

**Question 7.1:**

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

Answer

**General trends in group 15 elements**

**(i) Electronic configuration:** All the elements in group 15 have 5 valence electrons. Their general electronic configuration is  $ns^2 np^3$ .

**(ii) Oxidation states:** All these elements have 5 valence electrons and require three more electrons to complete their octets. However, gaining electrons is very difficult as the nucleus will have to attract three more electrons. This can take place only with nitrogen as it is the smallest in size and the distance between the nucleus and the valence shell is relatively small. The remaining elements of this group show a formal oxidation state of  $-3$  in their covalent compounds. In addition to the  $-3$  state, N and P also show  $-1$  and  $-2$  oxidation states.

All the elements present in this group show  $+3$  and  $+5$  oxidation states. However, the stability of  $+5$  oxidation state decreases down a group, whereas the stability of  $+3$  oxidation state increases. This happens because of the inert pair effect.

**(iii) Ionization energy and electronegativity**

First ionization decreases on moving down a group. This is because of increasing atomic sizes. As we move down a group, electronegativity decreases, owing to an increase in size.

**(iv) Atomic size:** On moving down a group, the atomic size increases. This increase in the atomic size is attributed to an increase in the number of shells.

**Question 7.2:**

Why does the reactivity of nitrogen differ from phosphorus?

Answer

Nitrogen is chemically less reactive. This is because of the high stability of its molecule,  $N_2$ . In  $N_2$ , the two nitrogen atoms form a triple bond. This triple bond has very high bond strength, which is very difficult to break. It is because of nitrogen's small size that it is able to form  $pn-pn$  bonds with itself. This property is not exhibited by atoms such as phosphorus. Thus, phosphorus is more reactive than nitrogen.

**Question 7.3:**

Discuss the trends in chemical reactivity of group 15 elements.

Answer

**General trends in chemical properties of group – 15****(i) Reactivity towards hydrogen:**

The elements of group 15 react with hydrogen to form hydrides of type  $\text{EH}_3$ , where  $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{or Bi}$ . The stability of hydrides decreases on moving down from  $\text{NH}_3$  to  $\text{BiH}_3$ .

**(ii) Reactivity towards oxygen:**

The elements of group 15 form two types of oxides:  $\text{E}_2\text{O}_3$  and  $\text{E}_2\text{O}_5$ , where  $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{or Bi}$ . The oxide with the element in the higher oxidation state is more acidic than the other. However, the acidic character decreases on moving down a group.

**(iii) Reactivity towards halogens:**

The group 15 elements react with halogens to form two series of salts:  $\text{EX}_3$  and  $\text{EX}_5$ . However, nitrogen does not form  $\text{NX}_5$  as it lacks the  $d$ -orbital. All trihalides (except  $\text{NX}_3$ ) are stable.

**(iv) Reactivity towards metals:**

The group 15 elements react with metals to form binary compounds in which metals exhibit  $-3$  oxidation states.

**Question 7.4:**

Why does  $\text{NH}_3$  form hydrogen bond but  $\text{PH}_3$  does not?

Answer

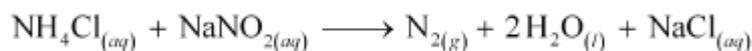
Nitrogen is highly electronegative as compared to phosphorus. This causes a greater attraction of electrons towards nitrogen in  $\text{NH}_3$  than towards phosphorus in  $\text{PH}_3$ . Hence, the extent of hydrogen bonding in  $\text{PH}_3$  is very less as compared to  $\text{NH}_3$ .

**Question 7.5:**

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

Answer

An aqueous solution of ammonium chloride is treated with sodium nitrite.



NO and HNO<sub>3</sub> are produced in small amounts. These are impurities that can be removed on passing nitrogen gas through aqueous sulphuric acid, containing potassium dichromate.

**Question 7.6:**

How is ammonia manufactured industrially?

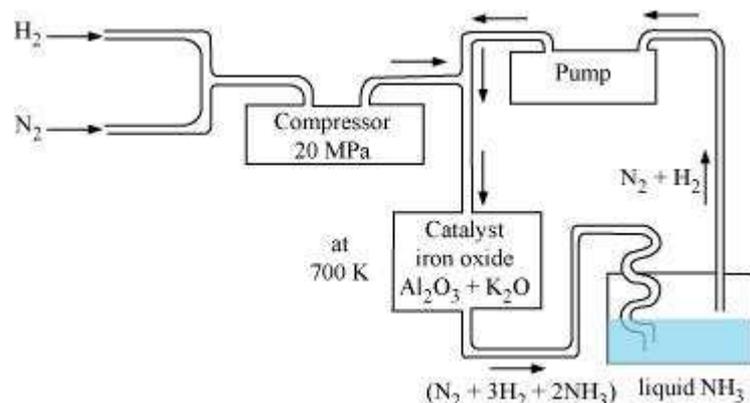
Answer

Ammonia is prepared on a large-scale by the Haber's process.



The optimum conditions for manufacturing ammonia are:

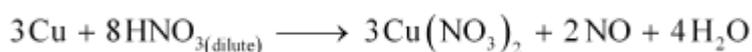
- (i) Pressure (around  $200 \times 10^5$  Pa)
- (ii) Temperature (4700 K)
- (iii) Catalyst such as iron oxide with small amounts of Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O

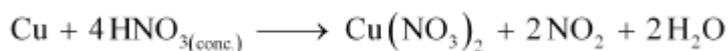
**Question 7.7:**

Illustrate how copper metal can give different products on reaction with HNO<sub>3</sub>.

Answer

Concentrated nitric acid is a strong oxidizing agent. It is used for oxidizing most metals. The products of oxidation depend on the concentration of the acid, temperature, and also on the material undergoing oxidation.

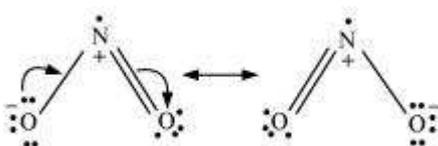


**Question 7.8:**

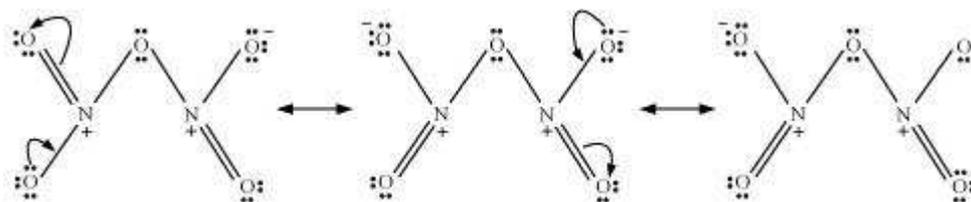
Give the resonating structures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$ .

Answer

(1)



(2)

**Question 7.9:**

The HNH angle value is higher than HPH, HAsH and HSbH angles. Why? [**Hint:** Can be explained on the basis of  $sp^3$  hybridisation in  $\text{NH}_3$  and only  $s-p$  bonding between hydrogen and other elements of the group].

Answer

Hydride  $\text{NH}_3$   $\text{PH}_3$   $\text{AsH}_3$   $\text{SbH}_3$

H–M–H angle  $107^\circ$   $92^\circ$   $91^\circ$   $90^\circ$

The above trend in the H–M–H bond angle can be explained on the basis of the electronegativity of the central atom. Since nitrogen is highly electronegative, there is high electron density around nitrogen. This causes greater repulsion between the electron pairs around nitrogen, resulting in maximum bond angle. We know that electronegativity decreases on moving down a group. Consequently, the repulsive interactions between the electron pairs decrease, thereby decreasing the H–M–H bond angle.

**Question 7.10:**



Why does  $R_3P=O$  exist but  $R_3N=O$  does not (R = alkyl group)?

Answer

N (unlike P) lacks the *d*-orbital. This restricts nitrogen to expand its coordination number beyond four. Hence,  $R_3N=O$  does not exist.

**Question 7.11:**

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

Answer

**$NH_3$  is distinctly basic while  $BiH_3$  is feebly basic.**

Nitrogen has a small size due to which the lone pair of electrons is concentrated in a small region. This means that the charge density per unit volume is high. On moving down a group, the size of the central atom increases and the charge gets distributed over a large area decreasing the electron density. Hence, the electron donating capacity of group 15 element hydrides decreases on moving down the group.

**Question 7.12:**

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

Answer

Nitrogen owing to its small size has a tendency to form *p* $\pi$ –*p* $\pi$  multiple bonds with itself. Nitrogen thus forms a very stable diatomic molecule,  $N_2$ . On moving down a group, the tendency to form *p* $\pi$ –*p* $\pi$  bonds decreases (because of the large size of heavier elements). Therefore, phosphorus (like other heavier metals) exists in the  $P_4$  state.

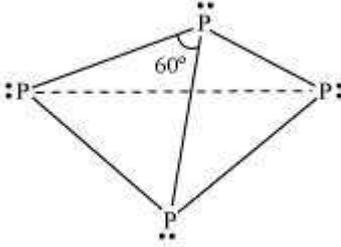
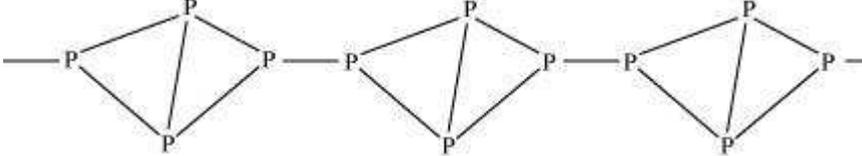
**Question 7.13:**

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

Answer

White phosphorus	Red Phosphorus
It is a soft and waxy solid. It possesses a garlic smell.	It is a hard and crystalline solid, without any smell.



It is poisonous.	It is non-poisonous.
It is insoluble in water but soluble in carbon disulphide.	It is insoluble in both water and carbon disulphide.
It undergoes spontaneous combustion in air.	It is relatively less reactive.
In both solid and vapour states, it exists as a $P_4$ molecule. 	It exists as a chain of tetrahedral $P_4$ units. 

**Question 7.14:**

Why does nitrogen show catenation properties less than phosphorus?

Answer

Catenation is much more common in phosphorous compounds than in nitrogen compounds. This is because of the relative weakness of the N–N single bond as compared to the P–P single bond. Since nitrogen atom is smaller, there is greater repulsion of electron density of two nitrogen atoms, thereby weakening the N–N single bond.

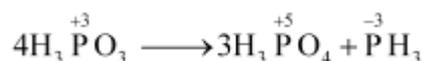
**Question 7.15:**

Give the disproportionation reaction of  $H_3PO_3$ .

Answer



On heating, orthophosphorus acid ( $\text{H}_3\text{PO}_3$ ) disproportionates to give orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and phosphine ( $\text{PH}_3$ ). The oxidation states of P in various species involved in the reaction are mentioned below.

**Question 7.16:**

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

Answer

$\text{PCl}_5$  can only act as an oxidizing agent. The highest oxidation state that P can show is +5. In  $\text{PCl}_5$ , phosphorus is in its highest oxidation state (+5). However, it can decrease its oxidation state and act as an oxidizing agent.

**Question 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.

Answer

The elements of group 16 are collectively called chalcogens.

**(i)** Elements of group 16 have six valence electrons each. The general electronic configuration of these elements is  $ns^2 np^4$ , where  $n$  varies from 2 to 6.

**(ii) Oxidation state:**

As these elements have six valence electrons ( $ns^2 np^4$ ), they should display an oxidation state of  $-2$ . However, only oxygen predominantly shows the oxidation state of  $-2$  owing to its high electronegativity. It also exhibits the oxidation state of  $-1$  ( $\text{H}_2\text{O}_2$ ), zero ( $\text{O}_2$ ), and  $+2$  ( $\text{OF}_2$ ). However, the stability of the  $-2$  oxidation state decreases on moving down a group due to a decrease in the electronegativity of the elements. The heavier elements of the group show an oxidation state of  $+2$ ,  $+4$ , and  $+6$  due to the availability of  $d$ -orbitals.

**(iii) Formation of hydrides:**

These elements form hydrides of formula  $\text{H}_2\text{E}$ , where  $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$ . Oxygen and sulphur also form hydrides of type  $\text{H}_2\text{E}_2$ . These hydrides are quite volatile in nature.

**Question 7.18:**



Why is dioxygen a gas but sulphur a solid?

Answer

Oxygen is smaller in size as compared to sulphur. Due to its smaller size, it can effectively form  $p\pi-p\pi$  bonds and form  $O_2$  ( $O=O$ ) molecule. Also, the intermolecular forces in oxygen are weak van der Waals, which cause it to exist as gas. On the other hand, sulphur does not form  $M_2$  molecule but exists as a puckered structure held together by strong covalent bonds. Hence, it is a solid.

**Question 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  $O^-$ ?

(Hint: Consider lattice energy factor in the formation of compounds).

Answer

Stability of an ionic compound depends on its lattice energy. More the lattice energy of a compound, more stable it will be.

Lattice energy is directly proportional to the charge carried by an ion. When a metal combines with oxygen, the lattice energy of the oxide involving  $O^{2-}$  ion is much more than the oxide involving  $O^-$  ion. Hence, the oxide having  $O^{2-}$  ions are more stable than oxides having  $O^-$ . Hence, we can say that formation of  $O^{2-}$  is energetically more favourable than formation of  $O^-$ .

**Question 7.20:**

Which aerosols deplete ozone?

Answer

Freons or chlorofluorocarbons (CFCs) are aerosols that accelerate the depletion of ozone. In the presence of ultraviolet radiations, molecules of CFCs break down to form chlorine-free radicals that combine with ozone to form oxygen.

**Question 7.21:**

Describe the manufacture of  $H_2SO_4$  by contact process?

Answer

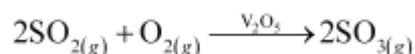
Sulphuric acid is manufactured by the contact process. It involves the following steps:

**Step (i):**

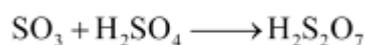
Sulphur or sulphide ores are burnt in air to form  $\text{SO}_2$ .

**Step (ii):**

By a reaction with oxygen,  $\text{SO}_2$  is converted into  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  as a catalyst.

**Step (iii):**

$\text{SO}_3$  produced is absorbed on  $\text{H}_2\text{SO}_4$  to give  $\text{H}_2\text{S}_2\text{O}_7$  (oleum).



This oleum is then diluted to obtain  $\text{H}_2\text{SO}_4$  of the desired concentration.

In practice, the plant is operated at 2 bar (pressure) and 720 K (temperature). The sulphuric acid thus obtained is 96-98% pure.

**Question 7.22:**

How is  $\text{SO}_2$  an air pollutant?

Answer

Sulphur dioxide causes harm to the environment in many ways:

1. It combines with water vapour present in the atmosphere to form sulphuric acid. This causes acid rain. Acid rain damages soil, plants, and buildings, especially those made of marble.
2. Even in very low concentrations,  $\text{SO}_2$  causes irritation in the respiratory tract. It causes throat and eye irritation and can also affect the larynx to cause breathlessness.
3. It is extremely harmful to plants. Plants exposed to sulphur dioxide for a long time lose colour from their leaves. This condition is known as chlorosis. This happens because the formation of chlorophyll is affected by the presence of sulphur dioxide.

**Question 7.23:**

Why are halogens strong oxidising agents?

Answer

The general electronic configuration of halogens is  $np^5$ , where  $n = 2-6$ . Thus, halogens need only one more electron to complete their octet and to attain the stable noble gas configuration. Also, halogens are highly electronegative with low dissociation energies



and high negative electron gain enthalpies. Therefore, they have a high tendency to gain an electron. Hence, they act as strong oxidizing agents.

**Question 7.24:**

Explain why fluorine forms only one oxoacid, HOF.

Answer

Fluorine forms only one oxoacid i.e., HOF because of its high electronegativity and small size.

**Question 7.25:**

Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Answer

Both chlorine and oxygen have almost the same electronegativity values, but chlorine rarely forms hydrogen bonding. This is because in comparison to chlorine, oxygen has a smaller size and as a result, a higher electron density per unit volume.

**Question 7.26:**

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

Answer

**Uses of  $\text{ClO}_2$ :**

- (i) It is used for purifying water.
- (ii) It is used as a bleaching agent.

**Question 7.27:**

Why are halogens coloured?

Answer

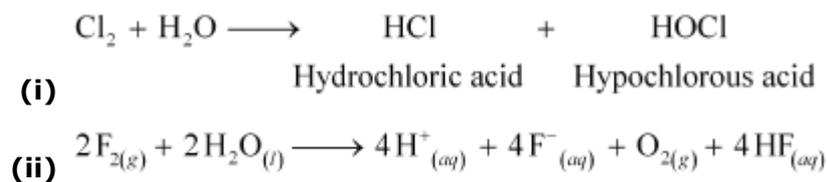
Almost all halogens are coloured. This is because halogens absorb radiations in the visible region. This results in the excitation of valence electrons to a higher energy region. Since the amount of energy required for excitation differs for each halogen, each halogen displays a different colour.

**Question 7.28:**



Write the reactions of  $F_2$  and  $Cl_2$  with water.

Answer

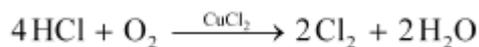


**Question 7.29:**

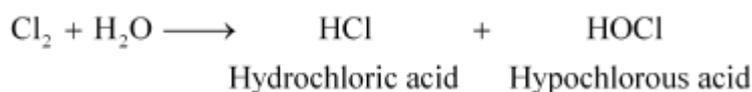
How can you prepare  $Cl_2$  from  $HCl$  and  $HCl$  from  $Cl_2$ ? Write reactions only.

Answer

**(i)**  $Cl_2$  can be prepared from  $HCl$  by Deacon's process.



**(ii)**  $HCl$  can be prepared from  $Cl_2$  on treating it with water.



**Question 7.30:**

What inspired N. Bartlett for carrying out reaction between  $Xe$  and  $PtF_6$ ?

Answer

Neil Bartlett initially carried out a reaction between oxygen and  $PtF_6$ . This resulted in the formation of a red compound,  $O_2^+[PtF_6]^-$ .

Later, he realized that the first ionization energy of oxygen (1175 kJ/mol) and  $Xe$  (1170 kJ/mol) is almost the same. Thus, he tried to prepare a compound with  $Xe$  and  $PtF_6$ . He was successful and a red-coloured compound,  $Xe^+[PtF_6]^-$  was formed.

**Question 7.31:**

What are the oxidation states of phosphorus in the following:

**(i)**  $H_3PO_3$  **(ii)**  $PCl_3$  **(iii)**  $Ca_3P_2$

**(iv)**  $Na_3PO_4$  **(v)**  $POF_3$ ?

Answer

Let the oxidation state of  $p$  be  $x$ .



(i)  $\text{H}_3\text{PO}_3$

$$3 + x + 3(-2) = 0$$

$$3 + x - 6 = 0$$

$$x - 3 = 0$$

$$x = +3$$

(ii)  $\text{PCl}_3$

$$x + 3(-1) = 0$$

$$x - 3 = 0$$

$$x = +3$$

(iii)  $\text{Ca}_3\text{P}_2$

$$3(+2) + 2(x) = 0$$

$$6 + 2x = 0$$

$$2x = -6$$

$$x = -3$$

(iv)  $\text{Na}_3\text{PO}_4$

$$3(+1) + x + 4(-2) = 0$$

$$3 + x - 8 = 0$$

$$x - 5 = 0$$

$$x = +5$$

(v)  $\text{POF}_3$

$$x + (-2) + 3(-1) = 0$$

$$x - 5 = 0$$

$$x = +5$$

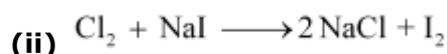
**Question 7.32:**

Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of  $\text{MnO}_2$ .

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

Answer

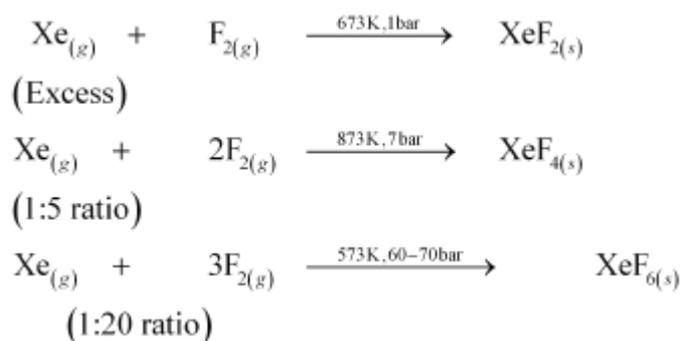


**Question 7.33:**

How are xenon fluorides  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  obtained?

Answer

$\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$  are obtained by a direct reaction between Xe and  $\text{F}_2$ . The condition under which the reaction is carried out determines the product.

**Question 7.34:**

With what neutral molecule is  $\text{ClO}^-$  isoelectronic? Is that molecule a Lewis base?

Answer

$\text{ClO}^-$  is isoelectronic to  $\text{ClF}$ . Also, both species contain 26 electrons in all as shown.

Total electrons  $\text{ClO}^- = 17 + 8 + 1 = 26$

In  $\text{ClF} = 17 + 9 = 26$

$\text{ClF}$  acts like a Lewis base as it accepts electrons from F to form  $\text{ClF}_3$ .

**Question 7.35:**

How are  $\text{XeO}_3$  and  $\text{XeOF}_4$  prepared?

Answer

(i)  $\text{XeO}_3$  can be prepared in two ways as shown.



(ii)  $\text{XeOF}_4$  can be prepared using  $\text{XeF}_6$ .



**Question 7.36:**

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.

Answer

(i) Bond dissociation energy usually decreases on moving down a group as the atomic size increases. However, the bond dissociation energy of  $F_2$  is lower than that of  $Cl_2$  and  $Br_2$ . This is due to the small atomic size of fluorine. Thus, the increasing order for bond dissociation energy among halogens is as follows:



- (ii)  $HF < HCl < HBr < HI$

The bond dissociation energy of H-X molecules where X = F, Cl, Br, I, decreases with an increase in the atomic size. Since H-I bond is the weakest, HI is the strongest acid.

- (iii)  $BiH_3 \leq SbH_3 < AsH_3 < PH_3 < NH_3$

On moving from nitrogen to bismuth, the size of the atom increases while the electron density on the atom decreases. Thus, the basic strength decreases.

**Question 7.37:**

Which one of the following does not exist?

- (i)  $XeOF_4$  (ii)  $NeF_2$   
(iii)  $XeF_2$  (iv)  $XeF_6$

Answer

$NeF_2$  does not exist.

**Question 7.38:**

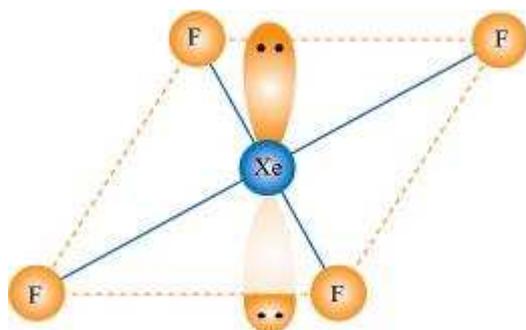
Give the formula and describe the structure of a noble gas species which is isostructural with:

- (i)  $ICl_4^-$   
(ii)  $IBr_2^-$   
(iii)  $BrO_3^-$

Answer

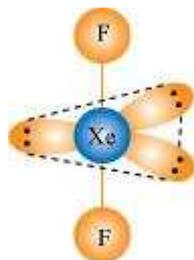
(i)

$\text{XeF}_4$  is isoelectronic with  $\text{ICl}_4^-$  and has square planar geometry.



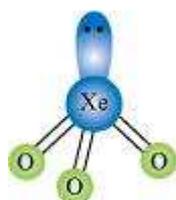
(ii)

$\text{XeF}_2$  is isoelectronic to  $\text{IBr}_2^-$  and has a linear structure.



(iii)

$\text{XeO}_3$  is isostructural to  $\text{BrO}_3^-$  and has a pyramidal molecular structure.



**Question 7.39:**

Why do noble gases have comparatively large atomic sizes?

Answer

Noble gases do not form molecules. In case of noble gases, the atomic radii corresponds to van der Waal's radii. On the other hand, the atomic radii of other elements correspond to their covalent radii. By definition, van der Waal's radii are larger than covalent radii. It



is for this reason that noble gases are very large in size as compared to other atoms belonging to the same period.

**Question 7.40:**

List the uses of Neon and argon gases.

Answer

**Uses of neon gas:**

- (i) It is mixed with helium to protect electrical equipments from high voltage.
- (ii) It is filled in discharge tubes with characteristic colours.
- (iii) It is used in beacon lights.

**Uses of Argon gas:**

- (i) Argon along with nitrogen is used in gas-filled electric lamps. This is because Ar is more inert than N.
- (ii) It is usually used to provide an inert temperature in a high metallurgical process.
- (iii) It is also used in laboratories to handle air-sensitive substances.

**Text solution****Question 7.1:**

Why are pentahalides more covalent than trihalides?

Answer

In pentahalides, the oxidation state is +5 and in trihalides, the oxidation state is +3. Since the metal ion with a high charge has more polarizing power, pentahalides are more covalent than trihalides.

**Question 7.2:**

Why is  $\text{BiH}_3$  the strongest reducing agent amongst all the hydrides of Group 15 elements?

Answer

As we move down a group, the atomic size increases and the stability of the hydrides of group 15 elements decreases. Since the stability of hydrides decreases on moving from  $\text{NH}_3$  to  $\text{BiH}_3$ , the reducing character of the hydrides increases on moving from  $\text{NH}_3$  to  $\text{BiH}_3$ .

**Question 7.3:**

Why is  $\text{N}_2$  less reactive at room temperature?

Answer

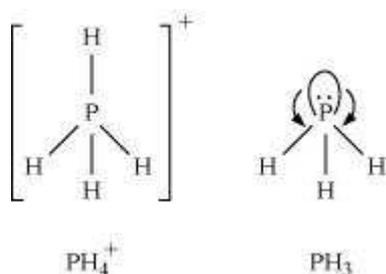
The two N atoms in  $\text{N}_2$  are bonded to each other by very strong triple covalent bonds. The bond dissociation energy of this bond is very high. As a result,  $\text{N}_2$  is less reactive at room temperature.

**Question 7.4:**

Mention the conditions required to maximise the yield of ammonia.

Answer

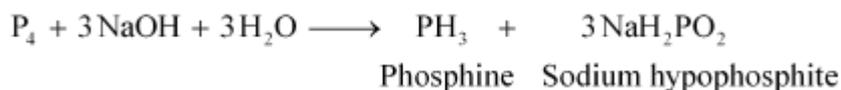


**Question 7.8:**

What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of  $\text{CO}_2$ ?

Answer

White phosphorous dissolves in boiling NaOH solution (in a  $\text{CO}_2$  atmosphere) to give phosphine,  $\text{PH}_3$ .

**Question 7.9:**

What happens when  $\text{PCl}_5$  is heated?

Answer

All the bonds that are present in  $\text{PCl}_5$  are not similar. It has three equatorial and two axial bonds. The equatorial bonds are stronger than the axial ones. Therefore, when  $\text{PCl}_5$  is heated strongly, it decomposes to form  $\text{PCl}_3$ .

**Question 7.10:**

Write a balanced equation for the hydrolytic reaction of  $\text{PCl}_5$  in heavy water.

Answer



Therefore, the net reaction can be written as

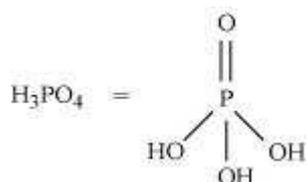


**Question 7.11:**

What is the basicity of  $\text{H}_3\text{PO}_4$ ?

Answer

$\text{H}_3\text{PO}_4$



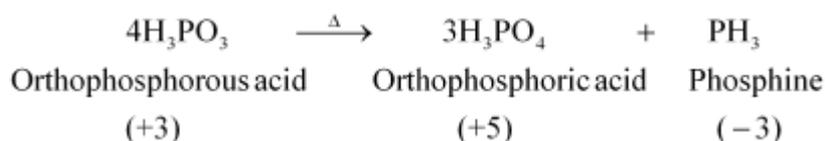
Since there are three OH groups present in  $\text{H}_3\text{PO}_4$ , its basicity is three i.e., it is a tribasic acid.

**Question 7.12:**

What happens when  $\text{H}_3\text{PO}_3$  is heated?

Answer

$\text{H}_3\text{PO}_3$ , on heating, undergoes disproportionation reaction to form  $\text{PH}_3$  and  $\text{H}_3\text{PO}_4$ . The oxidation numbers of P in  $\text{H}_3\text{PO}_3$ ,  $\text{PH}_3$ , and  $\text{H}_3\text{PO}_4$  are +3, -3, and +5 respectively. As the oxidation number of the same element is decreasing and increasing during a particular reaction, the reaction is a disproportionation reaction.

**Question 7.13:**

List the important sources of sulphur.

Answer

Sulphur mainly exists in combined form in the earth's crust primarily as sulphates [gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), baryte ( $\text{BaSO}_4$ )] and sulphides [(galena ( $\text{PbS}$ ), zinc blends ( $\text{ZnS}$ ), copper pyrites ( $\text{CuFeS}_2$ )).

**Question 7.14:**

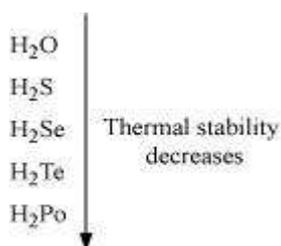
Write the order of thermal stability of the hydrides of Group 16 elements.

Answer



The thermal stability of hydrides decreases on moving down the group. This is due to a decrease in the bond dissociation enthalpy (H–E) of hydrides on moving down the group.

Therefore,



**Question 7.15:**

Why is H<sub>2</sub>O a liquid and H<sub>2</sub>S a gas?

Answer

H<sub>2</sub>O has oxygen as the central atom. Oxygen has smaller size and higher electronegativity as compared to sulphur. Therefore, there is extensive hydrogen bonding in H<sub>2</sub>O, which is absent in H<sub>2</sub>S. Molecules of H<sub>2</sub>S are held together only by weak van der Waal's forces of attraction.

Hence, H<sub>2</sub>O exists as a liquid while H<sub>2</sub>S as a solid.

**Question 7.16:**

Which of the following does not react with oxygen directly?

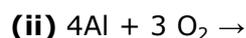
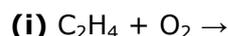
Zn, Ti, Pt, Fe

Answer

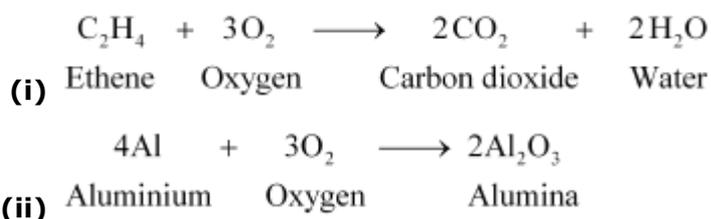
Pt is a noble metal and does not react very easily. All other elements, Zn, Ti, Fe, are quite reactive. Hence, oxygen does not react with platinum (Pt) directly.

**Question 7.17:**

Complete the following reactions:



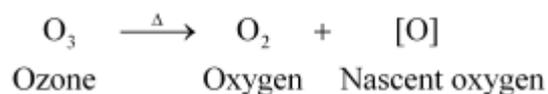
Answer

**Question 7.18:**

Why does O<sub>3</sub> act as a powerful oxidising agent?

Answer

Ozone is not a very stable compound under normal conditions and decomposes readily on heating to give a molecule of oxygen and nascent oxygen. Nascent oxygen, being a free radical, is very reactive.



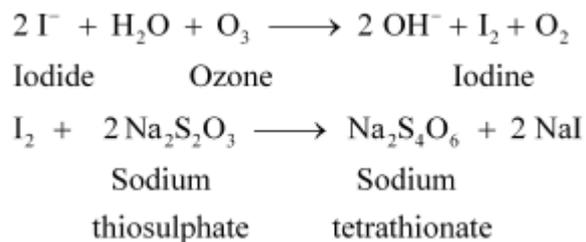
Therefore, ozone acts as a powerful oxidising agent.

**Question 7.19:**

How is O<sub>3</sub> estimated quantitatively?

Answer

Quantitatively, ozone can be estimated with the help of potassium iodide. When ozone is made to react with potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated. This liberated iodine can be titrated against a standard solution of sodium thiosulphate using starch as an indicator. The reactions involved in the process are given below.

**Question 7.20:**



What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

Answer

SO<sub>2</sub> acts as a reducing agent when passed through an aqueous solution containing Fe(III) salt. It reduces Fe(III) to Fe(II) i.e., ferric ions to ferrous ions.



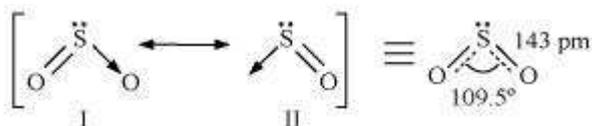
**Question 7.21:**

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?

Answer

The electronic configuration of S is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup>.

During the formation of SO<sub>2</sub>, one electron from 3p orbital goes to the 3d orbital and S undergoes sp<sup>2</sup> hybridization. Two of these orbitals form sigma bonds with two oxygen atoms and the third contains a lone pair. p-orbital and d-orbital contain an unpaired electron each. One of these electrons forms p<sub>n</sub>-p<sub>n</sub> bond with one oxygen atom and the other forms p<sub>n</sub>-d<sub>n</sub> bond with the other molecule. This is the reason SO<sub>2</sub> has a bent structure. Also, it is a resonance hybrid of structures **I** and **II**.



Both S–O bonds are equal in length (143 pm) and have a multiple bond character.

**Question 7.22:**

How is the presence of SO<sub>2</sub> detected?

Answer

SO<sub>2</sub> is a colourless and pungent smelling gas.

It can be detected with the help of potassium permanganate solution. When SO<sub>2</sub> is passed through an acidified potassium permanganate solution, it decolorizes the solution as it reduces MnO<sub>4</sub><sup>-</sup> ions to Mn<sup>2+</sup> ions.



**Question 7.23:**

Mention three areas in which  $\text{H}_2\text{SO}_4$  plays an important role.

Answer

Sulphuric acid is an important industrial chemical and is used for a lot of purposes. Some important uses of sulphuric acid are given below.

- (i) It is used in fertilizer industry. It is used to make various fertilizers such as ammonium sulphate and calcium super phosphate.
- (ii) It is used in the manufacture of pigments, paints, and detergents.
- (iii) It is used in the manufacture of storage batteries.

**Question 7.24:**

Write the conditions to maximize the yield of  $\text{H}_2\text{SO}_4$  by Contact process.

Answer

Manufacture of sulphuric acid by Contact process involves three steps.

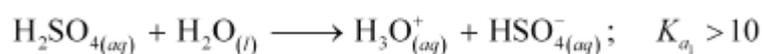
1. Burning of ores to form  $\text{SO}_2$
2. Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction of the former with  $\text{O}_2$   
( $\text{V}_2\text{O}_5$  is used in this process as a catalyst.)
3. Absorption of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give oleum ( $\text{H}_2\text{S}_2\text{O}_7$ )

The key step in this process is the second step. In this step, two moles of gaseous reactants combine to give one mole of gaseous product. Also, this reaction is exothermic. Thus, in accordance with Le Chatelier's principle, to obtain the maximum amount of  $\text{SO}_3$  gas, temperature should be low and pressure should be high.

**Question 7.25:**

Why is  $K_{a_2} \ll K_{a_1}$  for  $\text{H}_2\text{SO}_4$  in water?

Answer



It can be noticed that  $K_{a_1} \gg K_{a_2}$



This is because a neutral  $\text{H}_2\text{SO}_4$  has a much higher tendency to lose a proton than the negatively charged  $\text{HSO}_4^-$ . Thus, the former is a much stronger acid than the latter.

**Question 7.26:**

Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of  $\text{F}_2$  and  $\text{Cl}_2$ .

Answer

Fluorine is a much stronger oxidizing agent than chlorine. The oxidizing power depends on three factors.

1. Bond dissociation energy
2. Electron gain enthalpy
3. Hydration enthalpy

The electron gain enthalpy of chlorine is more negative than that of fluorine. However, the bond dissociation energy of fluorine is much lesser than that of chlorine. Also, because of its small size, the hydration energy of fluorine is much higher than that of chlorine. Therefore, the latter two factors more than compensate for the less negative electron gain enthalpy of fluorine. Thus, fluorine is a much stronger oxidizing agent than chlorine.

**Question 7.27:**

Give two examples to show the anomalous behaviour of fluorine.

Answer

**Anomalous behaviour of fluorine**

- (i) It forms only one oxoacid as compared to other halogens that form a number of oxoacids.
- (ii) Ionisation enthalpy, electronegativity, and electrode potential of fluorine are much higher than expected.

**Question 7.28:**

Sea is the greatest source of some halogens. Comment.

Answer



Sea water contains chlorides, bromides, and iodides of Na, K, Mg, and Ca. However, it primarily contains NaCl. The deposits of dried up sea beds contain sodium chloride and carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Marine life also contains iodine in their systems. For example, sea weeds contain upto 0.5% iodine as sodium iodide. Thus, sea is the greatest source of halogens.

**Question 7.29:**

Give the reason for bleaching action of  $\text{Cl}_2$ .

Answer

When chlorine reacts with water, it produces nascent oxygen. This nascent oxygen then combines with the coloured substances present in the organic matter to oxidize them into colourless substances.



Coloured substances +  $[\text{O}] \rightarrow$  Oxidized colourless substance

**Question 7.30:**

Name two poisonous gases which can be prepared from chlorine gas.

Answer

Two poisonous gases that can be prepared from chlorine gas are

- (i) Phosgene ( $\text{COCl}_2$ )
- (ii) Mustard gas ( $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ )

**Question 7.31:**

Why is ICl more reactive than  $\text{I}_2$ ?

Answer

ICl is more reactive than  $\text{I}_2$  because I–Cl bond in ICl is weaker than I–I bond in  $\text{I}_2$ .

**Question 7.32:**

Why is helium used in diving apparatus?

Answer

Air contains a large amount of nitrogen and the solubility of gases in liquids increases with increase in pressure. When sea divers dive deep into the sea, large amount of

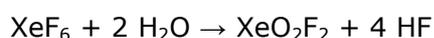


nitrogen dissolves in their blood. When they come back to the surface, solubility of nitrogen decreases and it separates from the blood and forms small air bubbles. This leads to a dangerous medical condition called bends. Therefore, air in oxygen cylinders used for diving is diluted with helium gas. This is done as He is sparingly less soluble in blood.

**Question 7.33:**

Balance the following equation:  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + \text{HF}$

Answer

**Balanced equation****Question 7.34:**

Why has it been difficult to study the chemistry of radon?

Answer

It is difficult to study the chemistry of radon because it is a radioactive substance having a half-life of only 3.82 days. Also, compounds of radon such as  $\text{RnF}_2$  have not been isolated. They have only been identified.

## CHAPTER-7 p-Block Elements

8 Marks Chapter

### Points to remember:-

The general valence shell electronic configuration of p-block elements  $ns^2 np^{1-6}$

### GROUP 15 ELEMENTS:-

Group 15 elements ; N, P, As, Sb & Bi

General electronic configuration:  $ns^2 np^3$

### Physical Properties:-

- Dinitrogen is a diatomic gas while all others are solids.
- N & P are non-metals. As & Sb metalloids & Bi is a metal. This is due to decrease in ionization enthalpy & increase in atomic size .
- Electro negativity decreases down the group .

### Chemical properties:-

- Common oxidation states : -3, +3 & +5.
- Due to inert effect, the stability of +5 state decreases down the group & stability of +3 state increases .

- In the case of Nitrogen all Oxidation states from +1 to +4 tend to disproportionate in acid solution , e.g.:-  $3\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2\text{NO}$   
Anomalous behavior of Nitrogen :- due to its small size, high electronegativity, high ionization enthalpy and absence of d-orbital.
- $\text{N}_2$  has unique ability to  $p\pi-p\pi$  multiple bonds whereas the heavier of this group do not form  $p\pi-p\pi$  because their atomic orbitals are so large & diffuse that they cannot have effective overlapping.
- Nitrogen exists as diatomic molecule with triple bond between the two atoms whereas other elements form single bonds in elemental state.
- N cannot form  $d\pi-p\pi$  due to the non-availability of d-orbitals whereas other elements can.

#### Trends In Properties:-

Stability -  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

Bond Dissociation Enthalpy-  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

Reducing character -  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$

Basic character-  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

Acidic character-  $\text{N}_2\text{O}_3 > \text{P}_2\text{O}_3 > \text{As}_2\text{O}_3 > \text{Sb}_2\text{O}_3 > \text{Bi}_2\text{O}_3$

#### Dinitrogen:-

##### Preparation

- Commercial preparation – By the liquefaction & fractional distillation of air.
- Laboratory preparation – By treating an aqueous solution  $\text{NH}_4\text{Cl}$  with sodium nitrate .  
 $\text{NH}_4\text{Cl} + \text{NaNO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{NaCl}$
- Thermal decomposition of ammonium dichromate also give  $\text{N}_2$ .  
 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
- Thermal decomposition of Barium or Sodium azide gives very pure  $\text{N}_2$ .

##### PROPERTIES

At high temperature nitrogen combines with metals to form ionic nitride ( $\text{Mg}_3\text{N}_2$ ) & with non-metals , covalent nitride.

##### AMMONIA PREPARATION

- In laboratory it is prepared by heating ammonium salt with  $\text{NaOH}$  or lime.  
 $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} + \text{CaCl}_2$
- In large scale it is manufactured by Haber 's process  
 $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$   
 $\Delta H^\circ = -46.1 \text{ kJ/mol}$   
Acc.to Lechatelier's principle the favorable conditions for the manufacture of  $\text{NH}_3$  are:-  
Optimum temperature: 700 K  
High pressure : 200 atm

Catalyst: Iron Oxides

Promoter :  $\text{K}_2\text{O}$  &  $\text{Al}_2\text{O}_3$

## PROPERTIES

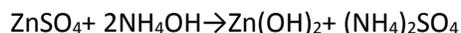
Ammonia is a colorless gas with pungent odour.

Highly soluble in water.

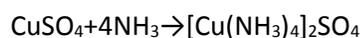
In solids & liquid states it exists as an associated molecule due to hydrogen bonding which accounts for high melting & boiling points of NH<sub>3</sub>

Trigonal Pyramidal shape NH<sub>3</sub> molecule.

Aqueous solution of ammonia is weakly basic due to the formation of OH<sup>-</sup> ion .



Ammonia can form coordinate bonds by donating its lone on nitrogen, ammonia forms complexes.



Name	Formula	Oxidation state	Chemical nature
Nitrous oxide or Laughing gas	N <sub>2</sub> O	+1	Neutral
Nitric oxide	NO	+2	Neutral
Dinitrogen trioxide	N <sub>2</sub> O <sub>3</sub>	+3	Acidic
Dinitrogen tetra oxide	N <sub>2</sub> O <sub>4</sub> or NO <sub>2</sub>	+4	Acidic
Dinitrogen pentaoxide	N <sub>2</sub> O <sub>5</sub>	+5	Acidic

## NITRIC ACID

PREPARATION: ostwald's process – it is based upon catalytic oxidation of ammonia by atmospheric oxidation . The main steps are

- 1)  $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[9\text{BAR}]{500\text{K, Pt}} 4\text{NO} + 6\text{H}_2\text{O}$
- 2)  $2\text{NO} + \text{O}_2 \rightarrow 2\text{HNO}_3 + \text{NO}$

## PROPERTIES:-

- (i) conc. HNO<sub>3</sub> is a strong oxidizing agent & attacks most metals gold & Pt. .
- (ii) Cr & Al do not dissolve HNO<sub>3</sub> because of the formation of a positive film of oxide on the surface.
- (iii) it oxidises non metals like I<sub>2</sub> to HNO<sub>3</sub>, C to CO<sub>2</sub>, S to H<sub>2</sub>SO<sub>4</sub>
- (iv) brown ring test is used to detect NO.

## PHOSPHOROUS:-

ALLOTROPIC FORMS: White , red  $\alpha$ -black &  $\beta$ -black .

White phosphorous is more reactive red phosphorous because white P exists as discrete  $P_4$  molecules .in red P several  $P_4$  molecules are linked to form a polymeric chain.

### PHOSPHINE

Preparation: It is prepared in laboratory by heating white P with concentrated NaOH solution in an

Inert atmosphere of  $CO_2$  [ $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ ]

### Phosphorous halides

Phosphorous forms two types of halides  $PX_3$  &  $PX_5$  ( $X = F, I, Br$ )

Trihalides have pyramidal shape and pentahalides have trigonalbipyramidal structure.

### OXOACIDS OF PHOSPHOROUS

- The acids in +3 oxidation state disproportionate to higher & lower oxidation.



- Acids which contain P-H bond have strong reducing properties. EX:  $-H_3PO_2$
- Hydrogen atoms which are attached with oxygen in P-OH form are ionisable and cause basicity.

### GROUP-16 ELEMENTS (CHALCOGENS)

Group 16 Elements: O, S, Se, Te, Po

General electronic configuration:  $ns^2np^4$

Element	Occurrence
Oxygen	Comprises 20.946% by volume of the atmosphere.
Sulphur	As sulphates such as gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Epsom salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and sulphides Such as galena $\text{PbS}$ , zinc blende $\text{ZnS}$ , copper pyrites $\text{CuFeS}_2$  As metal selenides and tellurides in sulphide ores.
Se&Te	as a decay product of thorium and uranium minerals.

### ATOMIC & PHYSICAL PROPERTIES

- Ionisation enthalpy decreases from oxygen to polonium.
- Oxygen atom has less negative electron gain enthalpy than S because of the compact nature of the oxygen atom. However from the S onwards the value again becomes less negative upto polonium.
- Electronegativity gradually decreases from oxygen to polonium, metallic character increases from oxygen to polonium.
- Oxygen & S are non-metals, selenium and tellurium are metalloids. Po is a radioactive metal.
- Oxygen is a diatomic gas while S, Se & Te are octa atomic  $\text{S}_8$ ,  $\text{Se}_8$  &  $\text{Te}_8$  molecules which has puckered 'ring' structure.

### CHEMICAL PROPERTIES

- Common oxidation state:-  $-2, +2, +4$  &  $+6$ .
- Due to inert effect, the stability of  $+6$  decreases down the group and stability of  $+4$  increases.

Oxygen exhibits  $+1$  state in  $\text{O}_2\text{F}_2$ ,  $+2$  in  $\text{OF}_2$ .

- Anomalous behavior of oxygen-due to its small size, high electronegativity and absence of d-orbitals.

### TREND IN PROPERTIES

Acidic character- $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

Thermal stability- $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

Reducing character- $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

Boiling point- $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$

Reducing property of dioxides- $\text{SO}_2 > \text{SeO}_2 > \text{TeO}_2$

Stability of halides- $\text{F} > \text{Cl} > \text{Br} > \text{I}$

## HALIDES

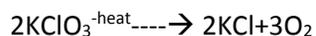
DI HALIDES: $\text{sp}^3$  hybridisation but angular structure.

TETRA HALIDES: $\text{sp}^3$  hybridisation-see-saw geometry

HEXA HALIDES: $\text{sp}^3\text{d}^2$ , octahedral  $\text{SF}_6$

## DIOXYGEN

Prepared by heating oxygen containing salts like chlorates, nitrates



## OXIDES

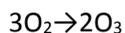
A binary compound of oxygen with another element is called oxide. Oxides can be classified on the basis of nature

- Acidic Oxides:-Non metallic oxides. Aqueous solutions are acids. Neutralize bases to form salts. Ex:  $\text{SO}_2, \text{CO}_2, \text{N}_2\text{O}_5$  etc.
- Basic Oxides:metallic oxides. Aqueous solutions are alkalis. Neutralize acids to form salts. Ex:  $\text{Na}_2\text{O}, \text{K}_2\text{O}$ , etc.
- Amphoteric oxides:-some metallic oxides exhibit a dual behavior. Neutralize both acids & bases to form salts. Ex:  $\text{Al}_2\text{O}_3, \text{SbO}_2, \text{SnO}$ , etc.....

## OZONE

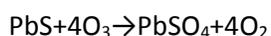
### PREPARATION

Prepared by subjecting cold, dry oxygen to silent electric discharge.



### PROPERTIES

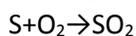
Due to the ease with which it liberates atoms of nascent oxygen, it acts as a powerful oxidizing agent. For eg:- it oxidises lead sulphide to lead sulphate and iodide ions to iodine.



## SULPHUR DIOXIDE

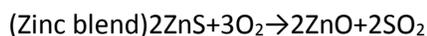
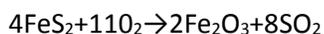
### PREPARATION

Burning of S in air



Roasting of sulphide minerals

(Iron pyrites)



### PROPERTIES

- Highly soluble in water to form solution of sulphurous acid  
 $SO_2 + H_2O \rightarrow H_2SO_3$
- $SO_2$  reacts with  $Cl_2$  to form sulphuryl chloride  
 $SO_2 + Cl_2 \rightarrow SO_2Cl_2$
- It reacts with oxygen to form  $SO_3$  in presence of  $V_2O_5$  catalyst  
 $2SO_2 + O_2 \rightarrow 2SO_3$
  
- Moist  $SO_2$  behaves as a reducing agent. It converts  $Fe(III)$  ions to  $Fe(II)$  ions & decolourises acidified potassium permanganate (VII) solution (It is the test for the gas).

### SULPHURIC ACID

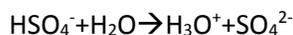
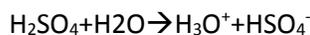
#### PREPARATION

It is manufactured by contact process which involves 3 steps

1. Burning of S or Sulphide ores in air to generate  $SO_2$ .
2. Conversion of  $SO_2$  to  $SO_3$  in presence of  $V_2O_5$  catalyst
3. Absorption of  $SO_3$  in  $H_2SO_4$  to give oleum.

#### PROPERTIES

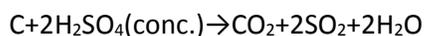
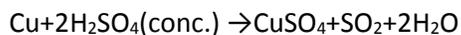
1. In aqueous solution it ionizes in 2 steps



2. It is a strong dehydrating agent Eg:- charring action of sugar



3. It is a moderately strong oxidizing agent.



### GROUP 17 ELEMENTS (HALOGENS)

Group 17 elements: F, Cl, Br, I, At

General electronic configuration:  $ns^2np^5$

Element	Occurrence
---------	------------

Fluorine	As insoluble fluorides (fluorspar $\text{CaF}_2$ , Cryolite and fluoroapatite)
Cl, Br, I	Sea water contains chlorides, bromides and iodides of Sodium, potassium magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass). Certain forms of marine life (various seaweeds)

### ATOMIC & PHYSICAL PROPERTIES

- i. Atomic & ionic radii increase from fluorine to iodine.
- ii. Ionization enthalpy gradually decreases from fluorine to iodine due to increase in atomic size.
- iii. Electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine & repulsion between newly added electron & electrons already present in its small 2p orbital.
- iv. Electronegativity decreases from fluorine to iodine. Fluorine is the most electronegative element in the periodic table.
- v. The color of halogens is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.
- vi. Bond dissociation enthalpy of fluorine is smaller than that of chlorine is due to electron-electron repulsion among the lone pair in fluorine molecules where they are much closer to each other than in case of chlorine. The trend:  $\text{Cl-Cl} > \text{Br-Br} > \text{F-F} > \text{I-I}$ .

### CHEMICAL PROPERTIES

OXIDATION STATES: -1. However, chlorine, bromine & iodine exhibit +1, +3, +5, +7 oxidation states also.

Fluorine forms two oxides  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$ . These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen.

**Anomalous behavior of fluorine-** due to its small size, highest electronegativity, low F-F bond dissociation enthalpy and absence of d-orbitals.

### TRENDS IN PROPERTIES

Oxidizing property –  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Acidic strength-  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

Stability & bond dissociation enthalpy-  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

Stability of oxides of halogens-  $\text{I} > \text{Cl} > \text{Br}$

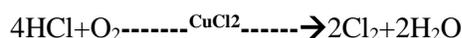
Ionic character of halides –  $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$

### CHLORINE

#### PREPARATION

1.  $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
2.  $4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{MnCl}_2 + 4\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$
3.  $2\text{KMnO}_4 + 16\text{HCl} \rightarrow 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 5\text{Cl}_2$

#### 4. DEACON'S PROCESS



5. By electrolysis of brine solution.  $\text{Cl}_2$  is obtained at anode.

## PROPERTIES

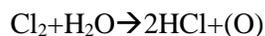
- i. With cold and dilute  $\text{Cl}_2$  produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.



- ii. With dry slaked lime it gives bleaching powder.



- iii. It is a powerful bleaching agent; bleaching action is due to oxidation



Colored substance + (O)  $\rightarrow$  colorless substance

- iv. Action of concentrated  $\text{H}_2\text{SO}_4$  on  $\text{NaCl}$  give  $\text{HCl}$  gas.



3:1 ratio of conc.  $\text{HCl}$  &  $\text{HNO}_3$  is known as aquaregia & it is used for dissolving noble metals like Au and Pt.

## OXOACIDS OF HALOGENS (SEE TABLE 7.10 & FIG. 7.8)

Interhalogen compounds are prepared by direct combination of halogens.

Ex:  $\text{ClF}$ ,  $\text{ClF}_3$ ,  $\text{BrF}_5$ ,  $\text{IF}_7$

They are more reactive than halogens because  $\text{X-X}'$  is weaker than  $\text{X-X}$  bonds in halogens (except  $\text{F-F}$ ).

TYPE	STRUCTURE
$\text{XX}'_3$	Bent T-shaped
$\text{XX}'_5$	Square pyramidal
$\text{XX}'_7$	Pentagonal bipyramidal

## GROUP 18 ELEMENTS

GROUP 18 ELEMENTS: He, Ne, Ar, Kr, Xe & Rn

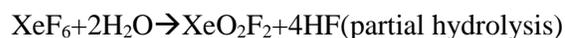
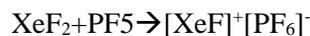
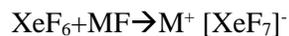
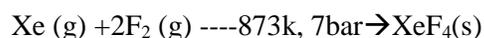
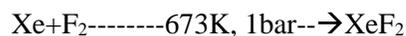
General electronic configuration:  $ns^2np^6$

Atomic radii- large as compared to other elements in the period since it corresponds to Vander Waal radii.

Inert – due to complete octet of outermost shell, very high ionization enthalpy & electron gain enthalpies are almost zero.

The first noble compound prepared by Neil Bartlett was  $XePtF_6$  & Xenon.  $O_2^+PtF_6^-$ . led to the discovery of  $XePtF_6$  since first ionization enthalpy of molecular oxygen ( $1175kJmol^{-1}$ ) was almost identical with that of xenon ( $1170kJmol^{-1}$ ).

### **PROPERTIES**



### **SOLVED QUESTIONS**

#### **1 MARK QUESTIONS**

1. Ammonia has higher boiling point than phosphine. Why?

-AMMONIA FORMS INTERMOLECULAR H-BOND.

2. Why  $BiH_3$  the strongest reducing agent amongst all the hydrides of group 15 elements ?
3. Why does  $PCl_3$  fume in moisture ?

In the presence of  $(H_2O)$ ,  $PCl_3$  undergoes hydrolysis giving fumes of  $HCl$ .



4. What Happens when  $H_3PO_3$  is Heated ?

It disproportionate to give orthophosphoric acid and Phosphine .



5. Why  $H_2S$  is acidic and  $H_2S$  is neutral ?

The S---H bond is weaker than O---H bond because the size of S atom is bigger than that of O atom. Hence H<sub>2</sub>S can dissociate to give H<sup>+</sup> ions in aqueous solution.

6. Name two poisonous gases which can be prepared from chlorine gas?

Phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub>NO<sub>2</sub>)

7. Name the halogen which does not exhibit positive oxidation state.

Fluorine being the most electronegative element does not show positive oxidation state.

8. Iodine forms I<sub>3</sub><sup>-</sup> but F<sub>2</sub> does not form F<sub>3</sub><sup>-</sup> ions. Why?

Due to the presence of vacant d-orbitals, I<sub>2</sub> accepts electrons from I<sup>-</sup> ions to form I<sub>3</sub><sup>-</sup> ions, but because of d-orbitals F<sub>2</sub> does not accept electrons from F<sup>-</sup> ions to form F<sub>3</sub><sup>-</sup> ions.

9. Draw the structure of peroxosulphuric acid.

10. Phosphorus forms PCl<sub>5</sub> but nitrogen cannot form NCl<sub>5</sub>. Why?

Due to the availability of vacant d-orbitals in P.

## 2 MARK QUESTION (SHORT ANSWER TYPE QUESTION)

1. Why is HF acid stored in wax coated glass bottles?

Ans. This is because HF does not attack wax but reacts with glass. It dissolves SiO<sub>2</sub> present in glass forming hydrofluorosilicic acid.



2. What is laughing gas? Why is it so called? How is it prepared?

Ans. Nitrous oxide (N<sub>2</sub>O) is called laughing gas, because when inhaled it produced hysterical laughter. It is prepared by gently heating ammonium nitrate.



3. Give reasons for the following:

(i) Conc. HNO<sub>3</sub> turns yellow on exposure to sunlight.

(ii) PCl<sub>5</sub> behaves as an ionic species in solid state.

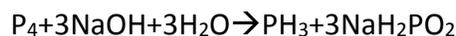
Ans. (i) Conc HNO<sub>3</sub> decomposes to NO<sub>2</sub> which is brown in color & NO<sub>2</sub> dissolves in HNO<sub>3</sub> to form

yellow.

(ii) It exists as  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  in solid state.

4. What happens when white P is heated with conc. NaOH solution in an atmosphere of  $\text{CO}_2$ ? Give equation.

Ans. Phosphine gas will be formed.



5. How is ozone estimated quantitatively?

Ans. When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodide is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating  $\text{O}_3$  gas.

6. Are all the five bonds in  $\text{PCl}_5$  molecule equivalent? Justify your answer.

$\text{PCl}_5$  has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

7.  $\text{NO}_2$  is coloured and readily dimerises. Why?

$\text{NO}_2$  contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerization; it is converted to stable  $\text{N}_2\text{O}_4$  molecule with even number of electrons.

8. Write the balanced chemical equation for the reaction of  $\text{Cl}_2$  with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify:



Yes, chlorine from zero oxidation state is changed to -1 and +5 oxidation states.

9. Account for the following.

(i)  $\text{SF}_6$  is less reactive than.

(ii) Of the noble gases only xenon chemical compounds.

Ans. (i) In  $\text{SF}_6$  there is less repulsion between F atoms than in  $\text{SF}_4$ .

(ii) Xe has low ionisation enthalpy & high polarising power due to larger atomic size.

10. With what neutral molecule is  $\text{ClO}^-$  isoelectronic? Is that molecule a Lewis base?

Ans.  $\text{ClF}$ . Yes, it is Lewis base due to presence of lone pair of electron.

11. Arrange the following in the order of property indicated against each set.

i)  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  (Increasing bond enthalpy)

ii)  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$  (Increasing acidic character)

Ans: i)  $HI < HBr < HCl < HF$

$H_2O < H_2S < H_2Se < H_2Te$

### 3 MARK QUESTIONS

1(i) why is He used in diving apparatus?

(ii) Noble gases have very low boiling points. Why?

(iii) Why is ICl more reactive than  $I_2$ ?

Ans. (i) It is not soluble in blood even under high pressure.

(ii) Being monoatomic they have weak dispersion forces.

(iii) I-Cl bond is weaker than I-I bond

2. Complete the following equations.

(i)  $XeF_4 + H_2O \rightarrow$

(ii)  $Ca_3P_2 + H_2O \rightarrow$  CBSE-2014

(iii)  $Cu + H_2SO_4$  (conc.)  $\rightarrow$

(iv)  $AgCl_{(s)} + NH_3$  (aq)  $\rightarrow$

Ans. (i)  $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(ii)  $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

(iii)  $Cu + H_2SO_4$  (conc.)  $\rightarrow CuSO_4 + SO_2 + 2H_2O$

(iv)  $AgCl_{(s)} + 2NH_3$  (aq)  $\rightarrow [Ag(NH_3)_2]Cl_{(aq)}$

3. (i) How is  $XeOF_4$  prepared? Draw its structure.

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

Ans. (i) Partial hydrolysis of  $XeOF_4$

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

Structure-square pyramidal. See Fig 7.9

(ii) Its reaction with iron produces  $H_2$

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

4. A) Draw the structure of the following molecules i)  $\text{XeOF}_4$  ii)  $\text{H}_2\text{SO}_4$   
b) Write the structural difference between white phosphorous and red phosphorous

Ans. a) Refer NCERT book

b) white phosphorous consist of discrete tetrahedral  $\text{P}_4$  molecule whereas red phosphorous is a polymeric structure..(Draw the structures)

5. Account for the following

- i.  $\text{PCl}_5$  is more covalent than  $\text{PCl}_3$
- ii. Iron on reaction with HCl forms  $\text{FeCl}_2$  and not  $\text{FeCl}_3$
- iii. The two O – O bond lengths in the ozone molecule are equal.

Ans.

- i. Since pentavalent metal ion has higher polarizing power than trivalent metal ion. Thus  $\text{PCl}_5$  is more covalent than  $\text{PCl}_3$ .
- ii. HCl reacts with Fe and produces  $\text{H}_2$ . Liberation of hydrogen prevents the formation of ferric chloride.
- iii.  $\text{O}_3$  is having resonance hybrid structure with 1.5 bond order.

#### 5 MARK QUESTION

1. Account for the following.

(i) Noble gas form compounds with  $\text{F}_2$  &  $\text{O}_2$  only.

(ii) Sulphur shows paramagnetic behavior.

(iii) HF is much less volatile than HCl.

(iv) White phosphorous is kept under water.

(v) Ammonia is a stronger base than phosphine.

Ans. (i)  $\text{F}_2$  &  $\text{O}_2$  are best oxidizing agents.

(ii) In vapour state sulphur partly exists as  $\text{S}_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $\text{O}_2$  and, hence, exhibit paramagnetism.

(iii) HF is associated with intermolecular H bonding.

(iv) Ignition temperature of white phosphorous is very low (303 K). Therefore on exposure to air, it spontaneously catches fire forming  $\text{P}_4\text{O}_{10}$ . Therefore to protect it from air, it is kept under water.

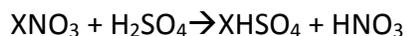
(v) Due to the smaller size of N, lone pair of electrons is readily available.

2. When Conc.  $\text{H}_2\text{SO}_4$  was added to an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were added in to test tube. On cooling gas (A) changed in to a colourless gas (B).

(a) Identify the gases 'A' and 'B'

(b) Write the equations for the reactions involved

The gas 'A' is  $\text{NO}_2$  whereas 'B' is  $\text{N}_2\text{O}_4$ .



Salt (conc.)



Blue Brown (A)



Colourless (B)

3. Arrange the following in the increasing order of the property mentioned.

(i)  $\text{HOCl}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$  (Acidic strength)

(ii)  $\text{As}_2\text{O}_3$ ,  $\text{ClO}_2$ ,  $\text{GeO}_3$ ,  $\text{Ga}_2\text{O}_3$  (Acidity)

(iii)  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$  (HEH bond angle)

(iv)  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  (Acidic strength)

(v)  $\text{MF}$ ,  $\text{MCl}$ ,  $\text{MBr}$ ,  $\text{MI}$  (ionic character)

Ans. (i) Acidic strength:  $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

(ii) Acidity:  $\text{Ga}_2\text{O}_3 < \text{GeO}_2 < \text{AsO}_3 < \text{ClO}_2$

(iii) Bond angle:  $\text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$

(iv) Acidic strength:  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

(v) Ionic character:  $\text{MI} < \text{MBr} < \text{MCl} < \text{MF}$

## ASSIGNMENTS

Very short answer type questions:

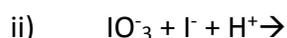
1. Which of  $\text{NH}_3$  and  $\text{H}_3\text{O}^+$  has higher bond angle and why?
2. Which of  $\text{PH}_4\text{I}$  and  $\text{PH}_4\text{Cl}$  is more stable and why?
3. What is the basicity of  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$ ?

4. NH<sub>3</sub> is easily liquefiable than PH<sub>3</sub>?
5. Which of NH<sub>3</sub> and PH<sub>3</sub> is stronger Lewis base and why?
6. PH<sub>3</sub> has lower boiling point than NH<sub>3</sub>. Explain.
7. Why are halogens coloured.
8. What are chalcogens?
9. Which noble gas is Radioactive?
10. Explain why fluorine always exhibit an oxidation state of - 1 only.
11. Which compound led to the discovery of compounds of noble gas?
12. Name the most electronegative element.
13. Why is OF<sub>6</sub> compound not known?
14. Why is N<sub>2</sub> not particularly reactive?
15. Ammonia acts as aligned. Explain.
16. Short answer type questions:
  - 1) Write Phosphorous is more reactive than red phosphorous. Explain.
  - 2) Why do noble gases have comparatively large atomic sizes?
  - 3) Arrange in decreasing order of Ionic character

M – F, M – Cl, M – Br, M – I

17. Phosphinic acid behaves as a monoprotic acid
18. Arrange the following in the order of property indicated:
  - a) AS<sub>2</sub>O<sub>3</sub>, ClO<sub>2</sub>, GeO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>\_\_\_ Increasing acidity
  - b) H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te\_\_\_ Increasing acid strength.
  - c) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> ---- Bond Energy

19. Complete the following:



20. How would you account for following?

i) Enthalpy of dissociation of F<sub>2</sub> is much less than that of Cl<sub>2</sub>.

ii) Sulphur in vapour state exhibits paramagnetism.

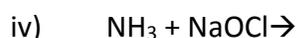
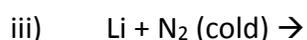
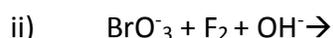
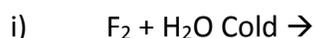
21. Draw structures of following:

a) Per-oxomonosalphuric acid - H<sub>2</sub>SO<sub>5</sub>

b) XeF<sub>4</sub>

22. Level – III

- 1) Complete and balance:



2) Despite lower electron affinity of F<sub>2</sub>, is stronger oxidising agent than Cl<sub>2</sub>. Explain.

23. Give reason for the following observations.

[i] Noble gases are mostly chemically inert

[ii] Nitrogen does not form pentahalide

[iii] Bismuth is a strong oxidising agent in pentavalent state

[iv] Nitric oxide becomes brown when released in air.

[v]  $\text{PCl}_5$  is ionic in nature in the solid state.

24. Identify hybridization state of central atom and use concept of VSEPR theory .also its shape (geometry) and draw the structure.

	LP	BP	Hybrid	Geometry	Shape
$\text{PCl}_3$					
$\text{PCl}_5$					
$\text{BrF}_3$					
$\text{XeF}_2$					
$\text{XeF}_4$					
$\text{XeOF}_4$					
$\text{XeO}_3$					
$\text{XeF}_6$					
$\text{XeO}_2\text{F}_2$					
$\text{SF}_4$					
$\text{PH}_3$					