(Chapter 7)(The p – Block Elements)

XII

Question 7.1:

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

Answer

General trends in group 15 elements

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

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

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

(iii) Ionization energy and electronegativity

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

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

Question 7.2:

Why does the reactivity of nitrogen differ from phosphorus?

Answer

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

Question 7.3:

Discuss the trends in chemical reactivity of group 15 elements.

Answer

General trends in chemical properties of group − 15

(i) Reactivity towards hydrogen:

The elements of group 15 react with hydrogen to form hydrides of type EH_3, where E = N, P, As, Sb, or Bi. The stability of hydrides decreases on moving down from NH_3 to BiH_3. **(ii) Reactivity towards oxygen:**

The elements of group 15 form two types of oxides: E_2O_3 and E_2O_5, where E = N, P, As, Sb, or Bi. The oxide with the element in the higher oxidation state is more acidic than the other. However, the acidic character decreases on moving down a group.

(iii) Reactivity towards halogens:

The group 15 elements react with halogens to form two series of salts: EX_3 and EX_5. However, nitrogen does not form NX_5 as it lacks the *d*-orbital. All trihalides (except NX_3) are stable.

(iv) Reactivity towards metals:

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

Question 7.4:

Why does NH_3 form hydrogen bond but PH_3 does not?

Answer

Nitrogen is highly electronegative as compared to phosphorus. This causes a greater attraction of electrons towards nitrogen in NH_3 than towards phosphorus in PH_3. Hence, the extent of hydrogen bonding in PH_3 is very less as compared to NH_3.

Question 7.5:

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

Answer

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

$$NH_4Cl_{(aq)} + NaNO_{2(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$$

NO and HNO_3 are produced in small amounts. These are impurities that can be removed on passing nitrogen gas through aqueous sulphuric acid, containing potassium dichromate.

Question 7.6:

How is ammonia manufactured industrially?

Answer

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

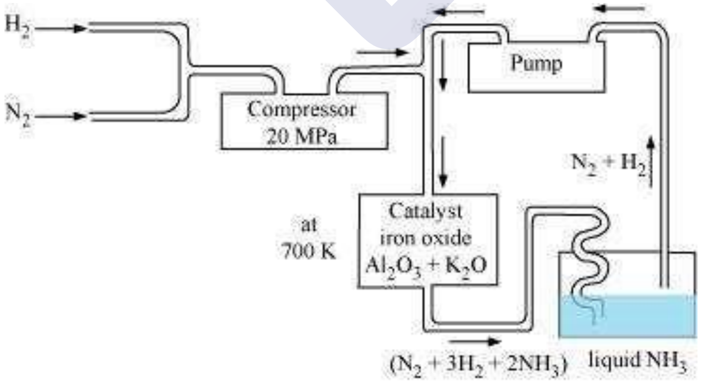
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta_f H^\circ = -46.1 \text{ kJ/mol}$$

The optimum conditions for manufacturing ammonia are:

(i) Pressure (around 200×10^5 Pa)

(ii) Temperature (4700 K)

(iii) Catalyst such as iron oxide with small amounts of Al_2O_3 and K_2O



Question 7.7:

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

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

$$3Cu + 8HNO_{3(dilute)} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

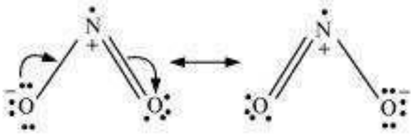
$$Cu + 4HNO_{3(conc)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Question 7.8:

Give the resonating structures of NO_2 and N_2O_5.

Answer

(1)



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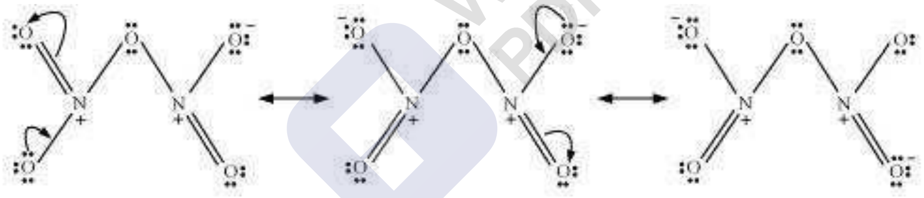


Question 7.9:

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

Answer

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

Question 7.10:

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

Answer

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

Question 7.11:

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

Answer

NH_3 is distinctly basic while BiH_3 is feebly basic.

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

Question 7.12:

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

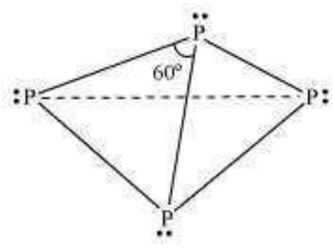
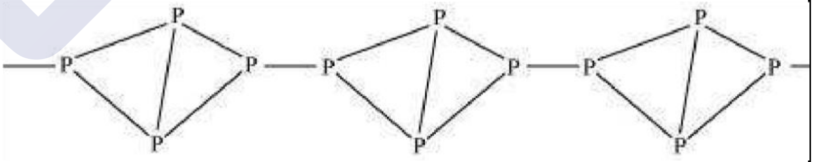
Answer

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

Question 7.13:

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

Answer

White phosphorus	Red Phosphorus
It is a soft and waxy solid. It possesses a garlic smell.	It is a hard and crystalline solid, without any smell.
It is poisonous.	It is non-poisonous.
It is insoluble in water but soluble in carbon disulphide.	It is insoluble in both water and carbon disulphide.
It undergoes spontaneous combustion in air.	It is relatively less reactive.
In both solid and vapour states, it exists as a P_4 molecule.  	It exists as a chain of tetrahedral P_4 units. 

Question 7.14:

Why does nitrogen show catenation properties less than phosphorus?

Answer

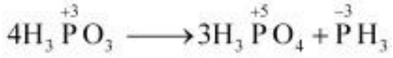
Catenation is much more common in phosphorous compounds than in nitrogen compounds. This is because of the relative weakness of the N−N single bond as compared to the P−P single bond. Since nitrogen atom is smaller, there is greater repulsion of electron density of two nitrogen atoms, thereby weakening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

Question 7.15:

Give the disproportionation reaction of H_3PO_3.

Answer

On heating, orthophosphorus acid (H_3PO_3) disproportionates to give orthophosphoric acid (H_3PO_4) and phosphine (PH_3). The oxidation states of P in various species involved in the reaction are mentioned below.



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

Question 7.16:

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

Answer

PCl_5 can only act as an oxidizing agent. The highest oxidation state that P can show is +5. In PCl_5, phosphorus is in its highest oxidation state (+5). However, it can decrease its oxidation state and act as an oxidizing agent.

Question 7.17:

Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

Answer

The elements of group 16 are collectively called chalcogens.

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

(ii) Oxidation state:

As these elements have six valence electrons ($ns^2\ np^4$), they should display an oxidation state of −2. However, only oxygen predominantly shows the oxidation state of −2 owing to its high electronegativity. It also exhibits the oxidation state of −1 (H_2O_2), zero (O_2), and +2 (OF_2). However, the stability of the −2 oxidation state decreases on moving down a group due to a decrease in the electronegativity of the elements. The heavier elements of the group show an oxidation state of +2, +4, and +6 due to the availability of *d*-orbitals.

(iii) Formation of hydrides:

These elements form hydrides of formula H_2E, where E = O, S, Se, Te, PO. Oxygen and sulphur also form hydrides of type H_2E_2. These hydrides are quite volatile in nature.

Question 7.18:

Why is dioxygen a gas but sulphur a solid?

Answer

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

Question 7.19:

Knowing the electron gain enthalpy values for O → 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^-?

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

Answer

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

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

Question 7.20:

Which aerosols deplete ozone?

Answer

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

Question 7.21:

Describe the manufacture of H_2SO_4 by contact process?

Answer

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

Step (i):

Sulphur or sulphide ores are burnt in air to form SO_2.

Step (ii):

By a reaction with oxygen, SO_2 is converted into SO_3 in the presence of V_2O_5 as a catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$

Step (iii):

SO_3 produced is absorbed on H_2SO_4 to give $H_2S_2O_7$ (oleum).

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

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

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

Question 7.22:

How is SO_2 an air pollutant?

Answer

Sulphur dioxide causes harm to the environment in many ways:

1. It combines with water vapour present in the atmosphere to form sulphuric acid. This causes acid rain. Acid rain damages soil, plants, and buildings, especially those made of marble.

2. Even in very low concentrations, SO_2 causes irritation in the respiratory tract. It causes throat and eye irritation and can also affect the larynx to cause breathlessness.

3. It is extremely harmful to plants. Plants exposed to sulphur dioxide for a long time lose colour from their leaves. This condition is known as chlorosis. This happens because the formation of chlorophyll is affected by the presence of sulphur dioxide.

Question 7.23:

Why are halogens strong oxidising agents?

Answer

The general electronic configuration of halogens is np^5, where n = 2-6. Thus, halogens need only one more electron to complete their octet and to attain the stable noble gas configuration. Also, halogens are highly electronegative with low dissociation energies and high negative electron gain enthalpies. Therefore, they have a high tendency to gain an electron. Hence, they act as strong oxidizing agents.

Question 7.24:

Explain why fluorine forms only one oxoacid, HOF.

Answer

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

Question 7.25:

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

Answer

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

Question 7.26:

Write two uses of ClO_2.

Answer

Uses of ClO_2:

(i) It is used for purifying water.

(ii) It is used as a bleaching agent.

Question 7.27:

Why are halogens coloured?

Answer

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

Question 7.28:

Write the reactions of F_2 and Cl_2 with water.

Answer

(i)

$$Cl_2 + H_2O \longrightarrow \underset{\text{Hydrochloric acid}}{HCl} + \underset{\text{Hypochlorous acid}}{HOCl}$$

(ii)

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + 4F^-_{(aq)} + O_{2(g)} + 4HF_{(aq)}$$

Question 7.29:

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

Answer

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

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

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

$$Cl_2 + H_2O \longrightarrow \underset{\text{Hydrochloric acid}}{HCl} + \underset{\text{Hypochlorous acid}}{HOCl}$$

Question 7.30:

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

Answer

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

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

Question 7.31:

What are the oxidation states of phosphorus in the following:

(i) H_3PO_3 **(ii)** PCl_3 **(iii)** Ca_3P_2 **(iv)** Na_3PO_4 **(v)** POF_3?

Answer

Let the oxidation state of p be x.

(i) H_3PO_3

$$3 + x + 3(-2) = 0$$
$$3 + x - 6 = 0$$
$$x - 3 = 0$$
$$x = +3$$

(ii) PCl_3

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

(iii) Ca_3P_2

$$3(+2)+2(x)=0$$
$$6+2x=0$$
$$2x=-6$$
$$x=-3$$

(iv) Na_3PO_4

$$3(+1)+x+4(-2)=0$$
$$3+x-8=0$$
$$x-5=0$$
$$x=+5$$

(v) POF_3

$$x+(-2)+3(-1)=0$$
$$x-5=0$$
$$x=+5$$

Question 7.32:

Write balanced equations for the following:

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

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

Answer

(i) $$4NaCl+MnO_2+4H_2SO_4 \longrightarrow MnCl_2+4NaHSO_4+2H_2O+Cl_2$$

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

Question 7.33:

How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

Answer

XeF_2, XeF_4, and XeF_6 are obtained by a direct reaction between Xe and F2. The condition under which the reaction is carried out determines the product.

$$\underset{\text{(Excess)}}{Xe_{(g)}} + F_{2(g)} \xrightarrow{673\text{K}, 1\text{bar}} XeF_{2(s)}$$

$$\underset{\text{(1:5 ratio)}}{Xe_{(g)} + 2F_{2(g)}} \xrightarrow{873\text{K}, 7\text{bar}} XeF_{4(s)}$$

$$\underset{\text{(1:20 ratio)}}{Xe_{(g)} + 3F_{2(g)}} \xrightarrow{573\text{K}, 60-70\text{bar}} XeF_{6(s)}$$

Question 7.34:

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

ClO^- is isoelectronic to ClF. Also, both species contain 26 electrons in all as shown.

Total electrons ClO^- = 17 + 8 + 1 = 26

In ClF = 17 + 9 = 26

ClF acts like a Lewis base as it accepts electrons from F to form ClF_3.

Question 7.35:

How are XeO_3 and $XeOF_4$ prepared?

Answer

(i) XeO_3 can be prepared in two ways as shown.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(ii) $XeOF_4$ can be prepared using XeF_6.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Question 7.36:

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

(i) F_2, Cl_2, Br_2, I_2 - increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI - increasing acid strength.

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

Answer

(i) Bond dissociation energy usually decreases on moving down a group as the atomic size increases. However, the bond dissociation energy of F2 is lower than that of Cl2 and Br2. This is due to the small atomic size of fluorine. Thus, the increasing order for bond dissociation energy among halogens is as follows:

$I_2 < F_2 < Br_2 < Cl_2$

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

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

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

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

Question 7.37:

Which one of the following does not exist?

(i) $XeOF_4$ **(ii)** NeF_2

(iii) XeF_2 **(iv)** XeF_6

Answer

NeF_2 does not exist.

Question 7.38:

Give the formula and describe the structure of a noble gas species which is isostructural with: **(i)** ICl_4^-

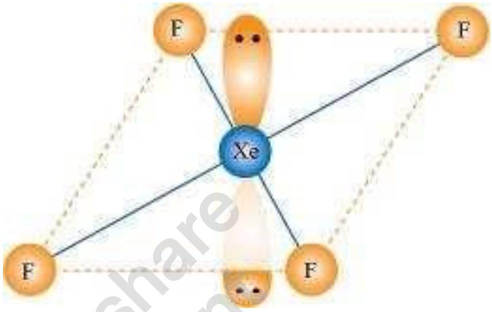
(ii) IBr_2^-

(iii) BrO_3^-

Answer

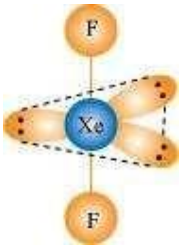
(i)

XeF_4 is isoelectronic with ICl_4^- and has square planar geometry.



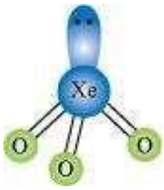
(ii)

XeF_2 is isoelectronic to IBr_2^- and has a linear structure.



(iii)

XeO_3 is isostructural to BrO_3^- and has a pyramidal molecular structure.



Question 7.39:

Why do noble gases have comparatively large atomic sizes?

Answer

Noble gases do not form molecules. In case of noble gases, the atomic radii corresponds to van der Waal's radii. On the other hand, the atomic radii of other elements correspond to their covalent radii. By definition, van der Waal's radii are larger than covalent radii. It is for this reason that noble gases are very large in size as compared to other atoms belonging to the same period.

Question 7.40:

List the uses of Neon and argon gases.

Answer

Uses of neon gas:

(i) It is mixed with helium to protect electrical equipments from high voltage.

(ii) It is filled in discharge tubes with characteristic colours.

(iii) It is used in beacon lights.

Uses of Argon gas:

(i) Argon along with nitrogen is used in gas-filled electric lamps. This is because Ar is more inert than N.

(ii) It is usually used to provide an inert temperature in a high metallurgical process.

(iii) It is also used in laboratories to handle air-sensitive substances.