Chapter: 7 (The p – Block Elements)

Exercise Questions

Question: 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 characteristics of group 15 elements:

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

ii.) Oxidation state: The common oxidation state of these elements are

-3, +3, +5. The tendency to exhibit -3 oxidation decreases down the group due to increase in size and metallic character (the last member of this group bismuth hardly forms any compound in -3 oxidation state). All the elements present in this group shows +3 and +5 oxidation states. However, the stability of +5 oxidation state decreases down a group, whereas the stability of +3 oxidation state increases due to inert pair effect.

iii.) Ionisation energy and electronegativity: Both the ionisation energy and electronegativity decreases as we moving down the group because of increase in size of atoms.

iv.) Atomic size: as we move down the group, atomic size of elements will increase due to increase in number of shells.

Question: 2 Why does the reactivity of nitrogen differ from phosphorus?

Answer: Nitrogen is chemically less reactive. This is because of the high stability of molecules, N_2. In N_2 the two nitrogen atoms are triply bonded, and have very high bond strength, which is very difficult to break. This high bond strength is because of nitrogen's small size that is able to form $p\pi \ldots p\pi$ bond with itself. This property is not exhibited by atoms such as phosphorous due to large size. Thus phosphorous is more reactive than nitrogen.

Question: 3 Discuss the trends in chemical reactivity of group 15 elements.

Answer: The trends in chemical reactivity of group 15 elements are given below:

(i) Reactivity with hydrogen: Group 15 elements form hydrides of the type MH_3 where M is group 15 element. On moving down the group, the stability of hydrides decreases.

(ii) Reactivity with oxygen: Group 15 elements form the oxides M_2O_3 and M_2O_5. In the oxide, when the oxidation state of group 15 element is higher, it is more acidic than the one with lower oxidation state. On moving down the group, the acidic character decreases.

(iii) Reactivity with halogens: Group 15 elements form the salts MX_3 and MX_5. Nitrogen only forms NX_3 but not NX_5 because of absence of the d-orbital. NX_3 is unstable and other trihalides are stable.

(iv) Reactivity towards metals: Group 15 elements form binary compounds with metals. In these compounds, the oxidation state of metal is -3.

Question: 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: 5 How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

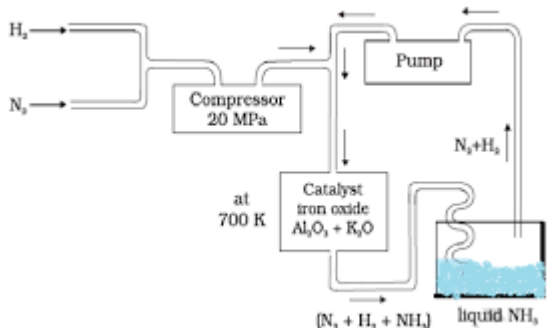
Answer: An aqueous solution of ammonium chloride is treated with sodium nitrite.

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

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: 6 How is ammonia manufactured industrially?

Answer: Ammonia is manufactured industrially by Haber's process. A mixture of dry nitrogen and hydrogen gases in the ratio of 1:3 by volume is compressed to about 200 to 300 atm. and passed over iron catalyst at a temperature of about 723 k to 773 k. Ammonia being formed is continuously removed by liquefying it.



Question: 7 Illustrate how copper metal can give different products on reaction with HNO_3.

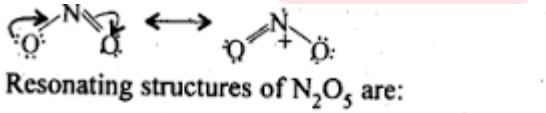
Answer: Concentrated nitric acid is a oxidising agent. It is used for oxidising most metals. The products of oxidation depends on the concentration of acid, and also on the material undergoing oxidation.

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

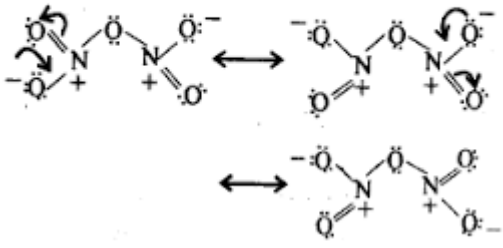
$Cu + 4HNO_{3(conc.)} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Question: 8 Give the resonating structures of NO_2 and N_2O_5?

Answer: The resonating structures are shown:



Resonating structures of N_2O_5 are:



Question: 9 The HNH angle value is higher than HPH, HAsH, and HSbH angles. Why?

Answer: The difference in the bond angles is based on the electronegativity and the size of the central atom. As a result, there is a gradual decrease in the electron density on the central atom resulting in decreased bond angles in the same order. Thus, the HNH angle value is higher than HPH, HAsH and HSbH angles.

Question: 10 Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

Answer: Nitrogen does not contains d-orbitals. As a result, it cannot expand its valency beyond four and cannot form pπ – dπ multiple bonds. In contrast, P contains the d-orbitals, and can expand its valency beyond 4 and can form pπ-dπ multiple bonds. Hence $R_3O = O$ exist but $R_3N = O$ does not.

Question: 11 Explain why NH_3 is basic while BiH_3 is only feebly basic?

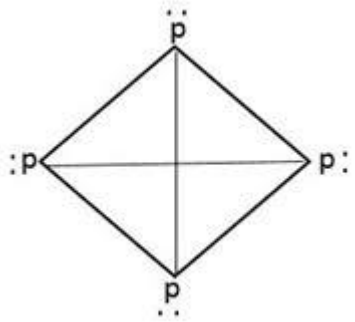
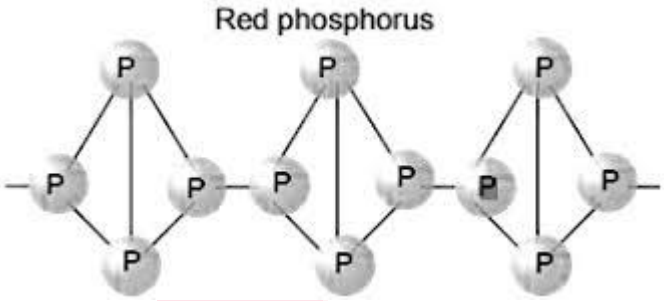
Answer: NH_3 is distinctly basic while BiH_3 is feebly basic. Nitrogen has a small size due to which the lone pair of electrons is concentrated in a small region. This means that the charge density per unit volume is high. Hence, the electron donating capacity of group 15 element hydrides decreases on moving down the group.

Question: 12 Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Answer: Because of its small size and high electronegativity nitrogen forms Pπ – pπ multiple bonds. Therefore, it exists as a diatomic molecule having a triple bond between the two N-atoms. But phosphorus prefers to form P – P single bonds because of its large size and hence it exists as tetrahedral, P_4 molecules.

Question: 13 Write main differences between the properties of white phosphorus and red phosphorus.

Answer:

White phosphorus	Red phosphorus
It is soft and waxy solid. It possesses garlic smell.	It is a hard and a 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 both water and carbon disulphide.
It undergoes spontaneous combustion in air.	It is relatively less reactive.
In both solid and vapour states, it exist as a P_4 molecule.	It exist as chain of tetrahedral P_4 units.
	

Question: 14 Why does nitrogen show catenation properties less than phosphorus?

Answer: The extent of catenation depends on strength of element-element bond. As N-N bond strength is weaker than P-P bond hence nitrogen shows less catenation properties than phosphorous.

Question: 15 Give the disproportionation reaction of H_3PO_3?

Answer: On heating, orthophosphorus acid disproportionates to give orthophosphoric acid and phosphine. The oxidation state of P in various species involved in the reaction are mentioned below:

$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

Question: 16 Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Answer: PCl_5 cannot act as reducing agent because it cannot increase its oxidation state beyond +5 and it can easily act as oxidising agent because it can decrease its oxidation state from +5 to +3.

Question: 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_2M, where M = O, S, Se, Te, PO. Oxygen and sulphur also form hydrides of type H_2M_2. These hydrides are quite volatile in nature.

Question: 18 Why is dioxygen a gas but sulphur a solid?

Answer: The intermolecular forces in oxygen are weak van der Waals forces, which causes it to exist as gas. On the other hand, sulphur does not form strong S=S double bonds hence exists as a puckered structure held together by strong covalent bonds and exists as a polyatomic molecule. So, it exists as a solid.

Question: 19 Which aerosols deplete ozone?

Answer: Chlorofluoro carbons, sulphur dioxide, nitrous oxide are some examples of ozone depleting substances. The aerosols that depletes ozone layer are chlorofluorocarbons such as freon. The chemical formula of freon is CCl_2F_2.

Question: 20 Describe the manufacture of H_2SO_4 by contact process?

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

Step 1: Sulphur or sulphide ores are burnt in air to form SO_2.

Step 2: By a reaction with oxygen, SO_2 is converted in SO_3 in the presence of V_2O_5 as a catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V2O5} 2SO_{3(g)}$$

Step 3: SO_3 produced is absorbed on H_2SO_4 of the desired concentration.

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

Question: 21 How is SO_2 an air pollutant?

Answer: Sulphur dioxide (SO_2) is an air pollutant made up of sulphur and oxygen atoms and is harmful to both plants and people. On dissolution in rain water, SO_2 produces acid rain. This SO_3 gets converted into H_2SO_4 in the presence of moisture, which comes down in the form acid rain.

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

Question: 22 Why are halogens strong oxidising agents?

Answer: Halogens act as strong oxidising agents because they have high tendency to accept electron, i.e., they have high electron affinity values. The reduction potentials are high (positive) and decreased from F to I.

Question: 23 Explain why fluorine forms only one oxoacids. HOF.

Answer: Fluorine forms only one oxoacid, HOF due to small atomic size and high electronegativity. Fluorine cannot act as central atom in higher oxoacids.

Question: 24 Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Answer: Atomic size of oxygen is smaller than the atomic size of chlorine. Small atomic size favours hydrogen bond formation.

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

Question: 25 Write two uses of ClO_2.

Answer: **Uses:**

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

Question: 26 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 differ for each halogen, each halogen displays a colour.

Question: 27 Write the reaction of F_2 and Cl_2 with water.

Answer:

i.) $Cl_2 + H_2O \rightarrow HCl + HOCl$
ii.) $2F_{2(g)} + 2H_2O \rightarrow O_{2(g)} + 4HF_{(aq)}$

Question: 28 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.

$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$

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

$Cl_2 + H_2O \rightarrow HCl + HOCl$.

Question: 29 What inspired N. Bartlett for carrying out reaction b/w Xe and PtF_6?

Answer: PtF_6, a powerful oxidizing agent combines with oxygen to form $O_2^+[PtF_6]^-$. This shows that PtF_6 has oxidized O_2 to O_2^+.

Following are the similarities between oxygen and xenon:

(i) They have similar first ionization enthalpies, 1170 kJ/mol and 1166 kJ/mol for oxygen and xenon respectively.

(ii) The molecular diameter of oxygen and the atomic radius of Xe are similar ($4A^0$).

This inspired N. Bartlett to carry out reaction between Xe and PtF_6.

Question: 30 What is the oxidation state 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 of x.

i.) H_3PO_3

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

$3 + x - 6 = 0$

$X = 3$

ii.) PCl_3

$X + 3(-1) = 0$

$X - 3 = 0$

$X = 3$

iii.) Ca_3P_2

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

$6 + 2x = 0$

$x = -3$

iv.) Na_3PO_4

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

$3 + x - 8 = 0$

$X = 5$

v.) POF_3

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

$X - 5 = 0$

$X = 5$

Question: 31 Write the balanced equation 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.) $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

ii.) $Cl_2 + NaI \rightarrow 2NaCl + I_2$

Question: 32 How are xenon fluoride XeF_2, XeF_4 and XeF_6 obtained?

Answer: The preparation of xenon fluorides are given below:

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

$Xe\ (g, 1\text{mole}) + 2F_2(g, 5\ \text{moles}) \xrightarrow[7\ \text{bar}]{873\ K} XeF_4(s)$

$Xe\ (g, 1\ \text{mole}) + 3F_2(g, 20\ \text{moles}) \xrightarrow{60-70\ \text{bar}} XeF_6(s)$

Question: 33 With what neutral molecule is ClO^- isoelectronic? Is that molecule a lewis base?

Answer: ClO^- is isoelectronic to ClF as both the compounds contain 26 electrons in all.

ClO^- : 17+8+1 = 26

ClF : 17+9 = 26.

Yes, ClF molecule is a Lewis base as it accepts electrons from F to form ClF_3.

Question: 34 How are XeO_3 and $XeOF_4$ prepared?

Answer:

i.) XeO_3 can be prepared in two ways:

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

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

ii.) $XeOF_4$ can be prepared using:

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

Question: 35 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) $I_2 < F_2 < Br_2 < Cl_2$

The electron affinity of Chlorine is maximum in the periodic table and so the bond dissociation enthalpy. Flourine has lower bond dissociation enthalpy than Br_2 and Cl_2. Due to small size electronic repulsion is very high. I_2 has lowest bond dissociation enthalpy due to quite larger size it is easiest to break the bond.

(ii) HF < HCl < HBr < HI ⇒ Acidic strength of Halogen acids increases down the group.

Iii.)$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$ ⇒ Basic strength decreases down the group because as we go down the group the size of the atom and thus the electron density decreases. These compounds are lewis base having 1 lone pair on the central atoms. As the electron density decrease the tendency to donate electron pair decreases.

Question: 36 Which one of the following does not exist?

i.) $XeFO_4$, ii.) NeF_2, iii.) XeF_2, iv.) XeF_6

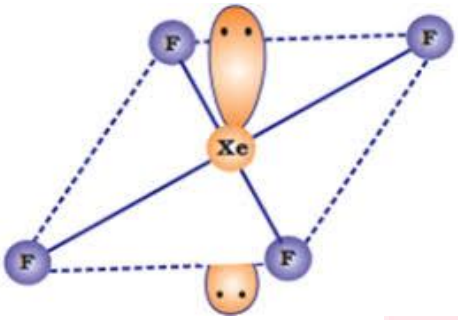
Answer: NeF_2, does not exist.

Question: 37 Give the formula and describe the structure of noble gas species which is isostructural with:

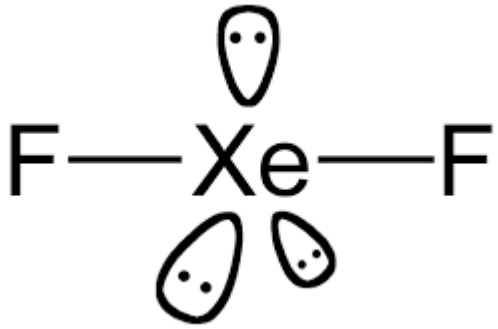
i.) ICl^-_4 ii.) IBr_2^- iii.) BrO_3^-

Answer:

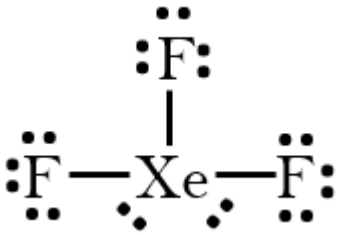
i.) XeF_4 is isostructural with ICl_4^- and has square planar geometry.



ii.) XeF_2 is isostructural with IBr_2^- and has a linear structure.



iii.) XeF_3 is isostructural with BrO_3^-



Question: 38 Why do noble gases have comparatively large atomic size?

Answer: All the electrons of noble gas elements are paired (ns^2np^6configuration), paired electrons produce inter electronic repulsions which weakens the effective nuclear force, so electrons tend to move away from the nucleus because of repulsions. So size of noble gases are bigger than the other elements in their respective periods.

Question: 39 List the uses of neon and argon gases.

Answer: Uses of Neon and Argon Gases -

Uses of neon gas:

i.) It is mixed with helium to protect electrical equipment's 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.

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.

Question: 40 Knowing the electron gain enthalpy value for O → O^- and O → O^{2-} as -141 and 702 $kJmol^{-1}$ respectively, how can you account for the formation of a large no. of oxides having O^{2-} species and not O^-?

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^-.