CH7 – THE P BLOCK ELEMENTS

6.1. Which of the ores mentioned can be concentrated by magnetic separation method?

Ans: 7.1. Why are pentahalides more covalent than trihalidcs?

Ans: The group 15 elements have 5 e^{-1} s in their valence shell. It is difficult to lose $3e^{-1}$s to form E^{3+} and even more difficult to lose $5e^{-1}$ s to form E^{5+}. Thus, they have very little tendency to form ionic compounds. Further, since the elements in +5 state have less tendency to lose e^{-1}s than in the +3 state, elements in +5 state have more tendency to share e^{-1} s and hence pentahalides are more covalent than trihalides.

7.2. Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15 elements? (C.B.S.E. 2013)

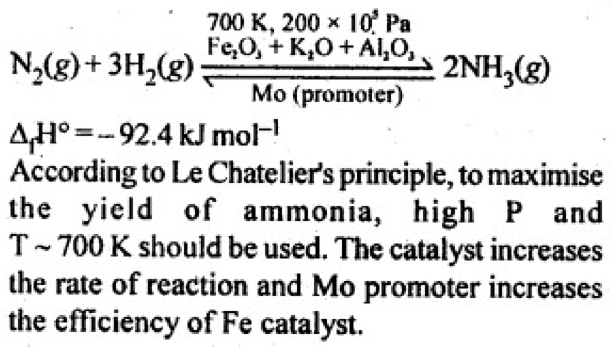
Ans: Down the group, the atomic size of the element (E) increases and the bond length of the corresponding E—H bond also increases. This adversely affects the bond dissociation enthalpy. This means that amongst the trihydrides of the members of nitrogen family, the bond dissociation enthalpy of Bi—H bond is the least. Therefore, BiH_3 is the strongest reducing agent among the hydrides of group 15 elements.

7.3. Why is N_2 less reactive at room temperature?

Ans: Due to presence of triple bond between two N-atoms (N = N), the bond dissociation energy of N_2 is very high. As a result, N_2 becomes less reactive at room temperature.

7.4. Mention the conditions required to maximise the yield of ammonia.

Ans: Ammonia is prepared by Haber's process as given below:



$$N_2(g) + 3H_2(g) \underset{\text{Mo (promoter)}}{\overset{\text{700 K, } 200 \times 10^5 \text{ Pa}}{\overset{Fe_2O_3 + K_2O + Al_2O_3}{\rightleftharpoons}}} 2NH_3(g)$$

$$\Delta_f H^\circ = -92.4 \text{ kJ mol}^{-1}$$

According to Le Chatelier's principle, to maximise the yield of ammonia, high P and T ~ 700 K should be used. The catalyst increases the rate of reaction and Mo promoter increases the efficiency of Fe catalyst.

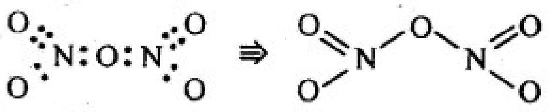
7.5. How does ammonia react with a solution of Cu^{2+}?

Ans:

$$Cu^{2+}(aq) + 4NH_4OH(aq) \rightarrow \underset{\text{tetrammine copper (II) ion (deep blue)}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$$

7.6. What is the covalence of nitrogen in N_2O_5 ?

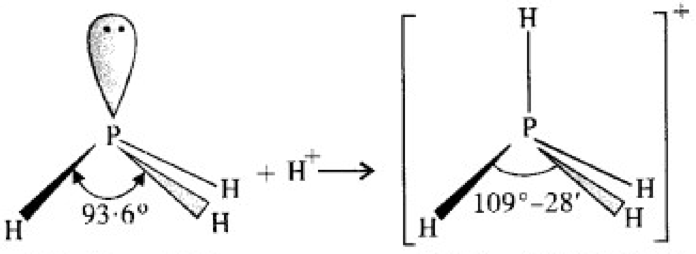
Ans: In N_2O_5 , each N-atom has four shared pairs of e-1 s as shown:



Thus, the covalency of N is 4.

7.7. Why is bond angle in PH+4 ion higher than in PH_3 ? (Pb. Board 2009)

Ans: In both PH_3 and PH+4 ion, the phosphorus atom is sp^3 hybridised. However, in PH_3 the central atom has apyramidal structure due to the presence of lone electron pair on the phosphorus atom.



PH_3 (Pyramidal) PH_4^+ ion (Tetrahedral)

Because of lone pair : shared pair repulsion which is more than that of shared pair : shared pair repulsion, the bond angle in PH_3 is nearly 93-6°. In PH+4 ion, there is no lone electron pair on the phosphorus atom. It has a tetrahedral structure with bond angle of 109°-28′. Thus, the bond angle in PH+4 ion is higher than in PH_3.

7.8. What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2?

Ans:

$$P_4 + 3NaOH + 3H_2O \xrightarrow[CO_2 atm]{\Delta} \underset{\text{Phosphine}}{PH_3} + \underset{\text{sod. hypo-phosphite}}{3NaHPO_2}$$

7.9. What happens when PCl_5 is heated?

Ans:

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

On heating, the less stable axial bonds break to form PCl_3.

7.10. Write a balanced equation for the hydrolytic reaction of PC is in heavy water.

Ans:

$$PCl_5 + D_2O \longrightarrow POCl_3 + 2DCl$$

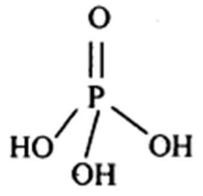
$$POCl_3 + 3D_2O \longrightarrow D_3PO_4 + 3DCl$$

$$PCl_5 + 4D_2O \longrightarrow D_3PO_4 + 5DCl$$

7.11. What is the basicity of H_3PO_4?

Ans:

H_3PO_4 is tribasic as shown below :



Due to three ionizable P–OH bonds, H_3PO_4 is tribasic.

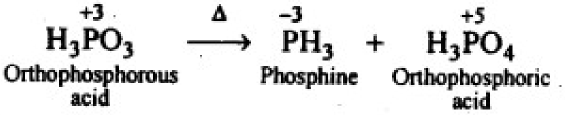
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$$

7.12. What happens when H_3PO_4 is heated?

Ans: On heating, H_3PO_3 disproportionates to form PH_3 and H_3PO_4 with O.S. of-3and + 5.



$$\underset{\text{Orthophosphorous acid}}{\overset{+3}{H_3PO_3}} \xrightarrow{\Delta} \underset{\text{Phosphine}}{\overset{-3}{PH_3}} + \underset{\text{Orthophosphoric acid}}{\overset{+5}{H_3PO_4}}$$

7.13. List the important sources of sulphur.

Ans: Sulphur mainly occurs in the combined states in earth's crust in the form of sulphates and sulphides.

Sulphates : gypsum ($CaSO_4.2H_2O$); epsom ($MgSO_4.7H_2O$); baryte ($BaSO_4$), etc.

Sulphides : Galena (PbS); zinc blende (ZnS); copper pyrites (CuFeS2); iron pyrites

(FeS_2), etc. Traces of sulphur occur'as H_2S and in organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool.

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

Ans: The thermal stability of hydrides of group 16 elements decreases down the group. This is because down the group, size of the element (M) increases, M-H bond length increases and thus, stability of M-H bond decreases so that it can be broken down easily. Hence, we have order of thermal stability as $H_2O > H_2S > H_2Se > H_2Te > H_2PQ$

7.15. Why is H_2O a liquid and H_2S a gas?

Ans: Due to high electronegativity of O than S, H_2O undergoes extensive intermolecular H-bonding. As a result, H_2O exists as an associated molecule in which each O is tetrahedrally surrounded by four H_2O molecules. Therefore, H_2O is a liquid at room temperature.

On the other hand,H_2S does not undergo H- bonding. It exists as discrete molecules which are held together by weak van der waals forces of attraction. A small amount of energy is required to break these forces of attraction. Therefore, H_2S is a gas at room temperature.

7.16. Which of the following does not react with oxygen directly? Zn, Ti, Pt, Fe

Ans: Platinum (Pt) is a noble metal and does not react with oxygen directly.

7.17. Complete the following reactions:

(i)$C_2H_2 + O_2$ -> (ii) 4Al + 3 O_2 ->

Ans:

(i) $C_2H_4 + 3O_2 \xrightarrow{\text{Heat}} 2CO_2 + 2H_2O$

(ii) $4Al + 3O_2 \xrightarrow{\text{Heat}} 2Al_2O_3$

7.18. Why does O_3 act as a powerful oxidising agent?

Ans: On heating, O_3 readily decomposes to give O_2 and nascent oxygen.

$$O_3 \xrightarrow{\text{Heat}} O_2 + O(\text{nascent oxygen})$$

Since nascent oxygen is very reactive, therefore, O_3 acts as a powerful oxidising agent.

7.19. How is O_3 estimated quantitatively?

Ans: When O_3 is treated with excess of KI solution buffered with borate buffer (pH = 9.2), I2 is liberated quantitatively.

$$2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

The I_2 thus liberated is titrated against a standard solution of sodium thiosulphate using starch as an indicator.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

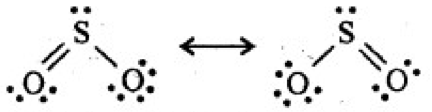
7.20. What happens when sulp'hur dioxide is passed through an aqueous solution of Fe(III) salt?

Ans: SO_2 acts as a reducing agent and reduces aqueous solution of Fe (III)salt to Fe (II) salt.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$
$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$$
$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

7.21. Comment on the nature of two S-O bonds formed in S02 molecule. Are the two S-O bonds in this molecule equal ?

Ans: SO_2 exists as an angular molecule with OSO bond angle of 119.5°. It a resonance hybrid of two canonical-forms:



Due to resonance, the two π-bonds are equal.

7.22. How is the presence of SO_2 detected?

Ans: SO_2 is a pungent smelling gas. It can be detected by two test:

7.23. Mention three areas in which H_2SO_4 plays an important role.

Ans: (i) Sulphuric acid is used for the manufacture of a number of chemicals like hydrochloric acid, phosphoric acid, nitric acid along with a large number of organic compounds.

(ii) A mixture of concentrated nitric acid and concentrated sulphuric acid is used in the manufacture of explosives like picric acid, T.N.T, dynamite etc.

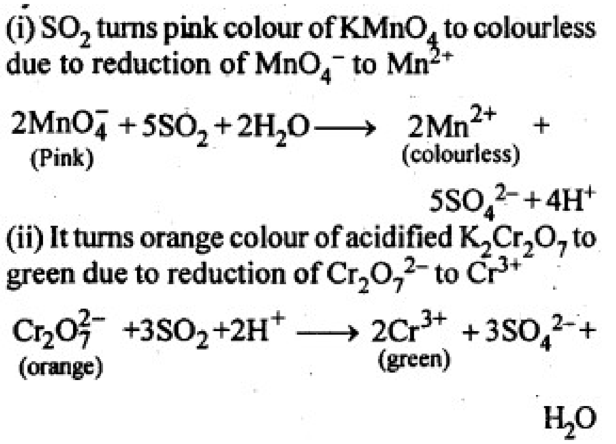
(iii) Dilute solution of acid is employed in petroleum refining in order to remove the unwanted impurities of sulphur.

Question 24.

Write the conditions to maximise the yield of H_2SO_4 by Contact process.

Solution:

The key step in the manufacture of sulphuric acid is oxidation of SO_2 to SO_3 in presence of V_2O_5 catalyst.



(i) SO_2 turns pink colour of $KMnO_4$ to colourless due to reduction of MnO_4^- to Mn^{2+}

$$\underset{\text{(Pink)}}{2MnO_4^-} + 5SO_2 + 2H_2O \longrightarrow \underset{\text{(colourless)}}{2Mn^{2+}} + 5SO_4^{2-} + 4H^+$$

(ii) It turns orange colour of acidified $K_2Cr_2O_7$ to green due to reduction of $Cr_2O_7^{2-}$ to Cr^{3+}

$$\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 3SO_2 + 2H^+ \longrightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O$$

The reaction is exothermic and reversible. Hence, low temperature and high pressure are the favourable conditions for maximum yield of SO_3. In practice a pressure of 2 bar and temperature of 720 K is maintained.

Question 25.

Why is $K_{a2} \ll K_{a1}$ for H_2SO_4 in water?

Solution:

H_2SO_4 is a very strong acid in water largely because of its first ionisation to H_3O^+ and HSO_4^- The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. That is why, $K_{a2} \ll K_{a1}$.

Question 26.

Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising powers of F_2 and Cl_2.

Solution:

The oxidising powers of both the members of halogen family are expressed in terms of their electron accepting tendency and can be compared as their standard reduction potential values.

$F_2 + 2e^- \rightarrow 2F^-$; $E° = 2\text{-}87$ V, $Cl_2 + 2e^- \rightarrow 2Cl^-$; $E° = 1\text{-}36$ V

Since the E° of fluorine is more than that of chlorine, it is a stronger oxidising agent.

Explanation : Three factors contribute towards the oxidation potentials of both the halogens. These are :

(i) Bond dissociation enthalpy: Bond dissociation enthalpy of F2 (158 kJ mol^{-1}) is less compared to that of Cl_2 (242·6 kJ mol^{-1}).

(ii) Electron gain enthalpy: The negative electron gain enthalpy of F (- 332·6 kJ mol^{-1}) is slightly less than of Cl (-348·5 kJ mol^{-1}).

(iii) Hydration enthalpy: The hydration enthalpy of F- ion (515 kJ mol^{-1}) is much higher than that of Cl- ion (381 kJ mol^{-1}) due to its smaller size.

From the available data, we may conclude that lesser bond dissociation enthalpy and higher hydration enthalpy compensate lower negative electron gain enthalpy of fluorine as compared to chlorine. Consequently, F_2 is a more powerful oxidising agent than Cl_2.

Question 27.

Give two examples to show the anomalous behaviour of fluorine.

Solution:

1. Ionisation enthalpy, electro-negativity and electrode potential are higher for fluorine than the expected trends of other halogen.
2. Fluorine does not show any positive oxidation state except in HOF.

Question 28.

Sea is the greatest source of some halogens. Comment.

Solution:

Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium but sodium chloride being the maximum makes sea water saline. Various sea weeds contain upto 0.5% iodine.

Question 29.

Give the reason for bleaching action of Cl_2.

Solution:

Chlorine bleaches by oxidation $Cl_2 + H_2O \rightarrow HCl + HOCl \rightarrow HCl + [O]$

The nascent oxygen reacts with dye to make it colourless.

Question 30.

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

Solution:

$COCl_2$ (phosgene), CCl_3NO_2 (tear gas)

Question 31.

Why is ICI more reactive than l2?

Solution:

In general, interhalogen compounds are more reactive than halogens due to weaker X-X’ bonding than X-X bond. Thus, ICI is more reactive than I_2.

Question 32.

Why is helium used in diving apparatus?

Answer:

Helium along with oxygen is used in the diving apparatus by the sea divers. Since it is very little soluble in blood, it reduces decompression and causes less discomfort to the diver in breathing. A mixture of helium and oxygen does not cause pain due to very low solubility of helium in blood as compared to nitrogen.

Question 33.

Balance the following equation :

$XeF_6 + H_2O \rightarrow XeO_2F_2 + 4HF$

Solution:

Question 34.

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

Solution:

Radon is radioactive with very short half-life which makes the study of chemistry of radon difficult.

NCERT EXERCISES

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

Sol: In group 15 of the Periodic Table, the elements, nitrogen ($_7N$), phosphorus ($_{15}P$), arsenic ($_{33}As$), antimony ($_{51}Sb$) and bismuth ($_{83}Bi$) are present. The elements of this group can exhibit various oxidation states ranging between -3 to + 5. Negative oxidation state will be exhibited when they combine with less electronegative element andpositive oxidation state will be exhibited with more electronegative element. Positive oxidation state becomes more favourable as we more down the group due to increasing metallic character & electropositivity. Although due to inert pair effect the stability of +5 state will also decrease. The only stable compound of Bi (V) is BiF_5.

The atomic (covalent) and ionic radii (in a particular oxidation state) of the elements of nitrogen family (group 15) are smaller than the corresponding elements of carbon family (group 14). On moving down the group, the covalent and ionic radii (in a particular oxidation state) increase with increase in atomic number. There is a considerable increase in covalent radius from N to P. However, from As to Bi, only a small increase is observed.

As the size increases on moving down the group, the ionisation enthalpy increases. The ionisation enthalpy of nitrogen group elements is more than the corresponding elements of oxygen group. This is because of more stable half-filled outermost p- subshell of nitrogen group elements. Electronegativity decreases down the group with increase in atomic size.

7.2. Why is the reactivity of nitrogen different from that of phosphorus?

Sol: Molecular nitrogen exists as a diatomic molecule (N_2) in which the two nitrogen atoms are linked to each other by triple bond ($N\equiv N$). It is a gas at room temperature. Multiple bonding is not possible in case of phosphorus due to its large size. It exists as P_4 molecule (solid) in which P atoms are linked to one another by single covalent bonds. Because of greater bond dissociation enthalpy (946 kJ mol^{-1}) of $N\equiv N$ bond, molecular nitrogen is very less reactive as compared to molecular phosphorus.

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

Sol: Hydrides: All elements of group 15 form gaseous hydrides of the type MH_3. In all the hydrides the central atom is sp^3 hybridized and their shape is pyramidal due to presence of lone pair of electrons.

(a)The basic strength of the hydrides decreases as we move down the group. Thus, NH_3 is the strongest base.

$NH_3 > PH_3 > AsH_3 > SbH_3$

(b)The thermal stability of the hydrides decreases as the atomic size increases, i.e., the M – H bond strength decreases which means reducing character increases.

(c)In the liquid state, the molecules of $NH_3$are associated due to hydrogen bonding. The molecules of other hydrides are not associated.

(d)NH_3 is soluble in water whereas other hydrides are insoluble.

(e)All the hydrides, except NH_3, are strong reducing agents and react with metal ions (Ag^+, Cu^{2+}, etc.) to form phosphides, arsenides or antimonides.

Halides: The elements of group 15 form two series of halides MX_3 and MX_5.

(a)All the elements of the group form trihalides. The ionic character of trihalides increases as we move down the group. Except NCl_3 all the trihalides are hydrolysed by water. This is due to the absence of d-orbitals in nitrogen.

(b)PF_3 is not hydrolysed because fluorine being more electronegative than oxygen forms more stable bonds with phosphorus than P – O bonds.

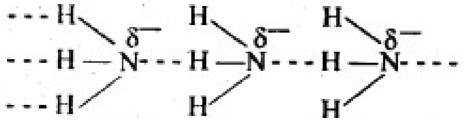
(c)N cannot form NX_5 because of non-availability of rforbitals. Bi cannot form BiX_3 because of reluctance of 6s electrons of Bi to participate in bond formation.
(d)The hybridisation of M in MX_3 is sp^3 and shape is pyramidal. M in MX_5 is sp^3 as hybridised and shape is trigonal pyramidal. The axial bonds in MX_5 are weaker and longer, So MX_5 are less stable and decompose on heating eg:

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

Oxides:
(a)Nitrogen forms a number of oxides. The rest of the members (P, As, Sb and Bi) of the group form two types of oxides : E_20_3 and E_2O_5.
(b)The reluctance of P, As, Sb and Bi to enter into pπ -pπ multiple bonding leads to cage structures of their oxides and they exist as dimers, E_4O_6 and E_5O_{10}.
(c)The basic nature of die oxides increases with increase in atomic number of the element. Thus, the oxides of nitrogen (except N_20 and NO), P (III) and As (III) are acidic, Sb (III) oxide is amphoteric and Bi (III) oxide is basic.

7.4. Why does NH_3 form hydrogen bond but PH_3 does not?

Sol: Nitrogen has an electronegativity value 3.0, which is much higher than that of H (2.1). As a result, N – H bond is quite polar and hence NH_3 undergoes intermolecular H – bonding.



Phosphorus have an electronegativity value 2-1. Thus, P – H bond is not polar and hence PH_3 does not undergo H – bonding.

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

Sol: In laboratory, nitrogen is prepared by heating an equimolar aqueous solution of ammonium chloride and sodium nitrite. As a result of double decomposition reaction, ammonium nitrite is formed. Ammonium nitrite is unstable and decompose to form nitrogen gas.

$$NH_4Cl\,(aq) + NaNO_2\,(aq) \longrightarrow NH_4NO_2\,(aq) + NaCl\,(aq)$$

$$NH_4NO_2\,(aq) \xrightarrow{\text{Heat}} N_2\,(g) + 2H_2O\,(l)$$

7.6. How is ammonia manufactured industrially?

Sol: Commercially, by Haber's process.

$$N_2(g)+3H_2(g) \underset{\Delta}{\overset{*}{\rightleftharpoons}} 2NH_3(g)$$

$$\Delta_f H = -46.1\,kJ\,mol^{-1}$$

iron oxide, K_2O, Al_20_3 The optimum conditions for the production of NH_3 are pressure of 200 atm and temperature of 100K.

7.7. Illustrate how copper metal can give different products on reaction with $HN0_3$.

Sol: On heating with dil $HN0_3$, copper gives copper nitrate and nitric oxide.

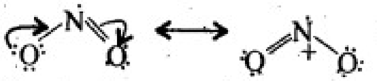
$$3Cu + 8HNO_3\,(dil) \xrightarrow{Heat} 3Cu(NO_3)_2 + 4H_2O + 2NO$$

With concentrated HNO_3, copper gives NO_2 instead of NO.

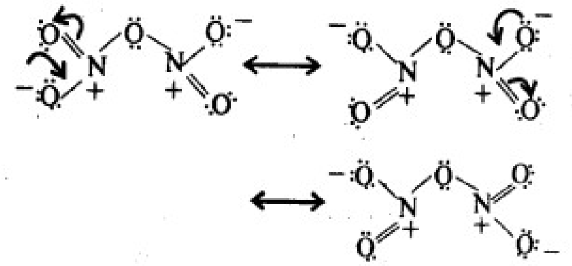
$$Cu + 4HNO_3(conc.) \xrightarrow{Heat} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

7.8. Give the resonating structures of $N0_2$ and N_2O_5.

Sol: Resonating structures of $N0_2$ are:



Resonating structures of N_2O_5 are:



7.9. The HNH angle value is higher than HPH, H AsH and HSbH angles. Why? (Hint: Can be explained on the basis of sp^3 hybridisation in NH_3 and only s-p bonding , between hydrogen and other elements of the group).

Sol: In all these cases, the central atom is sp^3 hybridized. Three of the four sp^3 orbitals form three σ-bonds, while the fourth contains the lone pair of electrons. On moving down from N to Sb, the electronegativity of the central atom goes on decreasing. As a result of this, bond pairs of electrons lie away and away from the central atom. This is because of the force of repulsion between the adjacent bond pairs goes on decreasing and the bond angles keep on decreasing from NH_3 to SbH_3. Thus, bond angles are in the order:

HNH (107·8°) > HPH (93·6°) > HAsH (91·8°) > HSbH (91·3°)

7.10. Why does $R_3P=0$ exist but $R_3N=0$ does not (R is an alkyl group) ?

Sol: Nitrogen does not have vacant d-orbitals on its valence shell. Therefore, it cannot extend its dπ-pπ bonding is not possible. As a result, the molecules of $R_3N = 0$ does not exist. However, phosphorus and rest of the members of the group 15 have vacant d-orbitals in the valence shell which can be involved in dπ-pπ bonding. Under the circumstances, $R_3P=0$ molecule can exist.

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

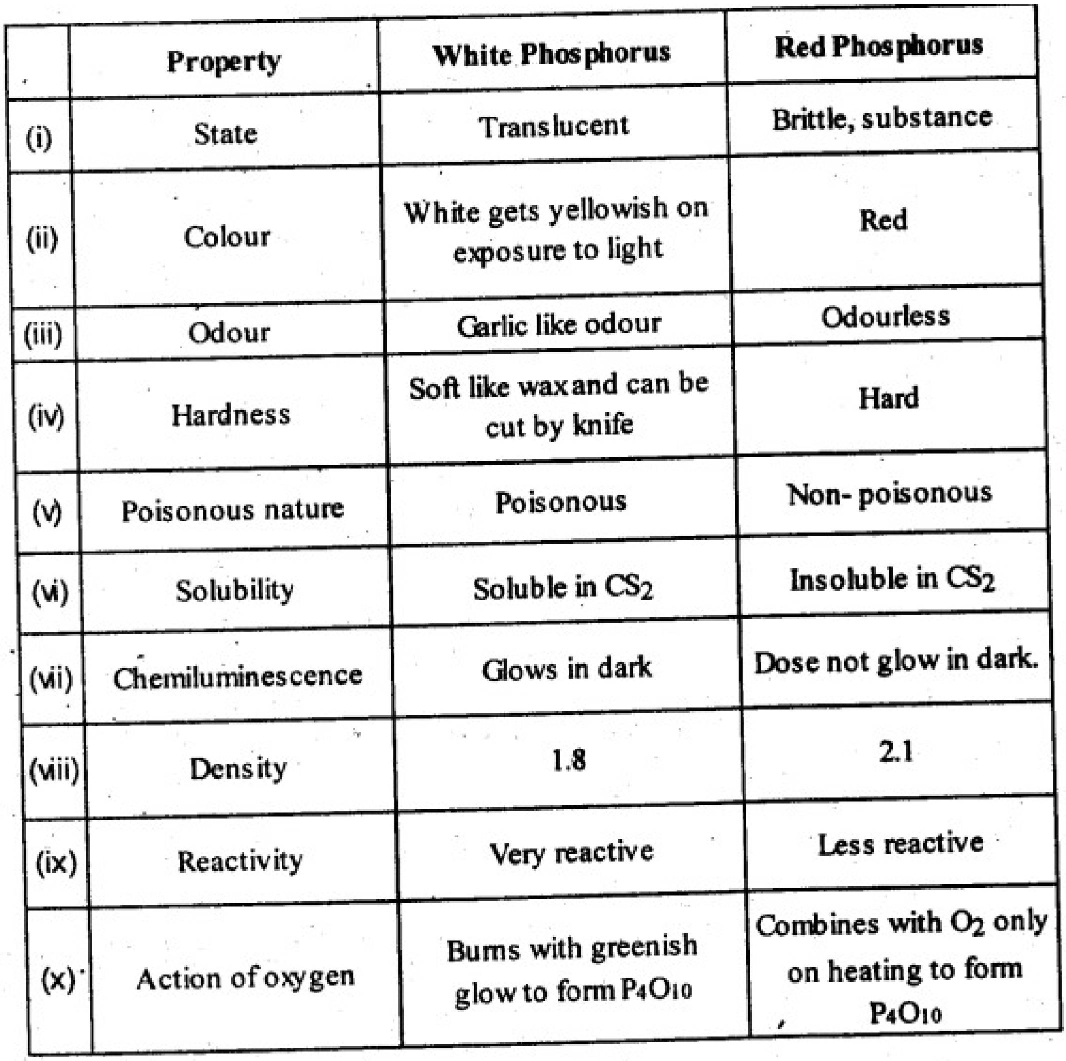
Sol: In both NH_3 and BiH_3, N and Bi have a lone paif of electrons on the central atom and hence should behave as Lewis bases. But NH_3 is much more basic than BiH_3. Since the atomic size of N is much smaller than that of Bi, therefore, electron density on N-atom is much higher than that on Bi-atom. Thus, the tendency of N in NH_3 to donate its lone pair of electrons is much more in comparison to tendency of Bi in BiH_3. Hence, NH_3 is more basic than BiH_3.

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

Sol: Nitrogen exists as a diatomic molecule having a triple bond between the two N-atoms, This is due its small size that it forms pπ-pπ multiple bonds with itself and with carbon /oxygen as well. On the other hand, phosphorus due to its larger size does not form multiple pπ-pπ bonds with itself. It prefers to form P – P single bonds and hence it exists as tetrahedral P_4 molecule.

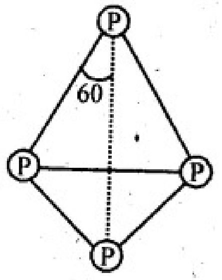
7.13. Write main differences between the properties of white phosphorus and red phosphorus.

Sol:

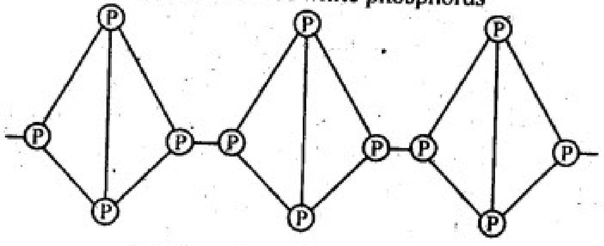


	Property	White Phosphorus	Red Phosphorus
(i)	State	Translucent	Brittle, substance
(ii)	Colour	White gets yellowish on exposure to light	Red
(iii)	Odour	Garlic like odour	Odourless
(iv)	Hardness	Soft like wax and can be cut by knife	Hard
(v)	Poisonous nature	Poisonous	Non- poisonous
(vi)	Solubility	Soluble in CS_2	Insoluble in CS_2
(vii)	Chemiluminescence	Glows in dark	Dose not glow in dark.
(viii)	Density	1.8	2.1
(ix)	Reactivity	Very reactive	Less reactive
(x)	Action of oxygen	Burns with greenish glow to form P_4O_{10}	Combines with O_2 only on heating to form P_4O_{10}

Structure of white and red phosphorus are given below:



(i) Structure of white phosphorus



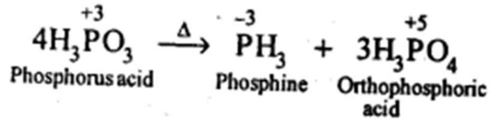
(ii) Structure of red phosphorus

7.14. Why does nitrogen show catenation properties less than phosphorus ? (C.B.S.E. Foreign 2009)

Sol: The valence shell electronic configuration of N is $2s^2 2p^3$. In order to complete the octet, the two nitrogen atoms share three electron pairs in the valence p-sub-shell and get linked by triple bond (N=N). Thus molecular nitrogen exists as discrete diatomic species and there is no scope of any self linking or catenation involving a number of nitrogen atoms. However, in case of phosphorus, multiple bonding is not feasible due to comparatively large atomic size of the element. Molecular phosphorus exists as tetra-atomic molecule (P4) in white phosphorus. These tetrahedrons are further linked by covalent bonds to form red variety which is in polymeric form. Thus, catenation in nitrogen is less than in phosphorus.

7.15. Give the disproportionation reaction of $H_3\,P0_3$.

Sol: On heating, $H_3\,P0_4$ undergoes self – oxidation-reduction, i.e: disproportionation to form PH_3.

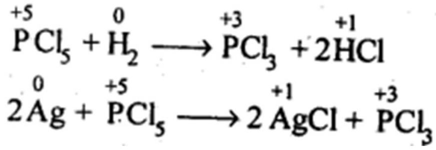


$$4H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} \overset{-3}{P}H_3 + 3H_3\overset{+5}{P}O_4$$

Phosphorus acid Phosphine Orthophosphoric acid

7.16. Can PCl_5 act as an oxidising as well as a reducing agent Justify.

Sol: The oxidation state of P in PCl_5 is+5. Since P has five electrons in its valence shell, therefore, it cannot donate electron and cannot increase its oxidation state beyond + 5, Thus, PCl_5 cannot act as a reducing agent. It can act as oxidizing agent by itself undergoing reduction.



$$\overset{+5}{P}Cl_5 + \overset{0}{H_2} \longrightarrow \overset{+3}{P}Cl_3 + 2\overset{+1}{H}Cl$$

$$2\overset{0}{Ag} + \overset{+5}{P}Cl_5 \longrightarrow 2\overset{+1}{Ag}Cl + \overset{+3}{P}Cl_3$$

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.

Sol: (1)Electronic configuration:

O (At. no. = 8) = [He] $2s^2\ 2p^4$

S (At. no. = 16) = [Ne] $3s^2\ 3p^4$

Se (At. no. = 34) = [Ar] $3d^{10}\ 4s^2\ 4p^4$

Te (At. no. = 52) = [Kr] $4d^{10}\ 5s^2\ 5p^4$,

Po (At. no. = 84) = [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$, Thus, all these elements have the same $ns^2\ np^4$ (n = 2 to 6) valence shell electronic configuration, hence are justified to be placed in group 16 of the Periodic Table.

(2)Oxidation state : Two more electrons are needed to acquire the nearest noble gas configuration. Thus, the minimum oxidation state of these elements should be – 2. O and to some extent S show – 2 oxidation state. Other element being more electropositive than O and S, do not show negative oxidation state. As these contain six electrons, thus, maximum oxidation state shown by them is+ 6. Other oxidation state shown by them are + 2 and + 4. O do not show+4 and + 6 oxidation state, due to the absence of d-orbitals. Thus, on the basis of maximum and minimum oxidation states, these elements are justified to be placed in the same group 16 of the periodic table.

(3)Hydride formation: All these elements share two of their valence electrons with 1 s- orbital of hydrogen to form hydrides of the general formula EH_2, i.e., H_20, H_2S, H_2Se, H_2Te and H_2Po. Thus, on the basis of hydride formation, these elements are justified to be placed in the same group 16 of the Periodic Table.

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

Sol: Due to the small size and high electronegativity, oxygen forms pπ- pπ multiple bonds. As a result, oxygen exists as diatomic (O_2) molecules. These molecules are held together by weak van der Waal's forces of attraction which can be overcome by collisions of the molecules at room temperature. Therefore, O_2 is a gas at room temperature. Due to its bigger size and lower electronegativity, sulphur does not form pn-pn multiple bonds. It prefers to form S – S single bonds. S – S single bond is stronger then O-O single bond. Thus, sulphur has higher tendency for catenation than oxygen. Due to higher tendency for catenation and lower tendency for pπ – pπ multiple bonds sulphur exits as octa-atomic (S_g) molecule. Due to bigger size, the force of attraction holding the S_g molecules together are much stronger which cannot be overcome by collisions of molecules at room temperature. Therefore, sulphur is solid at room temperature.

7.19. Knowing the electron gain enthalpy values of O—>O^- and O—>O^{2-} as -141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-?

Sol: Let us consider the reaction of oxygen with monopositve metal, we can have two compounds. MO(O in -1 state) and M_2O (O in -2 state). The energy required for formation of O^{-2} is compensated by increased coulombic attraction between M^+ and O^{-2}. Coulombic force of attraction, F_A is proportional to product of charges on ions i.e.

$$F_A \propto \frac{q_1 q_2}{r^2}$$

where q_1 and q_2 are charges on ions and r is distance between ions. Same logic can be applied if metal is dispositive.

7.20. Which aerosols deplete ozone?

Sol: Aerosols like chlorofluorocarbons (CFC's), i.e., freon (CCl_2F_2), depletes the ozone layer by supplying Cl* free radicals which convert O_3 to O_2

$$\underset{\text{Freon}}{CCl_2F_2}\,(g) \xrightarrow{h\nu} \cdot Cl(g) + \cdot CClF_2\,(g)$$
$$\cdot Cl\,(g) + O_3\,(g) \longrightarrow ClO\cdot(g) + O_2\,(g)$$
$$ClO\cdot(g) + \cdot O\,(g) \longrightarrow \cdot Cl\,(g) + O_2\,(g)$$

7.21. Describe the manufacture of H_2SO_4 by contact process?

Sol: Preparation of sulphuric acid:By Contact Process: Burning of sulphur or sulphide ores in presence of oxygen to produce SO_2. Catalytic oxidation of SO_2 with $O_2$to give SO_3 in the presence of V_2O_5.

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

Then SO_3 made to react with sulphuric acid of suitable normality to obtain a thick oily liquid called oleum.

$$SO_3(g) + H_2SO_4(\ell) \longrightarrow H_2S_2O_7(\ell)$$

Then oleum is diluted to obtain sulphuric acid of desired concentration.

$$H_2S_2O_7(\ell) + H_2O(\ell) \longrightarrow 2H_2SO_4(\ell)$$

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

7.22. How is SO_2 an air pollutant?

Sol: (1) SO_2 dissolves in moisture present in air to form H_2SO_4 which damages building materials especially marble (acid – rain).- $CaCO_3 + H_2SO_3$ ——->$CaSO_3 + H_20 + CO_2$

(2)It corrodes metals like Fe and steel. It also brings about fading and deterioration of fabrics, leather, paper, etc., and affecting the colour of paints.

(3)Even in low concentration (= 0.03 ppm), it has damaging effect on the plants. If exposed for a long time, i.e., a few days or weeks, it slows down the formation of chlorophyll i. e., loss of green colour. This is called chlorosis.

(4)It is strongly irritating to the respiratory track. It cause throat and eye irritation, resulting into cough, tears and redness in eyes. It also cause breathlessness and effects larynx i. e. „ voice box.

7.23. Why are halogens strong oxidising agents?

Sol: Members of the halogen family act as strong oxidising agents on account of their electron accepting tendency both in the molecular as well as atomic form.

$$\underset{(F_2,\ Cl_2,\ Br_2,\ I_2)}{X_2} + 2e^- \longrightarrow 2X^-$$

This is attributed to their high electronegativity, negative electron gain enthalpy values and alsp low bond dissociation enthalpies sinve they contain single covalent bonds(X — X) in their molecules. Fluorine is most reactive among the halogens and the reactivity down the group.

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

Sol: Cl, Br and I form four series of oxo acids of general formula HOX, HOXO, $HOXO_2$, and $H0XO_3$. In these oxo-adds, the oxidation states of halogens are + 1, + 3, + 5, and + 7 respectively. However, due to high electronegativity, small size and absence of d-orbitals, F does not form oxo-acids with + 3, + 5 and + 7, oxidation states. It just forms one oxo-acid (HOF).

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

Sol: Both .nitrogen (N) and chlorine (Cl) have electronegativity of 3.0. However, only nitrogen is involved in the hydrogen bonds (e.g., NH3) and not chlorine. This is due to smaller atomic size of nitrogen (atomic radius =70 pm) as compared to chlorine (atomic radius = 99) pm), therefore, N can cause greater polarisation of N-H bond than Cl in case of Cl—H bond.Consequently, N atom is involved in hydrogen bonding and not chlorine.

7.26. Write two uses of ClO_2

Sol: (1) ClO_2 is an excellent bleaching agent. It is 30 times stronger bleaching agent then the Cl_2. It is used as a bleaching agerit for paper pulp in paper industry and in textile industry. (2) ClO_2 is also a powerful oxidising agent and chlorinating agent. It acts as a germicide for disinfecting water. It is used for purifying drinking water.

7.27. Why are halogens coloured?

Sol: The halogens are coloured because their molecules absorb light in the visible region. As a result of which their electrons get excited to higher energy levels while the remaining light is transmitted. The color of halogens is the color of this transmitted light.

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

Sol:

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$3F_2(g) + 3H_2O(l) \longrightarrow 6H^+(aq) + 6F^-(aq) + O_3(g)$$

$$Cl_2(g) + H_2O(l) \longrightarrow HCl(aq) + HOCl(aq)$$

F_2 oxidisis water, whereas Cl_2 undergoes disproportion in water.

7.29. How can-you prepare Cl_2 from HCl and HCl from CI_2? Write reactions only.

Sol:

$$\underset{\text{Oxidising agent}}{MnO_2} + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

We can also used $KMnO_4$, $K_2Cr_2O_7$, etc., in place of MnO_2.

$$H_2 + Cl_2 \xrightarrow{\text{Diffused sunlight}} 2HCl$$

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

Sol: N. Bartlett observed that PtF_6 reacts with $O_2$to give an compound $O_2+ [PtF_6]^-$.

PtF_6 (g) + O_2 (g) ——–>$O_2+[PtF_6]^-$

Since the first ionization enthalpy of Xe (1170 kJ mol^{-1})is fairly close to that of 02 molecule (1175 kJ mol^{-1}), he thought that PtF_6 should also oxidise Xe to Xe^+. This inspired Bartlett to carryout the reaction between Xe and PtF_6. When PtF_6 and Xe were made to react, a rapid reaction took place and a red solid, $Xe+[PtF_6]^-$ was obtained.

$$Xe + PtF_6 \xrightarrow{278\text{ K}} Xe^+[PtF_6]^-$$

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

Sol:

(i) H_3PO_3

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

$\therefore x = +3$

(ii) PCl_3

$x + 3(-1) = 0$

$x = +3$

(iii) Ca_3P_2

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

$x = -3$

(iv) Na_3PO_4

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

$x = +5$

(v) POF_3

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

$x = +5.$

7.32. Write balanced equations for the following:

(i) NaCl is heated witlrsulphuric acid in the presence of MnO_2

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

Sol:

(i)

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$$
$$4HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$\overline{4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O}$$

i.e Cl^- is oxidized by MnO_2

(ii) $Cl_2(g) + 2NaI(aq) \longrightarrow 2NaCl(aq) + I_2(s)$

i.e. I^- is oxidized by Cl_2.

7.33. How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

Sol: XeF_2, XeF_4 and XeF_6 are obtained by direct reaction between Xe and F_2 as follows:

$$\underset{\text{excess}}{Xe(g)} + F_2(g) \xrightarrow[\text{Ni tube}]{673\text{ K, 1bar}} XeF_2(s)$$

$$\underset{\text{(In 1:5 ratio)}}{Xe(g) + 2F_2(g)} \xrightarrow{873\text{ K, 7 bar}} XeF_4(s)$$

$$\underset{\text{(In 1:20 ratio)}}{Xe(g) + 3F_2(g)} \xrightarrow{573\text{ K, 60 – 70bar}} XeF_6(s)$$

7.34. With which neutral molecule is ClO^- isoelectronic? Is this molecule Lewis acid or base ? (Pb. Board 2009)

Sol: ClO^- has (17 + 8 + 1) = 26 electrons. It is iso-electronic with two neutral molecules.

Oxygen difluoride (OF_2) : 8 + 18 = 26 electrons

Chlorine fluoride (ClF) : 17 + 9 = 26 electrons

Out of these, ClF can act as Lewis base. The atom chlorine has three lone electron pairs which it donates to form compounds like ClF_3, ClF_5 and ClF_7.

7.35. How are XeO_3 and $XeOF_4$prepared?

Sol:

$$(i)\ 6XeF_4 + 12H_2O \xrightarrow{\text{Hydrolysis}} 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \xrightarrow{\text{Hydrolysis}} XeO_3 + 6HF$$

$$(ii)\ XeF_6 + H_2O \xrightarrow{\text{Hydrolysis}} XeOF_4 + 2HF$$

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, HCI, HBr, HI – increasing acid . strength.

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 – increasing Sol. base strength.

Sol: (i) Bond dissociation enthalpy decreases as the bond distance increases from F_2 to I_2 due to increase in the size of the atom, on moving from F to I.

F – F bond dissociation enthalpy is smaller then the Cl – Cl and even smaller than Br – Br. This is because F atom is very small and have large electron-electron repulsion among the lone pairs of electrons in F_2 molecule where they are much closer to each other than in case of Cl_2. The increasing order of bond dissociation enthalphy is I, $< F_2 < Br_2 < Cl_2$

(ii) Acid strength of HF, HCI, HBr and HI depends upon their bond dissociation enthalpies. Since the bond dissociation enthalpy of H – X bond decreases from H – F to H-l as the size of atom increases from F to I.

Thus, the acid strength order is HF < HCI < HBr < HI

The weak acidic strength of HF is also due to H-bonding due to which release of H^+ becomes difficult.

(iii) NH_3, PH_3, ASH_3, SbH_3 and BiH_3 behaves as Lewis bases due to the presence of lone pair of electrons on the central atom. As we move from N to Bi, size of atom increases. Electron density on central atom decreases and hence the basic strength decreases from NH_3 to BiH_3. Thus basic strength order is

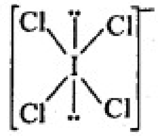
$BiH_3<SbH_3<AsH_3<PH_3<NH_3$

7.37. Which one of the following does not exist ?
(i)$XeOF_4$ (ii)NeF_2
(iii)XeF_4 (iv)XeF_6

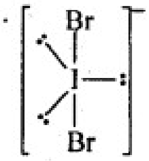
Sol: NeF_2 does not exist. This is because the sum of first and second ionization enthalpies of Ne are much higher than those of Xe. Consequently, F_2 can oxidise Xe to Xe^{2+} but cannot oxidise Ne to Ne^{2+}.

7.38. Give the formula and describe the structure of a noble gas species which is isostructural with: (i) ICI_4^- (ii) IBr_2^- (iii) $Br0_3^-$

Ans: (i) ICI_4^-: In ICI_4^-, central atom I has seven valence electrons and one due to negative charge. Four out of these 8 electrons are utilized in forming four single bonds with four Cl atoms. Four remaining electrons constitutes the two lone pairs. It is arranged in square planar structure. ICI_4^- has 36 valence electrons. A noble gas species having 36 valence electrons is XeF_4 ($8 + 4 \times 7 = 36$). XeF_4 is also square planar.



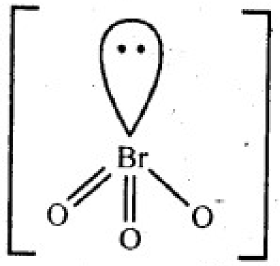
(ii) IBr_2^-: In IBr_2^-, central atom I has eight electrons. Two of these are utilized in forming two single bonds with two Br atom. Six remaining electrons constitutes three lone pairs. It is arranged in linear structure.

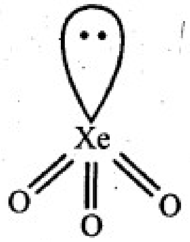


IBr_2^- has 22 valence electrons. A noble gas species having 22 valence electrons is XeF_2 ($8+2 \times 7=22$).

XeF_2 is also linear.

(iii) In $Br0_3^-$ ion the central Br atom has 8 valence electrons ($7 +1$). Out of these, it shares 4 with two atoms of O forming Br = O bonds. Out of the remaining four .electrons, 2 are donated to the third O atom which accounts for its negative charge. The remaining 2 electrons constitute one lone pair. In order to minimise the force of repulsion, the structure of $Br0_3^-$ ion must be pyramidal. $Br0_3^-$ ion has ($7 + 3 \times 6 + 1$) = 26 valence electrons and is isoelectronic as well as isostructural with noble gas species $Xe0_3$ which has also 26(8 + 3 x 6) electrons.





7.39. Why do noble gases have comparatively large atomic size?

Sol: The members of the noble gas family have comparatively large atomic size as compared to rest of the members present in the same period. Actually, for these elements, van der Waals' radii are considered while for rest of the elements either covalent radii or metallic radii are taken into account. Since van der Waals' radii arise simply due to van der Waals' forces of attraction, these are expected to have comparatively large magnitude.

7.40. List the uses of neoirand argon gases.

Sol: Uses of Neon

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Glow'of different colours 'neon signs' can be produced by mixing neon with other gases. Neon bulbs and used in botanical gardens and in green' houses.

Uses of Argon

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes such as arc welding of metals and alloys. In the laboratory, it is used for handling substance which are air sensitive.

It is used in filling incandescent and fluorescent lamps where its presence retards the sublimation of the filament and thus increases the life of the lamp.It is also used in "neon signs" for obtaining lights of different colours.

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