more electronegative than group 14 elements. Electronegativity of elements of group 15 shows a gradual decrease on moving down the group from N to Bi.
- **Group 16 Elements—Oxygen Family:** Group 16 of the periodic table consists of five elements: Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po). The elements of this group are commonly known as the oxygen family. These are also called chalcogens or ore forming elements because many metal ores occur as oxides and sulphides.

## TEXTBOOK QUESTIONS SOLVED

**7.1** Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.

**Ans.** Electronic configuration:  $ns^2np^3$ .

**Oxidation state:** +3, +5, -3 tendency to show -3 oxidation state decreases down the group.

**Atomic size:** It goes on increasing down the group due to increase in number of shells.

**Ionisation enthalpy:** It goes on decreasing down the group because atomic size goes on increasing.

**Electronegativity:** It goes on decreasing down the group as the atomic size increases.

**7.2** Why does the reactivity of nitrogen differ from phosphorus?

**Ans.** Nitrogen exists as a diatomic molecule ( $N \equiv N$ ). Due to the presence of a triple bond between the two N - atoms the bond dissociation energy is large ( $941.4 \text{ kJ mol}^{-1}$ ). As a result nitrogen is said to be chemical inert in its elemental state. In contrast P - P single bond is much weaker ( $213 \text{ kJ mol}^{-1}$ ) than  $N \equiv N$  bond therefore, Phosphorus is much more reactive than nitrogen.

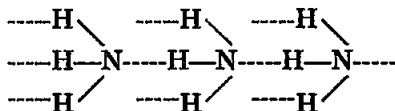
**7.3** Discuss the trends in chemical reactivity of group 15 elements.

**Ans.** Reactivity increases down the group due to increase in atomic size and decrease in ionisation energy. e.g., Nitrogen is least reactive at room temperature whereas white Phosphorus is more reactive. Among As, Sb and Bi, also reactivity increases due to decrease in ionisation energy and increase in electro positive character.

**7.4** Why does  $NH_3$  form hydrogen bond but  $PH_3$  does not?

**Ans.** The electronegativity of N is 3.0 and that of hydrogen 2.1. This difference in electronegativity values makes N-H bond

$\delta^- \quad \delta^+$   
polar (N-H) in  $NH_3$ . Because of these polar bonds  $NH_3$  forms intermolecular hydrogen bonds as:

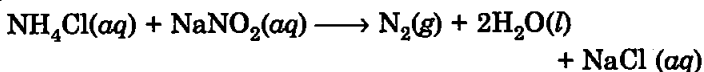


$\text{NH}_3$  molecule behaves as a dipole  $\overset{\delta-}{\text{N}}\overset{\delta+}{\text{H}_3}$

In the case of  $\text{PH}_3$ , P-H bonds are non-polar because both P and H have same value of electronegativity (2.1). Hence,  $\text{PH}_3$  does not form hydrogen bonds.

**7.5** How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

**Ans.** In the laboratory, nitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

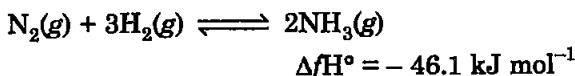


Small amounts of NO and  $\text{HNO}_3$  are also formed in this reaction, these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

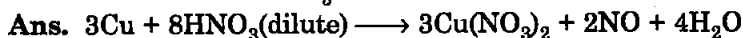
**7.6** How is ammonia manufactured industrially?

**Ans.** Ammonia is manufactured by Haber's process.

$\text{N}_2$  and  $\text{H}_2$  in presence of iron oxide mixed with  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  as catalyst at 700 K and high pressure  $20 \times 10^8$  Pa or 200 atm.

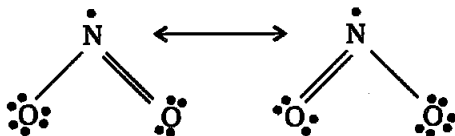


**7.7** Illustrate how copper metal can give different products on reaction with  $\text{HNO}_3$ .

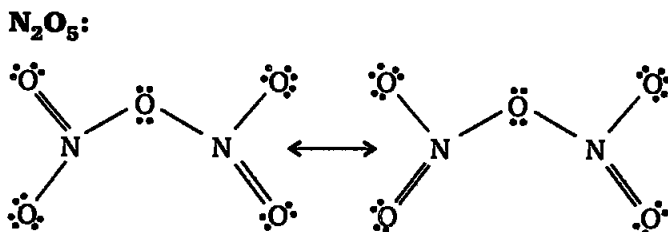


**7.8** Give the resonating structures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$ .

**Ans.**  $\text{NO}_2$ :



Resonating structure



Resonating structure

**7.9** The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

**Ans.** It is because 'N' is smaller in size and N-H bond is most polar than  $sp^3$  hybridised whereas in others these in  $s-p$  bonding polarity is higher in  $NH_3$  than in other hydrides.

**7.10** Why does  $R_3P = O$  exist but  $R_3N = O$  does not ( $R = \text{alkyl group}$ )?

**Ans.**  $R_3N=O$  molecule has five covalent bonds and for this situation N atom must expand its octet. The octet in N cannot be expanded as it does not have  $d$  orbitals for a formation of  $p\pi-d\pi$  bond. In the case of  $R_3P=O$ , P can expand its octet since it has  $d$ -orbitals in its valence shell and forms  $p\pi-d\pi$  bond. Hence  $R_3P = O$  can exist.

**7.11** Explain why  $NH_3$  is basic while  $BiH_3$  is only feebly basic.

**Ans.** Lewis basic nature of  $NH_3$  and  $BiH_3$  molecules is due to the presence of lone pairs on N and Bi atoms, respectively. Bi atom is much larger than N atom and also has empty  $d$  orbitals. Electron density due to lone pair on Bi gets defused because of the presence of  $d$  orbitals and so the lone pair is not easily available for donation. Hence  $BiH_3$  is less basic than  $NH_3$ .

**7.12** Nitrogen exists as diatomic molecule and phosphorus as  $P_4$ . Why?

**Ans.** Because of small size, high electronegativity and the presence of strong  $p\pi-p\pi$  multiple bonds, nitrogen exists as  $N_2$  molecule. These factors make the bond dissociation enthalpy of  $N_2$  molecule very high ( $941.4 \text{ kJ mol}^{-1}$ ). Also, because of these parameters catenation in nitrogen is prevented.

On the contrary, bigger phosphorus atoms do not form strong  $p\pi-p\pi$  multiple bond and also the electronegativity of P is much less than N.

However, single N–N bond is much weaker ( $160 \text{ kJ mol}^{-1}$ ) than that of P–P single bond ( $200 \text{ kJ mol}^{-1}$ ).

Hence, for nitrogen a tripple bond is preferred as it has more than 3 times the enthalpy of a single bond, whereas for phosphorus the triple bond enthalpy ( $490 \text{ kJ mol}^{-1}$ ) is much less than 3 times the single P–P bond enthalpy. Therefore, phosphorus forms  $\text{P}_4$  molecule with six single P–P bonds and exists as such.

**7.13** Write main differences between the properties of white phosphorus and red phosphorus.

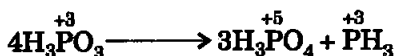
**Ans.** Chemically, red phosphorus is much less reactive than white phosphorus.

**7.14** Why does nitrogen show catenation properties less than phosphorus?

**Ans.** The single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result, the catenation tendency is weaker in nitrogen.

**7.15** Give the disproportionation reaction of  $\text{H}_3\text{PO}_3$ .

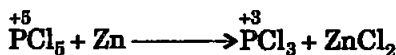
**Ans.** The disproportionation reaction is:



**7.16** Can  $\text{PCl}_5$  act as an oxidising as well as a reducing agent? Justify.

**Ans.** To act  $\text{PCl}_5$  as a *reducing agent* the oxidation number of phosphorus must *increase* from +5 in  $\text{PCl}_5$ . Phosphorus cannot increase its oxidation number beyond +5 since there are only five electrons in its valence shell.

However, the oxidation number of phosphorus can be decreased from +5 to +3.  $\text{PCl}_5$ , can thus, act as an *oxidising agent*. Examples are:



**7.17** 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.

**Ans.** (i) *Electronic configuration*

Electronic configuration of Group 16 elements (O, S, Se, Te and Po) is [Noble gas]  $ns^2 np^4$ . Hence, because of the similar electronic configuration these elements are placed in the same group.

(ii) *Oxidation states*

All the elements (except radioactive Po) show common oxidation states of  $-2$ ,  $+2$ ,  $+4$  and  $+6$ . Polonium shows  $+2$  and  $+4$  oxidation states. Oxygen, due to the absence of  $d$  orbitals does not show oxidation states of  $+4$  and  $+6$ . These common oxidation states supports their presence in the same group.

(iii) *Formation of hydrides*

All the elements form hydrides of the type  $H_2M$ . Because of the same general formula of hydrides these elements can be placed in the same group of the periodic table.

**7.18** *Why is dioxygen a gas but sulphur a solid?*

**Ans.** Due to small size and high electron gravity, oxygen forms  $\pi\pi - \pi\pi$  multiple bonds. As a result, oxygen exists as diatomic ( $O_2$ ) molecules. These molecules are held together by weak van der Waals' forces of attraction which can be easily overcome by collisions of the molecules at room temperature. Therefore,  $O_2$  is a gas at room temperature.

Sulphur on the other hand is octa atomic ( $S_8$ ) has high intermolecular force of attraction, that's why sulphur is solid at room temperature.

**7.19** *Knowing the electron gain enthalpy values for  $O \rightarrow O^-$  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  $O^-$ ?*

**Ans.** Formation of  $O^{2-}(g)$  ion is endothermic as the **electron gain enthalpy** values suggest. In this question the oxides formed with monovalent and bivalent metal ions are  $M_2O$  and  $MO$ , respectively. Since the charge on  $M$  in  $MO$  is  $+2$  and its size is also less than  $M^+$  ion with  $+1$  charge, Lattice enthalpy for the formation of  $M^{2+}O^{2-}$  (i.e.  $MO$ ) would be higher than  $(M^+)_2O$  (i.e.  $M_2O$ ) as small size and high charge cation gives more lattice enthalpy of formation. Higher lattice enthalpy values more than compensates the other enthalpy terms in

the formation of oxides. Hence more oxides with  $O^{2-}$  ion are formed.

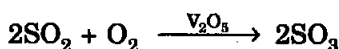
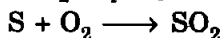
**7.20** Which aerosols deplete ozone?

**Ans.** Aerosols such as chlorofluorocarbons (CFC's), freon ( $CCl_2F_2$ ), depletes  $O_3$  layer by supplying Cl free radicals which convert  $O_3$  to  $O_2$ .

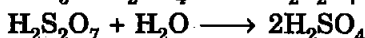
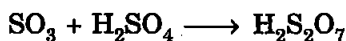
**7.21** Describe the manufacture of  $H_2SO_4$  by contact process

**Ans. Contact process:** It involves three steps:

- (i) Burning of sulphur or sulphide ores in presence of oxygen to produce  $SO_2$ .
- (ii)  $SO_2$  is reacted with  $O_2$  in presence of  $V_2O_5$  as a catalyst to form  $SO_3$ .
- (iii)  $SO_3$  is absorbed in  $H_2SO_4$  to give oleum which is  $H_2S_2O_7$ .



$$\Delta_r H = -196.6 \text{ kJ mol}^{-1}$$



The plant is operated at a pressure of 2 bar and a temperature of 720 K.

Dilution of oleum with water gives  $H_2SO_4$  of required concentration.

The sulphuric acid obtained by contact process is 96 – 98 % pure.

**7.22** How is  $SO_2$  an air pollutant?

**Ans.**  $SO_2$  is strongly irritating to the respiratory tract. It causes breathlessness and affects larynx, i.e. voice box.

It dissolves in rain water and produces acid rain which damages building material especially marbles. That is why  $SO_2$  is an air pollutant.

**7.23** Why are halogens strong oxidising agents?

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

**7.24** Explain why fluorine forms only one oxoacid, HOF.

**Ans.** Halogens, form oxoacids of the type HOX, HOXO, HOXO<sub>2</sub> and HOXO<sub>3</sub>. Fluorine forms only one oxoacid, HOX. For the formation of other oxoacids *d* orbitals are required for the



multiple  $p\pi-d\pi$  bonding between extra oxygen atoms and fluorine.

Hence, it forms only HOF and not other oxoacids. Other factors such as high electronegativity and small size of fluorine also favours only the formation of one oxoacid.

**7.25** Explain why in spite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

**Ans.** It is basically due to the larger size of chlorine than oxygen. Electron density on smaller atom is much more than the bigger atom thus attracting strongly other molecule containing hydrogen. This way oxygen forms stronger hydrogen bonds than chlorine even though their electronegativities are almost same.

**7.26** Write two uses of  $\text{ClO}_2$ .

**Ans.** Following are the two uses of  $\text{ClO}_2$ :

(i) It is a powerful oxidising and chlorinating agent and so is used as a bleach for wood pulp and cellulose and for purifying drinking water.

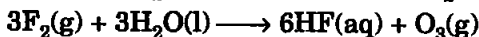
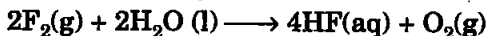
(ii) As a bleach it is used for bleaching flour in the manufacture of white bread.

**7.27** Why are halogens coloured?

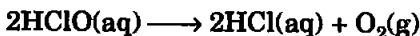
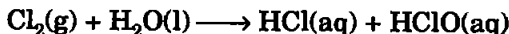
**Ans.** It is because they absorb light from visible region and radiate complementary colour.

**7.28** Write the reactions of  $\text{F}_2$  and  $\text{Cl}_2$  with water.

**Ans.**  $\text{F}_2$  is the strongest oxidising agent. It reacts with water producing  $\text{O}_2$  and also  $\text{O}_3$ :

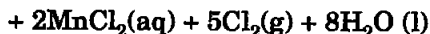


$\text{Cl}_2$  reacts with water to produce  $\text{HClO}$  which on keeping evolves  $\text{O}_2$ .

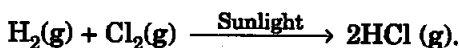


**7.29** How can you prepare  $\text{Cl}_2$  from  $\text{HCl}$  and  $\text{HCl}$  from  $\text{Cl}_2$ ? Write reactions only.

**Ans.** (i) Preparation of  $\text{Cl}_2$  from  $\text{HCl}$ :



(ii) Preparation of HCl from Cl<sub>2</sub>:



**7.30** What inspired N. Bartlett for carrying out reaction between Xe and PtF<sub>6</sub>?

**Ans.** The ionisation enthalpy of O<sub>2</sub> and Xe are nearly same.

**7.31** What are the oxidation states of phosphorus in the following

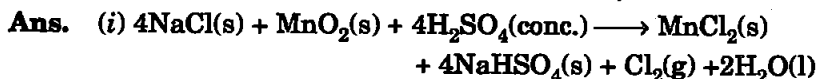
(i) H<sub>3</sub>PO<sub>3</sub> (ii) PCl<sub>3</sub> (iii) Ca<sub>3</sub>P<sub>2</sub> (iv) Na<sub>3</sub>PO<sub>4</sub> (v) POF<sub>3</sub>?

Ans.	S.N.	Compound	Oxidation state of P
	(i)	H <sub>3</sub> PO <sub>3</sub>	+3
	(ii)	PCl <sub>3</sub>	+3
	(iii)	Ca <sub>3</sub> P <sub>2</sub>	-3
	(iv)	Na <sub>3</sub> PO <sub>4</sub>	+5
	(v)	POF <sub>3</sub>	+5

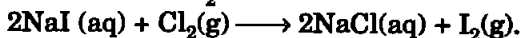
**7.32** Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO<sub>2</sub>.

(ii) Chlorine gas is passed into a solution of NaI in water.

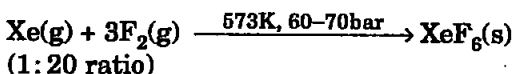
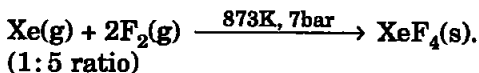
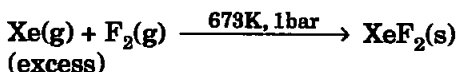


(ii) Cl<sub>2</sub> oxidises NaI to I<sub>2</sub>.



**7.33** How are xenon fluorides XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> obtained?

**Ans.** Xenon fluorides are obtained by the direct reaction between Xe and F<sub>2</sub> under different conditions:

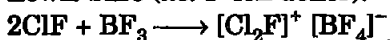


**7.34** With what neutral molecule is ClO<sup>-</sup> isoelectronic? Is that molecule a Lewis base?

**Ans.** (i) Number of electrons in ClO<sup>-</sup> is = 17 + 8 + 1 = 26. An isoelectronic neutral molecule should have 26 electrons. One such example in OF<sub>2</sub> molecule (8 + 9 + 9 = 26 electrons.).

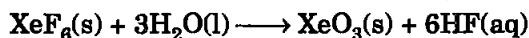
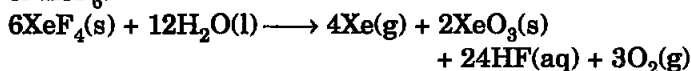
Since electronegativity of fluorine is very high, the non-bonding electron pairs on oxygen would be pulled towards fluorine making them less available for it to act as Lewis base. However, it can act as a Lewis base but very very weak.

- (ii) Another example can be of ClF (17 + 9 = 26 electrons). ClF acts as a Lewis base (i.e. F<sup>-</sup> ion donor):

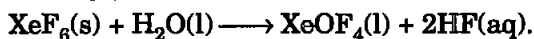


**7.35** How are XeO<sub>3</sub> and XeOF<sub>4</sub> prepared?

**Ans.** (i) XeO<sub>3</sub> can be obtained by the hydrolysis of either XeF<sub>4</sub> or XeF<sub>6</sub>.



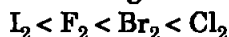
- (ii) XeOF<sub>4</sub> is obtained when XeF<sub>6</sub> reacts with small amount of water:



**7.36** Arrange the following in the order of property indicated for each set:

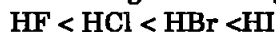
- (i) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> – increasing bond dissociation enthalpy.  
 (ii) HF, HCl, HBr, HI – increasing bond dissociation enthalpy  
 (iii) NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub> – increasing base strength.

**Ans.** (i) Increasing bond dissociation order is

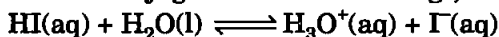


Bond dissociation enthalpy of F<sub>2</sub> is less than that of Br<sub>2</sub> and Cl<sub>2</sub> due to the lone pair-lone pair repulsions. It so happens that the magnitude of bond dissociation of F<sub>2</sub> becomes slightly more than that of I<sub>2</sub>.

- (ii) Increasing acid strength in water is



This order is due to the following order of bond dissociation enthalpies of H–X bond which decreases from H–F to H–I as the size of halogen atom increases. This question can also be answered on the basis of the formation of conjugate bases of acids e.g.,



Γ is the conjugate base of HI which is quite stable and also weak. A weak conjugate base has a strong conjugate acid. Strength of other conjugate bases is Γ < Br<sup>-</sup> < Cl<sup>-</sup> < F<sup>-</sup>.

(iii) Increasing (Lewis) base strength order is:



The reason for this order is that as we move from  $\text{NH}_3$  to  $\text{BiH}_3$  the size of the central atom increases resulting in the increased bond lengths. Electronegativity values also decrease  $\text{N} = 3.0$ ,  $\text{P} = 2.1$ ,  $\text{As} = 2.0$ ,  $\text{Sb} = 1.9$ ,  $\text{Bi} = 1.9$  and  $\text{H} = 2.1$ . It can be seen that in the case of  $\text{AsH}_3$ ,  $\text{SbH}_3$  and  $\text{BiH}_3$  the bond pairs are dragged more towards hydrogen making central atom positive. Hence lone-pair is not easily available for donation. In other words it can also be said that the electron density on the central atom decreases on moving from  $\text{NH}_3$  to  $\text{BiH}_3$  and so, the basic strength also decreases.

**7.37** Which one of the following does not exist?

(i)  $\text{XeOF}_4$  (ii)  $\text{NeF}_2$  (iii)  $\text{XeF}_2$  (iv)  $\text{XeF}_6$

**Ans.** Out of the four species  $\text{NeF}_2$  does not exist. For the formation of this compound very high amount of energy is required to convert  $\text{Ne}$  to  $\text{Ne}^{2+}$  (i.e., sum of first and second ionisation enthalpies of  $\text{Ne}$ ). This high value of ionisation enthalpy cannot be compensation by the sum of electron gain enthalpy of the formation of  $\text{F}^-$  ion. The compound is endothermic and thus cannot be formed.

Xenon is much larger in size than  $\text{Ne}$  and its ionisation enthalpies are much lower than those of  $\text{Ne}$ . Hence  $\text{Xe}$  fluorides and oxofluoride can be obtained.

**7.38** Give the formula and describe the structure of a noble gas species which is isostructural with:

(i)  $\text{ICl}_4^-$  (ii)  $\text{IBr}_2^-$  (iii)  $\text{BrO}_3^-$

**Ans.** (i)  $\text{ICl}_4^-$  (Number of valence electrons  
 $= 7 + (4 \times 7) + 1 = 36$ .)

It is isoelectronic with  $\text{XeF}_4$   
 (Number of valence electrons  
 $= 8 + (4 \times 7) = 36$ ).

Hence  $\text{ICl}_4^-$  is isoelectronic with  $\text{XeF}_4$ .

Structure of  $\text{XeF}_4$  is square planar.

(ii)  $\text{IBr}_2^-$  (Number of valence electrons  
 $= 7 + (2 \times 7) + 1 = 22$ )

It is isoelectronic with  $\text{XeF}_2$  (Number of valence electrons  
 $= 8 + (2 \times 7) = 22$ )

Structure of  $\text{XeF}_2$  is linear.

(iii)  $\text{BrO}_3^-$  (Number of valence electrons =  $7 + 3 \times 6 + 1 = 26$ )

It is isoelectronic with  $\text{XeO}_3$  (Number of valence electrons =  $8 + (3 \times 6) = 26$ )

Structure of  $\text{XeO}_3$  is trigonal pyramidal.

**7.39** *Why do noble gases have comparatively large atomic sizes?*

**Ans.** Atomic sizes of noble gases are largest in their respective periods. This is due to the reasons that noble gases exist as monatomic gases. Their atoms do not form molecules but are held by very weak van der Waals' forces. Their radii are often referred to as van der Waals' radii which have largest sizes in their respective periods.

**7.40** *List the uses of neon and argon gases.*

**Ans. Use of Argon:**

(i) It is used to provide inert atmosphere.

**Use of Neon:**

(i) Neon is used in discharge tubes and fluorescent bulbs.

□□□