Chapter.7
The p-block Elements
Class-XII
Subject-Chemistry

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

Answer 7.1

General characteristics of group 15 elements are:

a) Electronic configuration

Elements of group 15 have 5 valence electrons. Their general electronic configuration is $ns^2\ np^3$.

b) Ionization energy

On moving down a group, first ionization energy decreases. This happens because of increasing atomic sizes.

c) Electronegativity

On moving down a group, electronegativity decreases

d) Oxidation states

Elements of this group have 5 valence electrons and they require three more electrons to complete their octets. But, gaining electrons is very difficult in nitrogen as the nucleus will have to attract three more electrons. The remaining elements of this group show oxidation state of −3. In addition to the −3 state, N and P also show −1 & −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.

e) Atomic size:

On moving down a group, atomic size increases. This happens because of increase in the number of shells.

7.2 Why does the reactivity of nitrogen differ from phosphorus?

Answer 7.2

Electronic configuration of nitrogen is half filled & we know that fully filled & partially filled orbitals are quiet stable. Being, smaller in size, nitrogen is chemically less reactive. Whereas when we move down the group, size of atom increases, thus, other elements of this group do not exhibit this property. As size increases, effective nuclear charge of atom decreases & it can lose & gain electrons easily & show reactivity towards other elements. Thus, phosphorus is more reactive than nitrogen.

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

Answer 7.3

General trends in chemical properties of group – 15

a) Reactivity towards hydrogen:

Group 15 elements react with hydrogen & form hydrides having formula EH_3, where E = N, P, As, Sb, or Bi. The stability of hydrides decreases on moving down from NH_3 to BiH_3.

b) Reactivity towards oxygen:

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

c) Reactivity towards halogens:

The group 15 elements react with halogens to form two types of salts: EX_3 and EX_5. But, nitrogen does not form NX_5 as *d*-orbitals are absent in it.

d) Reactivity towards metals:

On reaction with metals, group 15 elements form binary compounds in which metals exhibit −3 oxidation states.

7.4 Why NH_3 form hydrogen bonds but PH_3 does not?

Answer 7.4

As we move down the group, electronegativity decreases. Thus, Nitrogen is highly electronegative as compared to phosphorus. This results in 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.

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

Answer 7.5

Laboratory preparation of nitrogen: -

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

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

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

7.6 How is ammonia manufactured industrially?

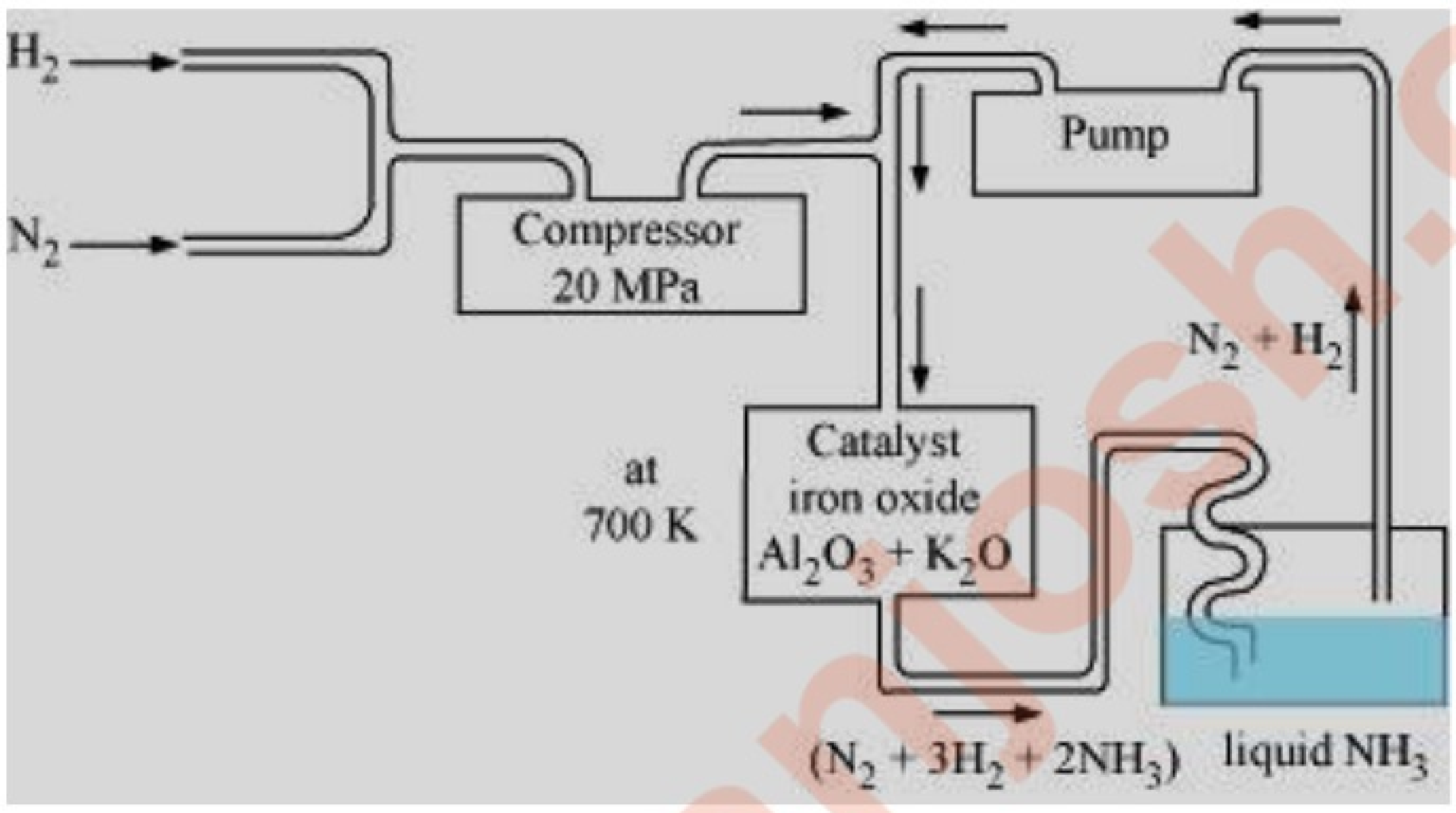
Answer 7.6

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

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

The optimum conditions for manufacturing ammonia are:

- Temperature = 4700 K
- Pressure = around 200 × 10^5 Pascal
- Catalyst such as iron oxide with small amounts of Al_2O_3 and K_2O



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

Answer 7.7

Concentrated nitric acid is used for oxidizing most metals. It is a strong oxidizing agent.

Reactions are:

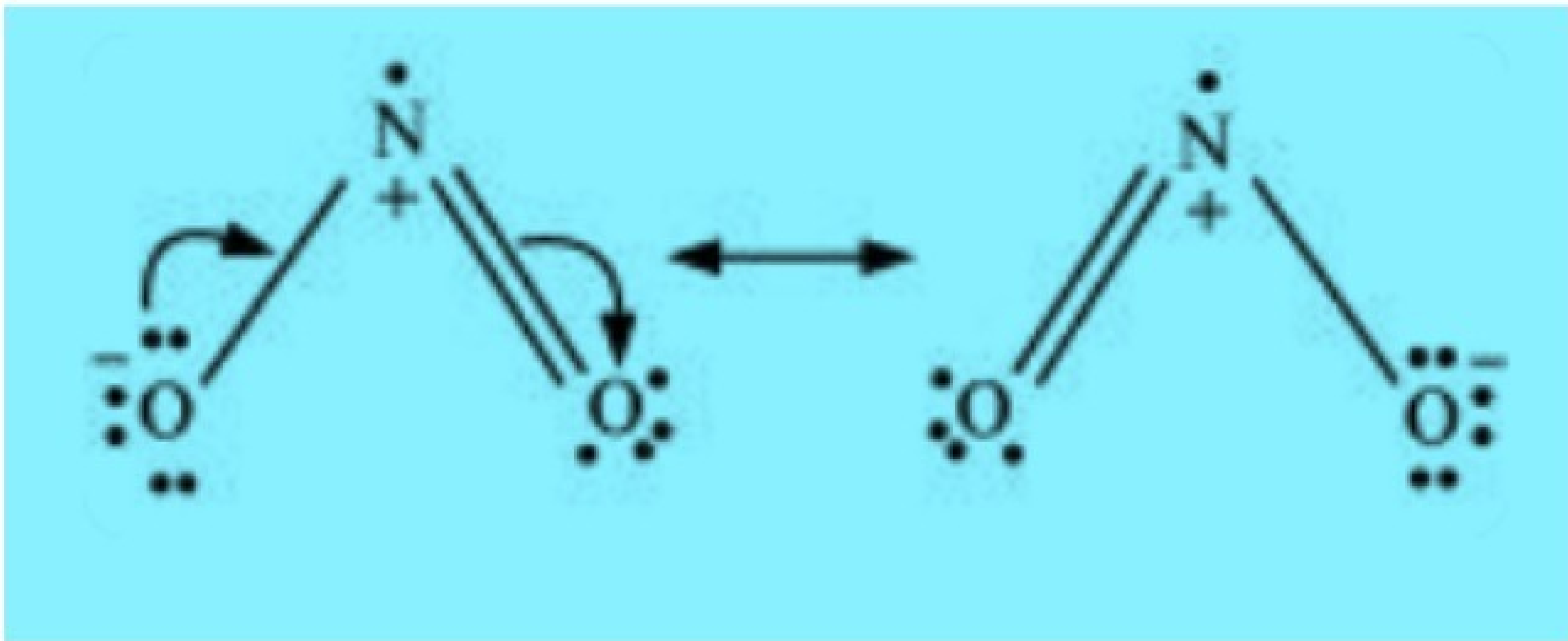
$$3Cu + 8HNO_{3(dilute)} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

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

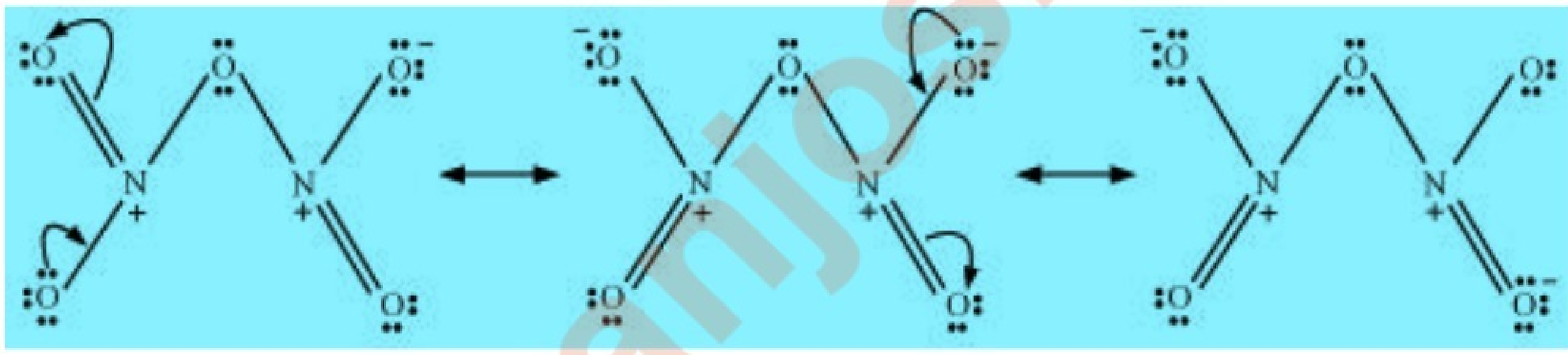
7.8 Give the resonating structures of NO_2 and N_2O_5.

Answer 7.8

a) NO_2



b) N_2O_5



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 7.9

This 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 leads to greater repulsion between the electron pairs around nitrogen. This results in greater bond angle.

We know that electronegativity decreases on moving down a group. Consequently, repulsive interactions between the electron pairs decrease, & thus decreasing the H−M−H bond angle.

Hydride NH_3 PH_3 AsH_3 SbH_3

H−M−H angle 107° 92° 91° 90°

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

Answer 7.10

D-orbitals are absent in the nitrogen atom. This restricts nitrogen to expand its coordination number beyond four. Hence, $R_3N=O$ does not exist.

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

Answer 7.11

Due to smaller size of Nitrogen, lone pair of electrons is concentrated in a small region. Due to this, the charge density per unit volume is high on nitrogen. On moving down a group, this charge density decreases as size of the central atom increases and the charge gets distributed over a large area. Thus, the electron donating capacity of group 15 element hydrides decreases on moving down the group.

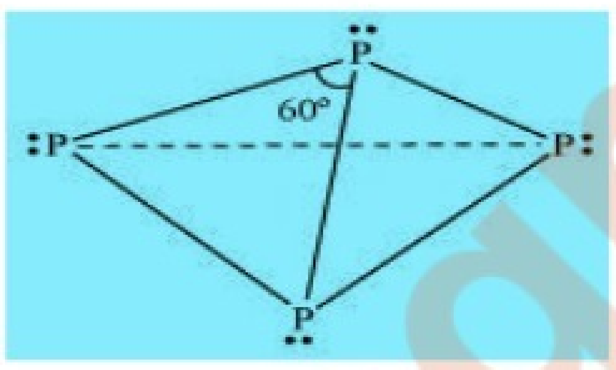
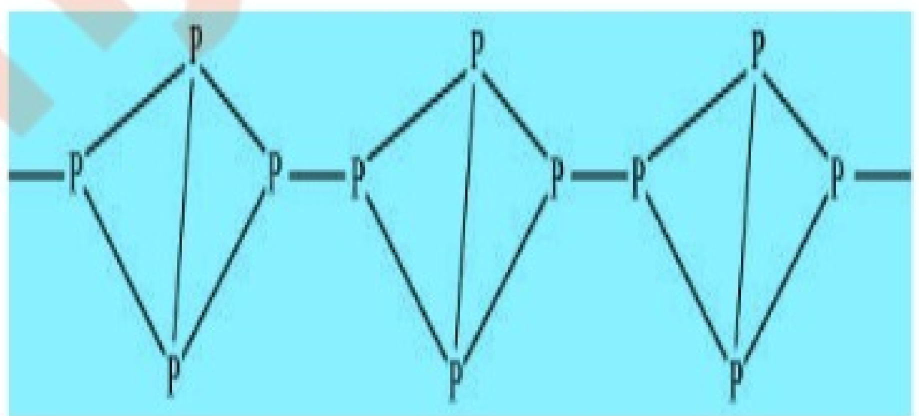
7.12 Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Answer 7.12

Due to smaller size, Nitrogen has a tendency to form $p\pi-p\pi$ multiple bonds with itself. Because of this Nitrogen 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. Thus, phosphorus exists in the P_4 state.

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

Answer 7.13

White phosphorus	Red Phosphorus
Soft and waxy solid	Hard and crystalline solid
Possesses a garlic smell	Without any smell
Insoluble in water but soluble in carbon disulphide.	Insoluble in both water and carbon disulphide
Poisonous in nature	Non-poisonous
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. 

7.14 Why does nitrogen show catenation properties less than phosphorus?

Answer 7.14

Because of smaller size of Nitrogen, N−N single bond is weaker than P−P single bond. Since, there is greater repulsion of electron density of two nitrogen atoms, thereby weakening the N−N single bond. Thus, catenation is much more common in phosphorous compounds than in nitrogen compounds.

7.15 Give the disproportionation reaction of H_3PO_3.

Answer 7.15

On heating, following disproportionate reaction takes place.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

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

Answer 7.16

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

Thus, PCl_5 can only act as an oxidizing 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.

Answer 7.17

Group 16 elements are collectively known as chalcogens. Characteristics of this group are:

a) Group 16 elements have six valence electrons. The general electronic configuration of these elements is $ns^2\, np^4$, where n varies from 2 to 6.

b) Oxidation state: - because of six valence electrons, they should display an oxidation state of −2. In additionally, they also show the oxidation state of −1, zero, and +2.

But, 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 presence of *d*-orbitals.

c) 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 volatile in nature.

7.18 Why is dioxygen a gas but sulphur a solid?

Answer 7.18

Size of Oxygen is small as compared to sulphur. Because of which, it can effectively form $p\pi - p\pi$ bonds and form O_2 molecule. The intermolecular forces in oxygen are weak van der Wall's, which cause it to exist as gas. Whereas, sulphur does not form M_2 molecule but exists as a puckered structure held together by strong covalent bonds. Hence, 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 large number of oxides having O^{2-} species and not O^-? (Hint: Consider lattice energy factor in the formation of compounds).

Answer 7.19

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.

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

Thus, the oxide having O^{2-} ions are more stable than oxides having O^-.

7.20 Which aerosols deplete ozone?

Answer 7.20

Chlorofluorocarbons or Freons (CFCs) are an aerosol that depletes ozone layer. In the presence of u-v radiations, molecules of CFCs break down to form chlorine-free radicals that combine with ozone to form oxygen & deplete the ozone layer.

7.21 Describe the manufacture of H_2SO_4 by contact process?

Answer 7.21

Sulphuric 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: With the help of 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 3: SO_3 produced is absorbed on H_2SO_4 to give $H_2S_2O_7$ (oleum).

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

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

The sulphuric acid thus obtained is 96-98% pure.

7.22 How is SO_2 an air pollutant?

Answer 7.22

Sulphur dioxide act as an air pollutant in many ways:

a) It is extremely harmful to plants. When plants get exposed to sulphur dioxide for a long time, they lose colour from their leaves. This is known as chlorosis. This happens because sulphur dioxide affects the formation of chlorophyll.

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

c) On combination with water vapour present in the atmosphere, sulphur dioxide forms sulphuric acid. This results in acid rain which in turn damages soil, plants, and buildings.

7.23 Why are halogens strong oxidising agents?

Answer 7.23

The general electronic configuration of halogens is np^5, where n = 2-6.

Because of this configuration, they need only one more electron to complete their octet and achieve the stable noble gas configuration. Additionally, they are highly electronegative, having high negative electron gain enthalpies & low dissociation energies. Thus, they have a high tendency to gain an electron. Therefore, they act as strong oxidizing agents.

7.24 Explain why fluorine forms only one oxoacid, HOF.

Answer 7.24

Fluorine is smaller in size & it is highly electronegative in nature. Because of which, it forms only one oxoacid i.e., HOF

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

Answer 7.25

Although, chlorine and oxygen have almost the same electronegativity, but chlorine rarely forms hydrogen bonding. This happens because oxygen has a smaller size as compared to chlorine. As a result, a higher electron density per unit volume is present on oxygen.

7.26 Write two uses of ClO_2.

Answer 7.26

Uses of ClO_2 are:

- It is used for purifying water.
- It is used as a bleaching agent.

7.27 Why are halogens coloured?

Answer 7.27

When a halogen absorbs radiations in the visible region, their valence electrons get excited to a higher energy region. When those valence electrons get back to ground state, energy is released in the form of radiations. Since, the amount of energy required for excitation differs for each halogen, thus, each halogen displays a different colour.

7.28 Write the reactions of F_2 and Cl_2 with water.

Answer 7.28

a) $Cl_2 + H_2O \rightarrow HCl + HOCl$

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

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

Answer 7.29

a) **<u>Deacon's process:</u>** - Cl_2 can be prepared from HCl by this process

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

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

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

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

Answer 7.30

Neil Bartlett initially carried out following reaction:

$$O_2 + PtF_6 \rightarrow O_2^+\left[PtF_6\right]^-$$

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 was formed.

$$Xe + PtF_6 \rightarrow Xe^+\left[PtF_6\right]^-$$

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 7.31

i. H_3PO_3

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

ii.

PCl_3

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

iii.

Ca_3P_2

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

iv.

Na_3PO_4

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

v.

POF_3

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

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.**

Answer 7.32

i. $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

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

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

Answer 7.33

Following reactions are involved: -

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

$(excess)$

$$Xe_{(g)} + 2F_{2(g)} \xrightarrow{873K,\ 7\ bar} XeF_{4(s)}$$

$(1:5 \text{ ratio})$

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

$(1:20 \text{ ratio})$

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

Answer 7.34

ClO^- is isoelectronic with ClF

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

Total electrons in $ClF = 17 + 9 = 26$

Both species contain 26 electrons.

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

7.35 How are XeO_3 and $XeOF_4$ prepared?

Answer 7.35

a) XeO_3 can be prepared in two ways:

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

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

b) $XeOF_4$ can be prepared as:

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

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

i. F_2, Cl_2, Br_2, I_2 - increasing bond dissociation enthalpy.
ii. HF, HCl, HBr, HI - increasing acid strength.
iii. NH_3, PH_3, AsH_3, SbH_3, BiH_3 − increasing base strength.

Answer 7.36

i. On moving down the group, bond dissociation energy decreases as the atomic size increases. But, the bond dissociation energy of F2 is lower than that of Cl2 and Br2. This is because of smaller size of fluorine. Hence, the order for bond dissociation energy is:

$I_2 < F_2 < Br_2 < Cl_2$

ii. With increase in the atomic size, the bond dissociation energy of H-X decreases. HI is the strongest acid.

HF < HCl < HBr < HI

iii. With the increase in atomic size, electron density on the atom decreases. Thus, the basic strength decreases.

$$BiH_3 \leq SbH_3 < AsH_3 < PH_3 < NH_3$$

7.37 Which one of the following does not exist?

i. $XeOF_4$
ii. NeF_2
iii. XeF_2
iv. XeF_6

Answer 7.31

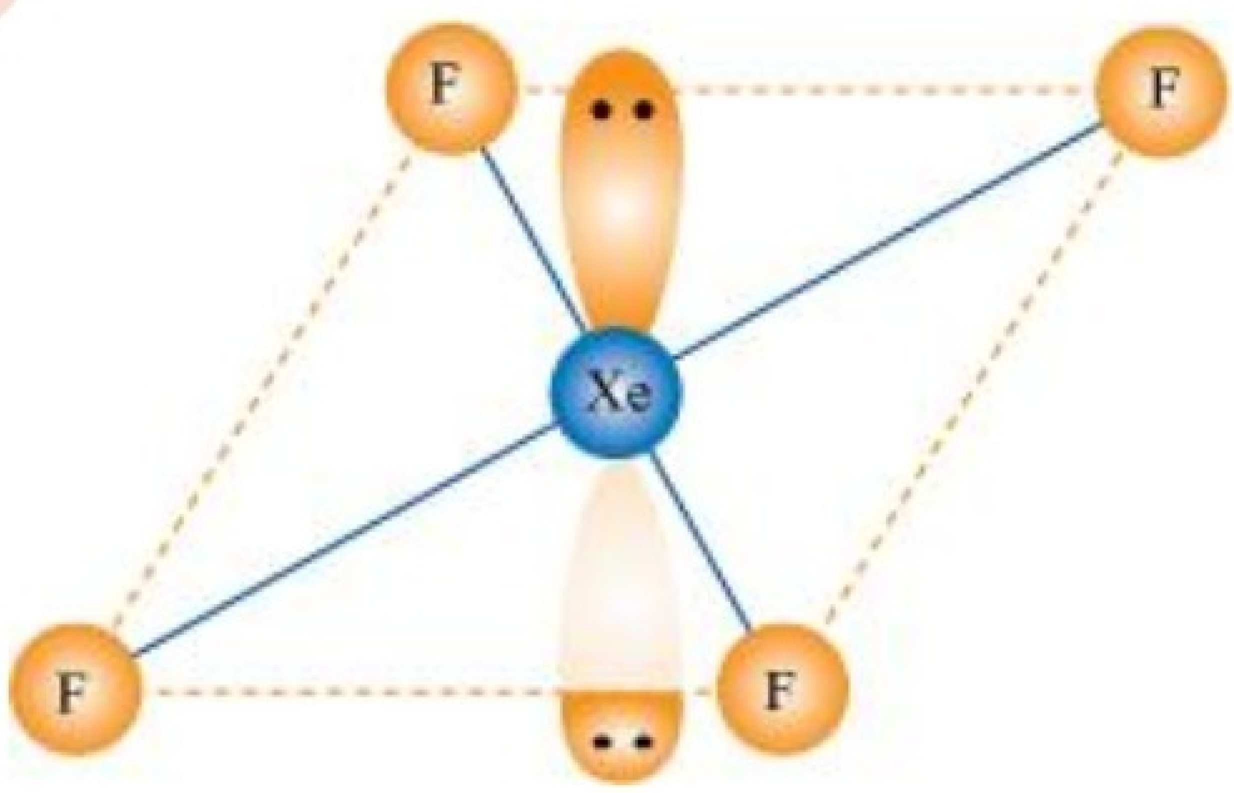
NeF_2 does not exist

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

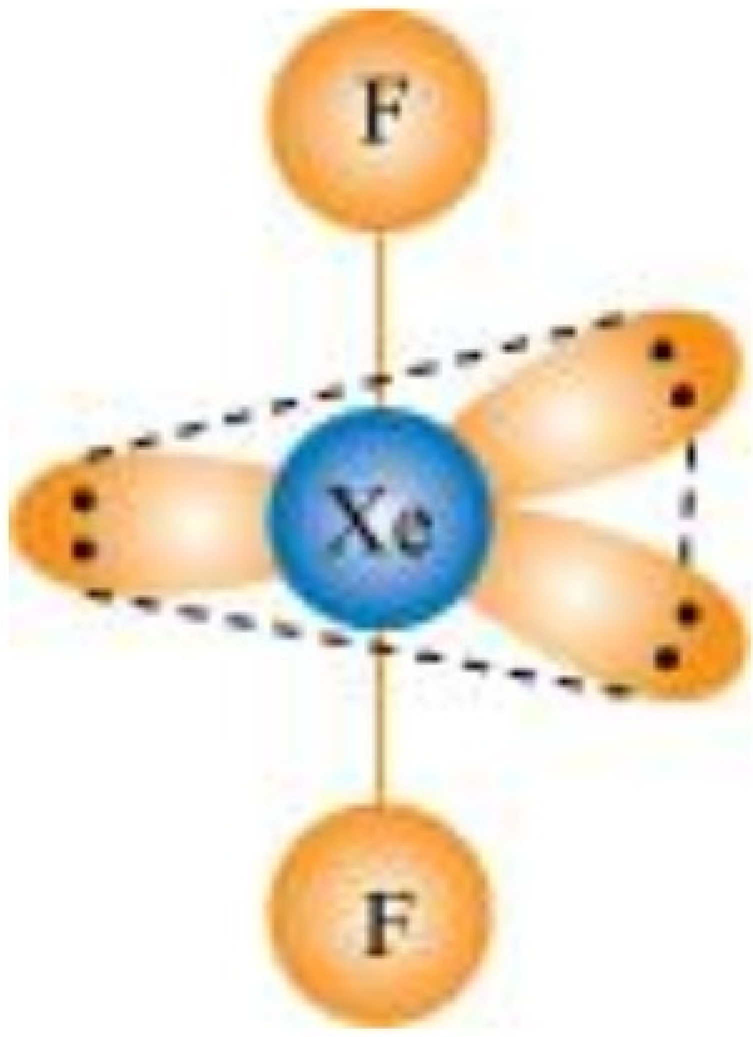
i. ICl_4^-
ii. IBr_2^-
iii. BrO_3^-

Answer 7.31

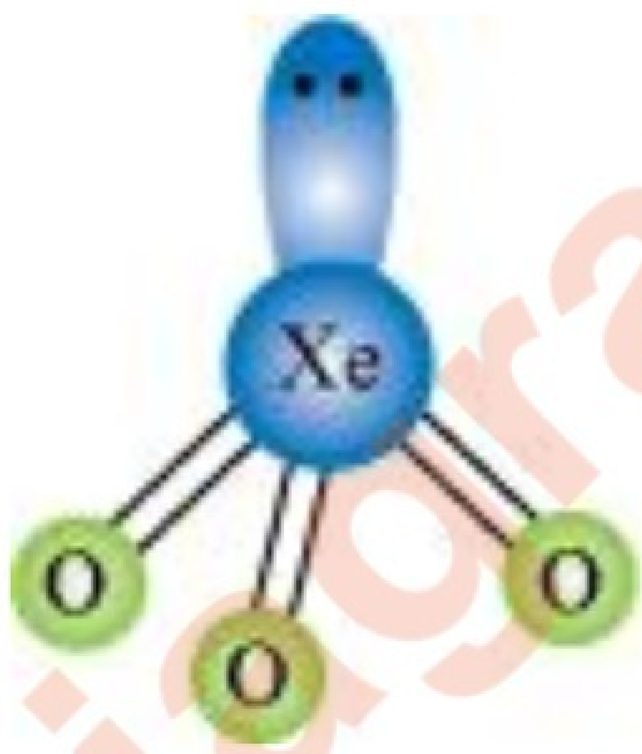
i. XeF_4 is isoelectronic with ICl_4^- and has square planar geometry.



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.



7.39 Why do noble gases have comparatively large atomic sizes?

Answer 7.39

Because of fully filled octet, Noble gases do not form molecules. Their atomic radii correspond to vander Waal's radii. On the other hand, atomic radii of other elements correspond to their covalent radii.

We know that, vander Waal's radii are larger than covalent radii. Thus, noble gases are very large in size as compared to other atoms belonging to the same period.

7.40 List the uses of Neon and argon gases.

Answer 7.40

Uses of neon gas:

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

Uses of Argon gas:

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