

Chapter 7: The p – Block Elements

Exercise Questions

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

Solution:

The general trends in the elements of Group 15 are shown below.

(i) Electronic configuration: Group 15 elements all have 5 valence electrons. They have a ns^2np^3 general electronic configuration.

(ii) Oxidation states: All of these elements have 5 valence electrons and need three more to complete their octets. However, gaining electrons is extremely difficult because the nucleus must attract three more electrons. Only nitrogen can do this because it is the smallest in size and the distance between the nucleus and the valence shell is relatively small. In their covalent compounds, the remaining elements in this group have a formal oxidation state of 3. N and P, in addition to the -3 state, have -1 and -2 oxidation states. This group's elements all have +3 and +5 oxidation states. However, the stability of the +5 oxidation state decreases as one descends, whereas the stability of the +3 oxidation state increases.

(iii) Ionization energy and electronegativity:

Moving down a group reduces first ionization. This is due to the increasing size of atomic nuclei. Electronegativity decreases as we move down a group due to an increase in size.

(iv) Atomic size: The atomic size increases as one moves down a group. The increase in atomic size is attributed to a greater number of shells.

7.2 Why does the reactivity of nitrogen differ from phosphorus?

Solution: Nitrogen has a lower chemical reactivity. This is due to the high stability of its N_2 molecule. The two nitrogen atoms in N_2 form a triple bond. This triple bond has an extremely high bond strength and is extremely difficult to break. Nitrogen is able to form $p\pi - p\pi$ bonds with itself because of its small size. Atoms such as phosphorus do not have this property. Phosphorus is thus more reactive than nitrogen.

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

Solution: The trends in the chemical properties of group 15 are shown below.

(i) Reactivity towards Hydrogen: Group 15 elements react with hydrogen to form hydrides of type EH_3 , where $E = N, P, As, Sb, \text{ or } Bi$. The stability of hydrides decreases as one progresses from NH_3 to BiH_3 .

(ii) Oxygen reactivity: Group 15 elements form two types of oxides: E_2O_3 and E_2O_5 , where $E = N, P, As, Sb, \text{ or } Bi$. The oxide with the higher oxidation state of the element is more acidic than the other. Moving down a group, however, the acidic character decreases.

(iii) Reactivity towards Halogen: The group 15 elements react with halogens to form two salt series: EX_3 and EX_5 . Nitrogen, on the other hand, does not form NX_5 because it lacks the d-orbital. Except for NX_3 , all trihalides are stable.

(iv) Reactivity towards metals:

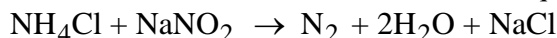
The elements of group 15 react with metals to form binary compounds in which metals have -3 oxidation states.

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

Solution: Nitrogen is more electronegative than phosphorus. This attracts electrons more towards nitrogen in NH_3 than towards phosphorus in PH_3 . As a result, the extent of hydrogen bonding in PH_3 is much lower than in NH_3 .

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

Solution: Sodium nitrite is used to treat an aqueous solution of ammonium chloride.



Small amounts of NO and HNO_3 are produced. These are impurities that can be removed by passing nitrogen gas through potassium dichromate-containing aqueous sulphuric acid.

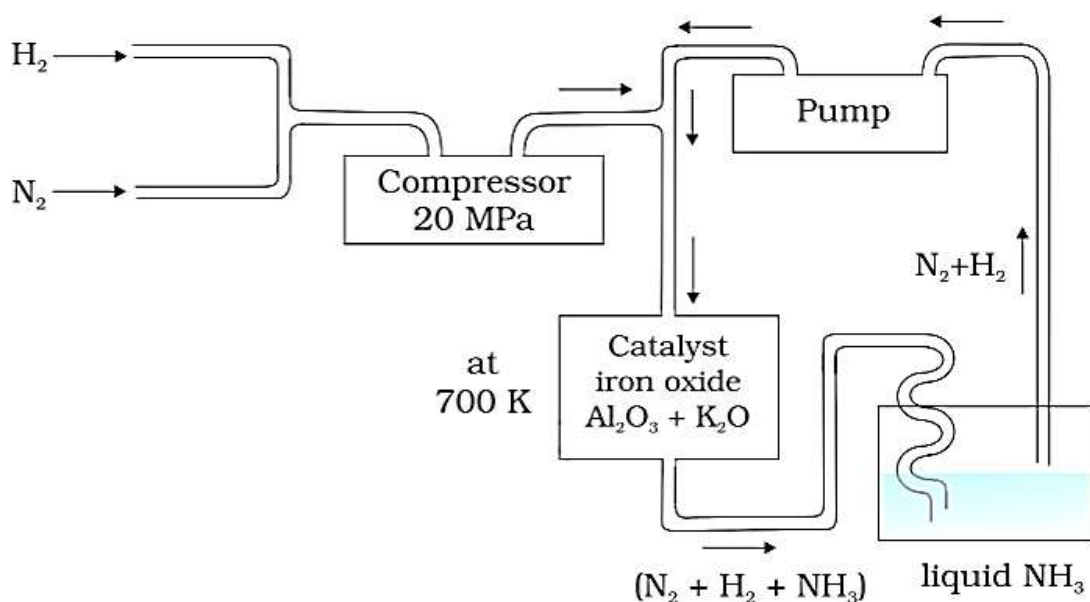
7.6. How is ammonia manufactured industrially?

Solution: The Haber method is used to prepare ammonia on a large scale.



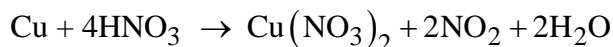
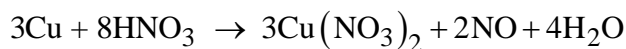
The best conditions for manufacturing ammonia are:

- (i) Pressure (around $200 \times 10^5 \text{ Pa}$)
- (ii) Temperature (4700 K)
- (iii) A catalyst, such as iron oxide, with trace amounts of Al_2O_3 and K_2O .



7.7. Illustrate how copper metal can give different products on reaction with HNO_3 .

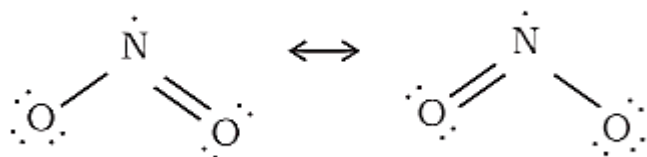
Solution: Nitric acid in concentrated form is a powerful oxidizing agent. Most metals are oxidized with it. The oxidation products are affected by the acid concentration, temperature, and the material being oxidized.



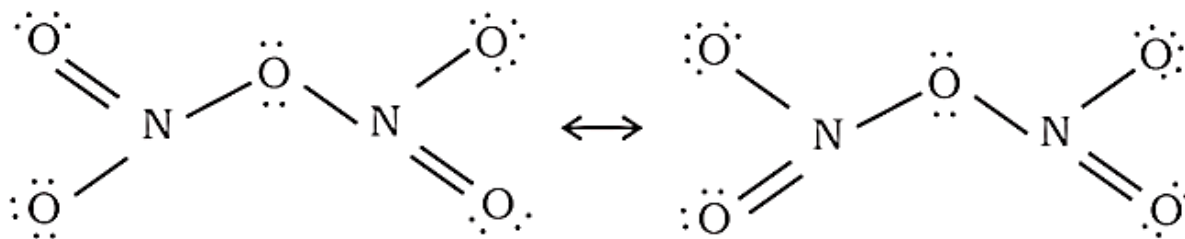
7.8. Give the resonating structures of NO_2 and N_2O_5 .

Solution:

(1)



(2)



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 NH_3 and only $s-p$ bonding between hydrogen and other elements of the group.]

Solution:

Hydride NH_3 PH_3 AsH_3 SbH_3

H–M–H angle 107° 92° 91° 90°

The above trend in the H–M–H bond angle can be explained by the central atom's electronegativity. Nitrogen has a high electron density because it is highly electronegative. As a result of the increased repulsion between the electron pairs surrounding nitrogen, the bond angle is maximized. We already know that electronegativity decreases as one moves down the group. As a result, the repulsive interactions between electron pairs decrease, resulting in a decrease in the H–M–H bond angle.

7.10. Why does $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not (R = alkyl group)?

Solution:

N, with exception of P, does not have a d -orbital. This limits nitrogen's ability to increase its coordination number beyond four. As a result, $\text{R}_3\text{N}=\text{O}$ does not exist.

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

Solution: NH_3 is clearly basic, whereas BiH_3 is feebly basic. Because nitrogen has a small size, the lone pair of electrons is concentrated in a small region. This indicates a high charge density per

unit volume. Moving down a group increases the size of the central atom and distributes the charge over a larger area, lowering the electron density. As a result, as one moves down the group, the electron donating capacity of group 15 element hydrides decreases.

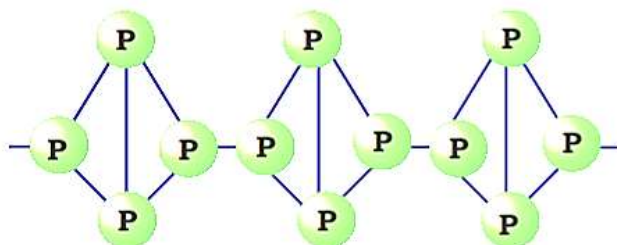
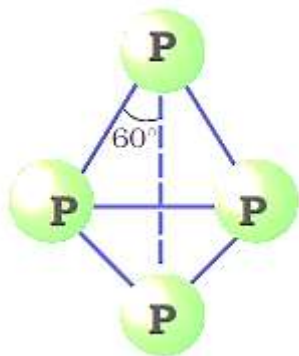
7.12. Nitrogen exists as diatomic molecule and phosphorus as P_4 . Why?

Solution: Nitrogen, due to its small size, has a proclivity to form $p\pi - p\pi$ multiple bonds with itself. As a result, nitrogen forms a very stable diatomic molecule, N_2 . The tendency to form $p\pi - p\pi$ bonds decreases as one moves down the group (because of the large size of heavier elements). As a result, phosphorus (along with other heavier metals) exists in the P_4 state.

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

Solution:

White phosphorus	Red Phosphorus
1. It is a waxy, soft solid. It has a garlic smell to it.	1. It is a hard, crystalline solid with no odor.
2. It is toxic.	2. It is non-toxic.
3. It is water insoluble but soluble in carbon disulphide.	3. It is insoluble in water as well as carbon disulphide.
4. It spontaneously burns in the air.	4. It has a lower reactivity.
5. It exists as a P_4 molecule in both solid and vapour states.	5. It exists in the form of a chain of tetrahedral P_4 units.



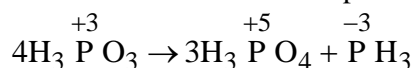


7.14. Why does nitrogen show catenation properties less than phosphorus?

Solution: Catenation occurs far more frequently in phosphorus compounds than in nitrogen compounds. This is due to the N-N single bond's relative weakness in comparison to the P-P single bond. Because the nitrogen atom is smaller, the repulsion of electron density between two nitrogen atoms is greater, weakening the N-N single bond.

7.15. Give the disproportionation reaction of H_3PO_3 .

Solution: When heated, orthophosphoric acid (H_3PO_4) and phosphine (PH_3) are formed as a result of the disproportionate reaction of orthophosphorus acid (H_3PO_3). The oxidation states of P in the reaction's various species are listed below.



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

Solution:

PCl_5 can only behave as an oxidizing agent. P has a maximum oxidation state of +5. Phosphorus is in the highest oxidation state (+5) in PCl_5 . It can, however, decrease its oxidation state and act as a reducing agent.

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.

Solution: Chalcogens are the collective name for the elements in Group 16.

(i) Each element in group 16 has six valence electrons. These elements' general electronic configuration is ns^2np^4 , where n ranges from 2 to 6.

(ii) Oxidation state: Because these elements have six valence electrons (ns^2np^4), their oxidation state should be -2. However, due to its high electronegativity, only oxygen exhibits the oxidation state of -2. It also has the oxidation states of -1 (H_2O_2), 0 (O_2), and +2 (H_2O_2) (OF_2). However, as one moves down a group, the stability of the -2 oxidation state decreases due to a decrease in the electronegativity of the elements. Because of the availability of d-orbitals, the heavier elements of the group have oxidation states of +2, +4, and +6.

(iii) Formation of hydrides:

These elements combine to form hydrides with the formula H_2E , where

E = O, S, Se, Te, and PO. Oxygen and sulfur also combine to form hydrides of the type H_2E_2 . These hydrides are highly flammable in nature.

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

Solution: When compared to sulphur, oxygen is smaller in size. Because of its smaller size, it is capable of forming $p\pi-p\pi$ bonds and forming an O_2 ($O=O$) molecule. Furthermore, the intermolecular forces in oxygen are van der Waals's weak, causing it to exist as a gas. Sulphur, on the other hand, does not form an M_2 molecule and instead exists as a puckered structure held together by strong covalent bonds. As a result, it is a solid.

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

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

Solution: The stability of an ionic compound is determined by its lattice energy. The higher a compound's lattice energy, the more stable it will be.

The charge carried by an ion is directly proportional to its lattice energy. When a metal combines with oxygen, the lattice energy of the oxide containing O^{2-} ion is much greater than the lattice energy of the oxide containing O^- ion. As a result, oxides containing O^{2-} ions are more stable than oxides containing O^- . As a result, we can say that the formation of O^{2-} is more energetically favorable than the formation of O^- .

7.20. Which aerosols deplete ozone?

Solution: Freons, also known as chlorofluorocarbons (CFCs), are aerosols that hasten the depletion of ozone. When exposed to ultraviolet radiation, CFC molecules degrade to form chlorine-free radicals, which combine with ozone to form oxygen.

7.21. Describe the manufacture of H_2SO_4 by contact process?

Solution: The contact process is used to produce sulphuric acid. It consists of the following steps:

Step (i): Sulphur or sulphide ore is burned in air to produce SO_2 .

Step (ii): SO_2 is converted to SO_3 by a reaction with oxygen in the presence of V_2O_5 as a catalyst.



Step (iii): The SO_3 produced is absorbed by H_2SO_4 , yielding $H_2S_2O_7$ (oleum).



This oleum is then diluted to obtain the desired concentration of H_2SO_4 .

In practice, the plant is run at a pressure of 2 bar and a temperature of 720 K. (temperature). The resulting sulphuric acid is 96-98 percent pure.

7.22. How is SO_2 an air pollutant?

Solution: Sulphur dioxide harms the environment in a variety of ways:

1. It reacts with water vapour in the atmosphere to produce sulphuric acid. This results in acid rain. Acid rain harms soil, plants, and structures, particularly those made of marble.
2. SO_2 causes respiratory tract irritation even at very low concentrations. It irritates the throat and eyes, and it can also affect the larynx, causing shortness of breath.
3. It is extremely toxic to plants. Plants that have been exposed to sulphur dioxide for an extended

period of time lose the color of their leaves. Chlorosis is the medical term for this condition. This occurs because the presence of sulphur dioxide interferes with the formation of chlorophyll.

7.23. Why are halogens strong oxidising agents?

Solution: Halogens have a general electronic configuration of np^5 , where $n = 2-6$. As a result, halogens require only one more electron to complete their octet and achieve the stable noble gas configuration. Furthermore, halogens are extremely electronegative, with low dissociation energies and high negative electron gain enthalpies. As a result, they have a high proclivity to gain an electron. As a result, they are powerful oxidizing agents.

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

Solution: Because of its high electronegativity and small size, fluorine only forms one oxoacid, HOF.

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

Solution: Although chlorine and oxygen have nearly identical electronegativity values, chlorine rarely forms hydrogen bonds. This is due to the fact that oxygen has a smaller size than chlorine and, as a result, a higher electron density per unit volume.

7.26. Write two uses of ClO_2 .

Solution:

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

7.27. Why are halogens coloured?

Solution: Almost all halogens have a color. This is due to the fact that halogens absorb visible radiation. This causes valence electrons to be excited to a higher energy region. Because the amount of energy required for excitation varies by halogen, each halogen has a distinct color.

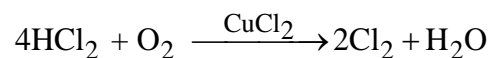
7.28. Write the reactions of F_2 and Cl_2 with water.

Solution:

- (i) $Cl_2 + H_2O \rightarrow \underset{\text{Hypochloric acid}}{HCl} + \underset{\text{Hypochlorous acid}}{HOCl}$
- (ii) $2F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2 + 4HF$

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

Solution: (i) Deacon's process can be used to produce Cl_2 from HCl.



(ii) By treating Cl_2 with water, HCl can be produced.



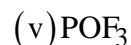
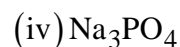
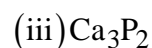
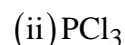
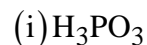
7.30. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6 ?

Solution: Neil Bartlett began by performing an oxygen- PtF_6 reaction. This caused the formation

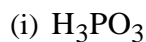
of a red compound, $\text{O}_2^+ [\text{PtF}_6]^-$.

He later discovered that the first ionization energy of oxygen (1175 kJ/mol) and Xe (1170 kJ/mol) is nearly identical. As a result, he attempted to synthesize a compound containing Xe and PtF_6 . He was successful, and a red-colored compound $\text{Xe}^+ [\text{PtF}_6]^-$ was formed as a result.

7.31. What are the oxidation states of phosphorus in the following:



Solution:



Let the oxidation state of P be x.

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

$$3 + x - 6 = 0$$

$$x - 3 = 0$$

$$x = +3$$



Let the oxidation state of P be x.

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

$$x - 3 = 0$$

$$x = +3$$



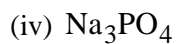
Let the oxidation state of P be x.

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

$$6 + 2x = 0$$

$$2x = -6$$

$$x = -3$$



Let the oxidation state of P be x.

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

$$3 + x - 8 = 0$$

$$x - 5 = 0$$

$$x = +5$$

(v) POF_3

Let the oxidation state of P be x.

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

$$x - 5 = 0$$

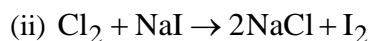
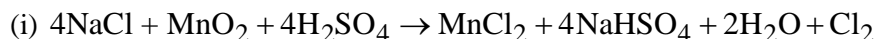
$$x = +5$$

7.32. Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO_2 .

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

Solution:

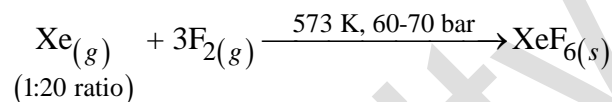
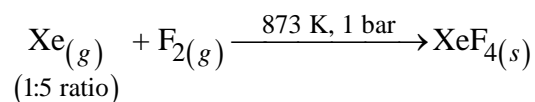
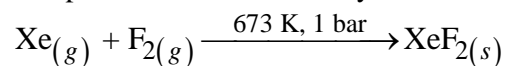


7.33. How are xenon fluorides XeF_2 , XeF_4 and XeF_6 obtained?

Solution:

XeF_2 , XeF_4 and XeF_6 are produced by a direct reaction of Xe and F_2 .

The product is determined by the conditions under which the reaction is carried out.



7.34. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Solution: ClO^- is isoelectronic to ClF . Also, they both have 26 electrons in all as shown below.

$$\begin{aligned} \text{Total electrons in } \text{ClO}^- &= 17 + 8 + 1 \\ &= 26 \end{aligned}$$

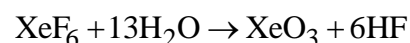
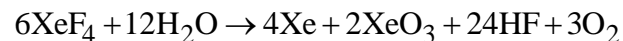
$$\begin{aligned} \text{Total electrons in } \text{ClF} &= 17 + 9 \\ &= 26 \end{aligned}$$

ClF behaves as a Lewis base, accepting electrons from F to form ClF_3 .

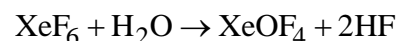
7.35. How are XeO_3 and XeOF_4 prepared?

Solution:

(i) There are two methods to prepare XeO_3 as shown below.



(ii) There is only one method to prepare XeOF_4 that is using XeF_6 .

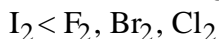


7.36. Arrange the following in the order of property indicated for each set:

- (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.

Solution:

(i) Bond dissociation energy typically decreases as atomic size increases as one moves down a group. F_2 bond dissociation energy, on the other hand, is lower than that of Cl_2 and Br_2 . This is due to fluorine's small atomic size. Thus, among halogens, the increasing order for bond dissociation energy is as follows:



(ii) The bond dissociation energy of H-X molecules where X = F, Cl, Br, I decreases as atomic size increases. Because the H-I bond is the weakest, HI is the most powerful acid.



(iii) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

Moving from nitrogen to bismuth causes the atom's size to increase while its electron density to decrease. As a result, the basic strength decreases.

7.37. Which one of the following does not exist?

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

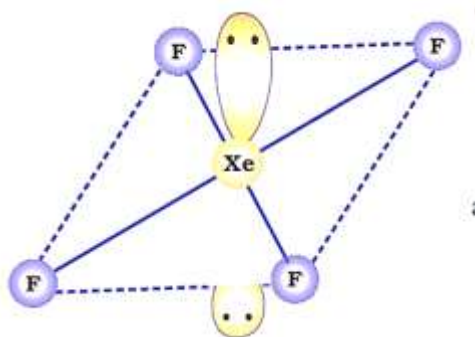
Solution: NeF_2 does not exist.

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

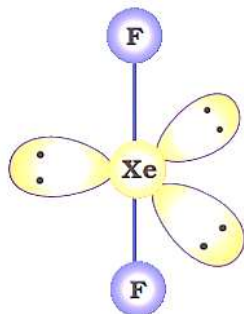
- (i) ICl_4^-
- (ii) IBr_2^-
- (iii) BrO_3^-

Solution:

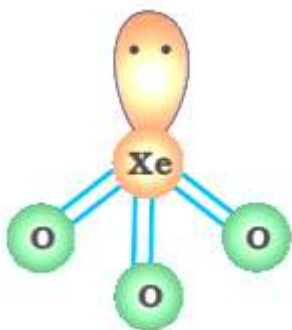
(i) XeF_4 is isoelectronic with ICl_4^- and the geometry is square planar.



(ii) XeF_2 is isoelectronic and the geometry is linear.



(iii) XeO_3 is isostructural to BrO_3^- and the geometry is pyramidal.



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

Solution:

Noble gases do not combine to form molecules. The atomic radii of noble gases correspond to van der Waal's radii. Other elements' atomic radii, on the other hand, correspond to their covalent radii. Van der Waal radii are, by definition, larger than covalent radii. As a result, noble gases are very large in size when compared to other atoms from the same period.

7.40. List the uses of Neon and argon gases.

Solution:

Uses of neon gas:

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

Uses of argon gas:

- (i) Argon and nitrogen are both used in gas-filled electric lamps. This is due to the fact that Ar is more inert than N.
- (ii) It is commonly used in high metallurgical processes to provide an inert temperature.
- (iii) In laboratories, it is also used to handle air-sensitive substances.

Intext questions

7.1. Why are pentahalides more covalent than trihalides?

Solution: The oxidation state of pentahalides is +5, while that of trihalides is +3. Pentahalides are more covalent than trihalides because metal ions with a higher charge have more polarizing power.

7.2. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements?

Solution:

Down a group, the atomic size grows and the stability of group 15 hydrides decreases. Because hydride stability decreases as one moves from NH_3 to BiH_3 , the reducing character of the hydrides increases as one moves from NH_3 to BiH_3 .

7.3. Why is N_2 less reactive at room temperature?

Solution: The two nitrogen atoms in N_2 are held together by extremely strong triple covalent bonds. This bond's bond dissociation energy is extremely high. As a result, at room temperature, N_2 is less reactive.

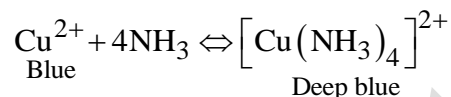
7.4. Mention the conditions required to maximise the yield of ammonia.

Solution: The Haber process is used to produce ammonia. The following conditions can be used to maximize ammonia yield:

- (i) High pressure (200 atm)
- (ii) A temperature of 700 K.
- (iii) Catalysts such as iron oxide mixed with trace amounts of K_2O and Al_2O_3 are used.

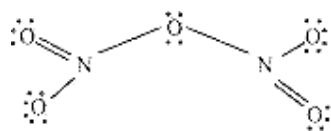
7.5. How does ammonia react with a solution of Cu^{2+} ?

Solution: NH_3 behaves as Lewis base. It gives up its electron pair and forms a bond with a metal ion.



7.6. What is the covalence of nitrogen in N_2O_5 ?

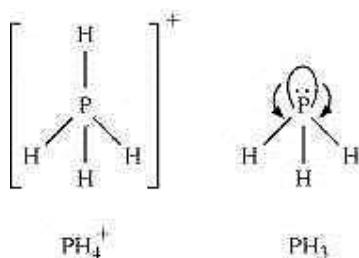
Solution: The structure of N_2O_5 shows that the covalence of nitrogen is 4.



7.7. Bond angle in PH_4^+ is higher than that in PH_3 . Why?

Solution: Phosphorus is sp^3 hybridized in PH_3 . Bonding with three hydrogen atoms involves three orbitals, with the fourth containing a lone pair. Because lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the sp^3 bonding tetrahedral shape is changed to pyramidal. PH_3 combines with a proton to form PH_4^+ , which lacks the lone pair. There is no lone pair-bond pair repulsion in PH_4^+ because there is no lone pair.

As a result, the bond angle in PH_4^+ is greater than the bond angle in PH_3 .



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

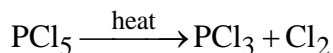
Solution:

In a CO_2 atmosphere, white phosphorous dissolves in boiling NaOH solution to form phosphine, PH_3 .



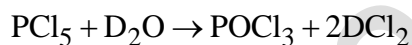
7.9. What happens when PCl_5 is heated?

Solution: All of the bonds in PCl_5 are distinct from one another. It has two axial bonds and three equatorial bonds. The axial bonds are weaker than the equatorial bonds. As a result, when PCl_5 is heated to a high temperature, it decomposes to form PCl_3 .

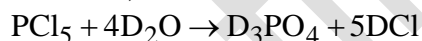


7.10. Write a balanced equation for the hydrolytic reaction of PCl_5 in heavy water.

Solution:

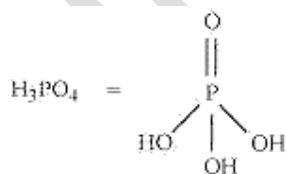


Therefore, the net reaction can be given as



7.11. What is the basicity of H_3PO_4 ?

Solution:

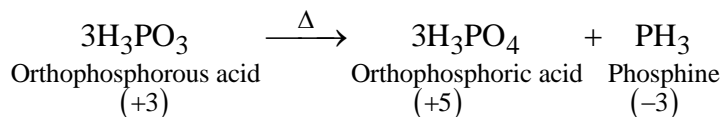


In H_3PO_4 , three OH or hydroxyl groups are present. So, its basicity will be three, that is, it is known as tribasic acid.

7.12: What happens when H_3PO_4 is heated?

Solution: When heated, H_3PO_4 undergoes a disproportionation reaction, yielding PH_3 and H_3PO_3 . P has oxidation numbers of +3, 3, and 5 in H_3PO_3 , PH_3 , and H_3PO_4 , respectively. A disproportionation reaction occurs when the oxidation number of the same element decreases and

increases during a specific reaction.

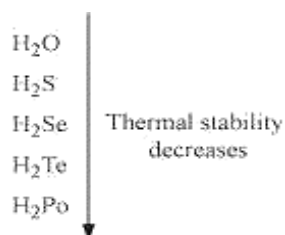


7.13. List the important sources of sulphur.

Solution: Sulphur is mostly found in the earth's crust in the form of 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 (BaSO_4)] and sulphides [galena (PbS), zinc blends (ZnS), copper pyrites (CuFeS_2)].

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

Solution: Moving down the group, the thermal stability of hydrides decreases. This is due to hydrides' bond dissociation enthalpy (HE) decreasing as they move down the group. Therefore, the order of the thermal stability of the hydrides of group 16 elements are shown below.



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

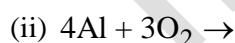
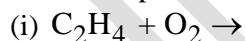
Solution: The central atom in H_2O is oxygen. When compared to sulfur, oxygen has a smaller size and a higher electronegativity. As a result, H_2O has extensive hydrogen bonding, whereas H_2S does not. H_2S molecules are only held together by weak van der Waal forces of attraction. As a result, H_2O exists as a liquid, whereas H_2S exists as a solid.

7.16. Which of the following does not react with oxygen directly?

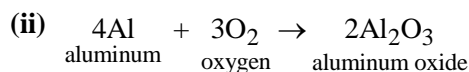
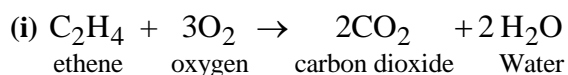
Zn, Ti, Pt, Fe

Solution: Pt is a noble metal that does not corrode easily. All of the other elements, Zn, Ti, and Fe, are highly reactive. As a result, oxygen does not directly react with platinum (Pt).

7.17. Complete the following reactions:



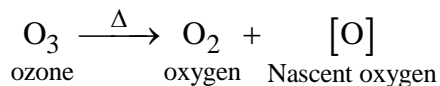
Solution:



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

Solution: Under normal conditions, ozone is not a very stable compound and readily decomposes on heating to give a molecule of oxygen and nascent oxygen. Nascent oxygen, as a free radical, is

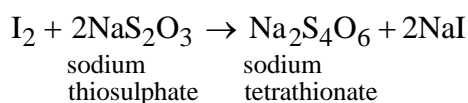
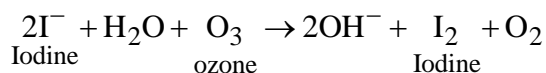
extremely reactive.



Therefore, ozone acts as a powerful oxidising agent.

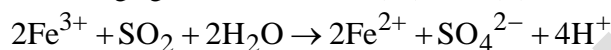
7.19. How is O_3 estimated quantitatively?

Solution: Ozone can be measured quantitatively using potassium iodide. Iodine is liberated when ozone reacts with potassium iodide solution buffered with a borate buffer (pH 9.2). Using starch as an indicator, this liberated iodine can be titrated against a standard solution of sodium thiosulphate. The reactions that occur during the process are listed below.



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

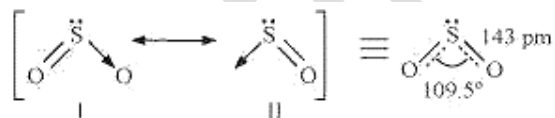
Solution: When sulphur dioxide is passed through an aqueous solution containing Fe(III) salt, it acts as a reducing agent. It converts Fe(III) to Fe(II), converting ferric ions to ferrous ions.



7.21. Comment on the nature of two S-O bonds formed in SO_2 molecule. Are the two S-O bonds in this molecule equal?

Solution: The ground state electronic configuration of S is $1s^2 2s^2 2p^6 3s^2 3p^4$.

SO_2 is formed when one electron from the $3p$ orbital moves to the $3d$ orbital and S undergoes sp^2 hybridization. Two of these orbitals have sigma bonds with two oxygen atoms, while the third has a single pair. Each p-orbital and d-orbital has an unpaired electron. One of these electrons forms a $p\pi - p\pi$ bond with one of the oxygen atoms, while the other forms a $p\pi - d\pi$ bond with the other molecule. This is why SO_2 has a curved structure. It is also a resonance hybrid of structures I and II.



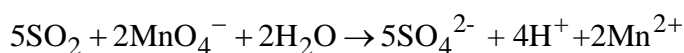
Both S-O bonds have the same length (143 pm) and a multiple bond character.

7.22. How is the presence of SO_2 detected?

Solution: SO_2 is a colorless gas with a strong odor.

It can be detected using a potassium permanganate solution. When SO_2 is passed through an acidified potassium permanganate solution, it decolorizes it by reducing MnO_4^- ions to Mn^{2+} ions.

The reaction is shown below.



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

Solution: Sulphuric acid is a vital industrial chemical that serves a variety of functions. The following are some of the most important applications for sulphuric acid.

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

7.24. Write the conditions to maximize the yield of H_2SO_4 by Contact process.

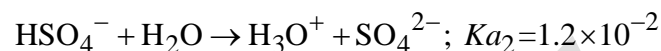
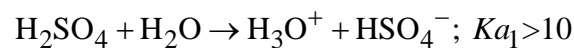
Solution: Three steps are involved in the Contact process of producing sulphuric acid.

1. Ore combustion to produce SO_2
2. SO_2 to SO_3 conversion via reaction of the former with O_2 (V_2O_5 is used in this process as a catalyst.)
3. SO_3 absorption in H_2SO_4 to produce oleum ($\text{H}_2\text{S}_2\text{O}_7$).

The second step is crucial in this process. Two moles of gaseous reactants are combined in this step to yield one mole of gaseous product. This reaction is also exothermic. Thus, according to Le Chatelier's principle, in order to obtain the greatest amount of SO_3 gas, the temperature should be low and the pressure should be high.

7.25. Why is $Ka_2 \ll Ka_1$ for H_2SO_4 in water?

Solution:



It can be noticed that $Ka_2 \ll Ka_1$. This is due to the fact that neutral H_2SO_4 has a much higher tendency to lose a proton than negatively charged HSO_4^- . As a result, the former is a far more potent acid than the latter.

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

Solution: Fluorine is a much more potent oxidizer than chlorine. Three factors influence oxidizing power.

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

Chlorine has a more negative electron gain enthalpy than fluorine. The bond dissociation energy of fluorine, on the other hand, is much lower than that of chlorine. Furthermore, due to its small size, fluorine has a much higher hydration energy than chlorine. As a result, the latter two factors more than compensate for fluorine's less negative electron gain enthalpy. As a result, fluorine is a much more powerful oxidizing agent than chlorine.

7.27. Give two examples to show the anomalous behaviour of fluorine.

Solution: Anomalous behaviour of fluorine:

- (i) It only produces one oxoacid, as opposed to other halogens, which produce a number of oxoacids.
- (ii) Fluorine's ionisation enthalpy, electronegativity, and electrode potential are much higher than expected.

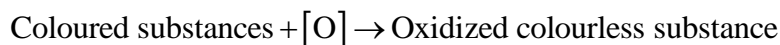
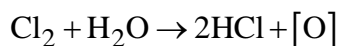
7.28. Sea is the greatest source of some halogens. Comment.

Solution: Na, K, Mg, and Ca chlorides, bromides, and iodides are found in sea water. It does, however, primarily contain NaCl. Sodium chloride and carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, are found

in dried up sea bed deposits. Iodine is also found in the systems of marine life. Seaweeds, for example, contain up to 0.5 percent iodine in the form of sodium iodide. As a result, the sea is the most abundant source of halogens.

7.29. Give the reason for bleaching action of Cl_2 .

Solution: When chlorine reacts with water, nascent oxygen is formed. This nascent oxygen then reacts with the colored substances in organic matter, oxidizing them into colorless substances.



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

Solution: Phosgene (COCl_2) and mustard gas are two poisonous gases that can be made from chlorine gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$)

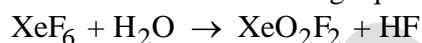
7.31. Why is ICl more reactive than I_2 ?

Solution: Since the bond of $\text{I}-\text{Cl}$ bond in ICl is weaker than $\text{I}-\text{I}$ bond in I_2 , ICl is more reactive than I_2 .

7.32. Why is helium used in diving apparatus?

Solution: Air includes a lot of nitrogen, and the solubility of gases in liquids increases as pressure rises. When deep sea divers dive, a large amount of nitrogen dissolves in their blood. When they resurface, the solubility of nitrogen decreases, and it separates from the blood, forming small air bubbles. This results in bends, a potentially fatal medical condition. As a result, the air in diving oxygen cylinders is diluted with helium gas. This is done because helium is only sparingly soluble in blood.

7.33. Balance the following equation:



Solution: The balanced equation is given as:



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

Solution: The chemistry of radon is difficult to study because it is a radioactive substance with a half-life of only 3.82 days. Furthermore, radon compounds such as RnF_2 have not been isolated. They've only been identified so far.

Examples

7.1. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Solution: Nitrogen has only s and p orbitals when $n = 2$. It lacks d orbitals, which would allow it to expand its covalence beyond four. As a result, it does not form pentahalide.

7.2. PH_3 has lower boiling point than NH_3 . Why?

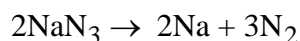
Solution: With exception of NH_3 , PH_3 molecules do not form hydrogen bonds in the liquid state.

As a result, the boiling point of PH_3 is lower than that of NH_3 .

7.3. Write the reaction of thermal decomposition of sodium azide.

Solution: Dinitrogen gas is produced during the thermal decomposition of sodium azide.

The reaction is shown below.



7.4. Why does NH_3 act as a Lewis base?

Solution: The nitrogen atom in NH_3 has one lone pair of electrons that can be donated. As a result, it serves as a Lewis base.

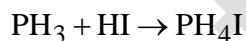
7.5. Why does NO_2 dimerise?

Solution: NO_2 has an even number of valence electrons. It behaves like any other odd molecule.

Dimerisation converts it to a stable N_2O_4 molecule with an even number of electrons.

7.6. In what way can it be proved that PH_3 is basic in nature?

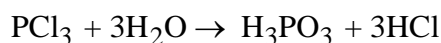
Solution: PH_3 reacts with acids such as HI to form PH_4I , indicating that it is basic in nature.



In the above reaction, PH_3 acts as a Lewis base due to the lone pair on the phosphorus atom.

7.7. Why does PCl_3 fume in moisture?

Solution: In the presence of moisture, PCl_3 hydrolyzes, producing HCl fumes.



7.8. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Solution: The structure of PCl_5 is trigonal bipyramidal, and the three equatorial P-Cl bonds are equivalent, whereas the two axial bonds are distinct and longer than equatorial bonds.

7.9. How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?

Solution: Two H atoms are directly bonded to a phosphorus atom in H_3PO_2 , giving the acid a reducing character.

7.10. Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

Solution: Group 15 elements require more energy to remove electrons than Group 16 elements due to their extra stable half-filled p orbitals electronic configurations.

7.11. H_2S is less acidic than H_2Te . Why?

Solution: Acidic character increases due to a decrease in bond (E–H) dissociation enthalpy down the group.

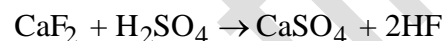
7.12. Which form of sulphur shows paramagnetic behaviour?

Solution: Sulphur partially exists in the vapour state as the S_2 molecule, which has two unpaired electrons in the antibonding π^* orbitals like O_2 and thus exhibits paramagnetism.

7.13. What happens when (i) Concentrated H_2SO_4 is added to calcium fluoride (ii) SO_3 is passed through water?

Solution: (i) When concentrated H_2SO_4 is added to calcium fluoride, hydrogen fluoride is formed.

The reaction is given as



(ii) When SO_3 is passes through water, H_2SO_4 is produced.



7.14. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Solution: Halogens have the smallest size and thus the highest effective nuclear charge in their respective periods. As a result, they readily accept one electron in order to acquire noble gas electronic configuration.

7.15. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

Solution: It is due to

(i) low enthalpy of dissociation of F - F bond

(ii) high hydration enthalpy of F^-

7.16. Fluorine exhibits only -1 oxidation state whereas other halogens exhibit $+1$, $+3$, $+5$ and $+7$ oxidation states also. Explain.

Solution: Fluorine is the most electronegative element, with no positive oxidation states. Other halogens with d orbitals can also expand their octets and show $+1$, $+3$, $+5$, and $+7$ oxidation states.

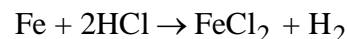
7.17. Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated $NaOH$. Is this reaction a disproportionation reaction? Justify.

Solution: $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine is converted from its zero oxidation state to the -1 and $+5$ oxidation states.

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

Solution: When HCl reacts with finely powdered iron, it produces hydrogen and ferrous chloride.



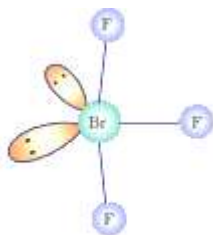
The formation of ferric chloride is prevented by the liberation of hydrogen.

7.19. Discuss the molecular shape of BrF_3 on the basis of VSEPR theory.

Solution: In the valence shell of the central atom Br, there are seven electrons. Three of these will form electron-pair bonds with three fluorine atoms, leaving four electrons behind. There are three bond pairs and two lone pairs as a result. These will occupy the corners of a trigonal bipyramid, according to VSEPR theory. The two lone pairs will occupy equatorial positions in order to minimize lone pair-lone pair and bond pair-lone pair repulsions that are greater than bond pair-bond pair repulsions.

Furthermore, the axial fluorine atoms will be bent towards the equatorial fluorine to reduce lone-pair-lone pair repulsions. The shape would be a slightly bent 'T.'

The structure is shown below.



7.20. Why are the elements of Group 18 known as noble gases?

Solution: Since the elements in Group 18 have completely filled valence shell orbitals, they can only react with a few other elements under certain conditions. As a result, they are now referred to as noble gases.

7.21. Noble gases have very low boiling points. Why?

Solution: Since noble gases are monoatomic and have no interatomic forces other than weak dispersion forces, they can be liquefied at very low temperatures. As a result, they have low boiling points.

7.22. Does the hydrolysis of XeF_6 lead to a redox reaction?

Solution: No, the hydrolysis products are XeOF_4 and XeO_2F_2 , and the oxidation states of all the elements remain the same as they were in the reacting state.



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