Q 1: Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity

Solution:
General trends in group 15 elements
(i) Electronic configuration: There are 5 valence electrons for all the elements in group 15.
$ns^2\ np^3$ is their general electronic configuration.

(ii) Oxidation states: All these elements require three or more electrons to complete their octets and have 5 valence electrons. It is difficult in gaining electrons as the nucleus will have to attract three more electrons. This happens 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:
Ionization decreases as we move down the group. This happens because of increase in atomic sizes. Moving down the group, electronegativity decreases due to increase in size.

(iv) Atomic size: As we move down the group atomic size increases. This increase in the atomic size is attributed to an increase in the number of shells.

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

Solution:
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 $p\pi-p\pi$ bonds with itself. This property is not exhibited by atoms such as phosphorus. Thus, phosphorus is more reactive than nitrogen.

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

Solution:
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.

Q 4: Why does NH_3 form hydrogen bond but PH_3 does not?

Solution:
When compared to phosphorus nitrogen is highly electronegative. This results in 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.

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

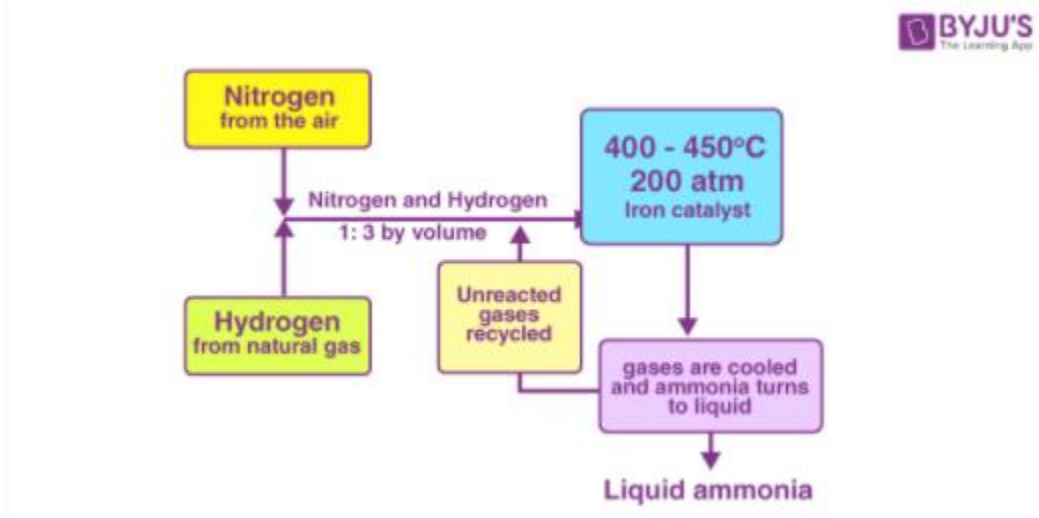
Solution:
An aqueous solution of ammonium chloride is treated with sodium nitrite.

$$NH_4Cl\ (aq\ ) + NaNO_2 \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

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.

Q 6: How is ammonia manufactured industrially?

Solution:
Ammonia is prepared on a large-scale by the Haber's process.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

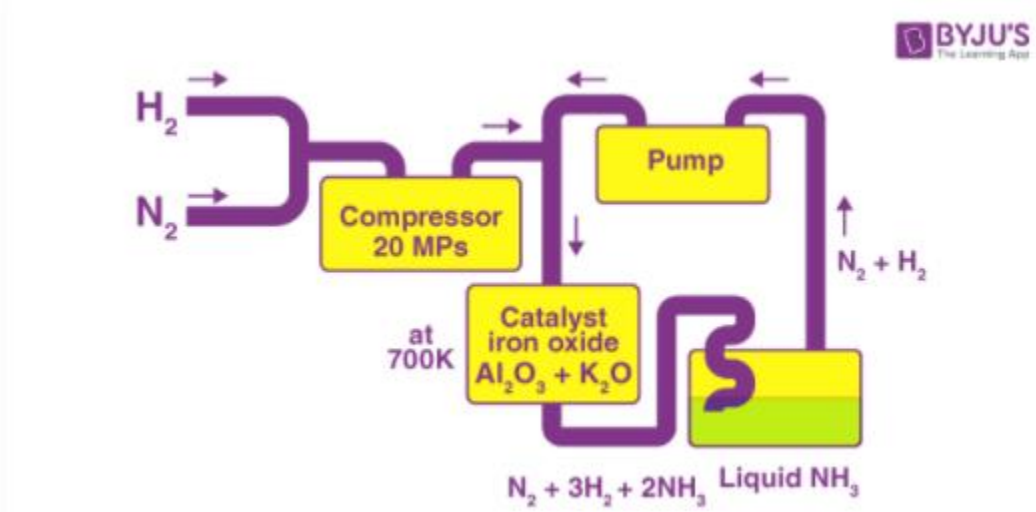


The optimum conditions for manufacturing ammonia are:

(i) Pressure (around 200 x 10^5 Pa)

(ii) Temperature (700 K)

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



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

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

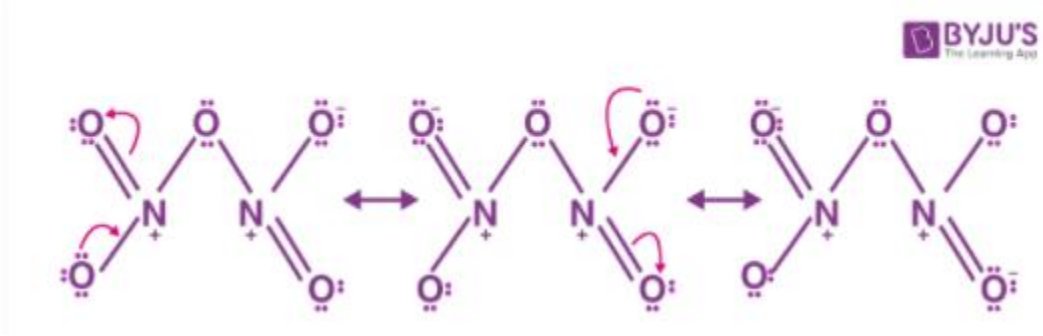
$3Cu + 8HNO_3(\text{dil.}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

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

Q 8: Give the resonating structures of NO_2 and N_2O_5

Solution:
NO_2

N_2O_5



Q 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 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.

Q 10: Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkylgroup)?

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

Q 11: Explain why NH_3 is basic while BiH_3 is only feebly basic.

Solution:
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 decrease on moving down the group.

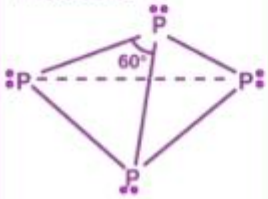
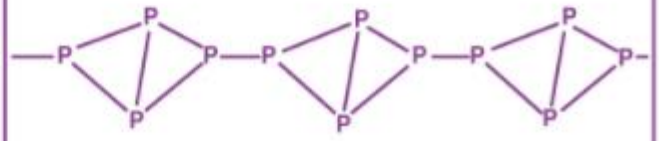
Q 12: Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Solution:
Nitrogen owing to its small size has a tendency to form pπ−pπ multiple bonds with itself.

Nitrogen thus forms a very stable diatomic molecule, N_2. On moving down a group, the tendency to form pπ−pπ bonds decreases (because of the large size of heavier elements). Therefore, phosphorus (like other heavier metals) exists in the P_4 state.

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

Solution:

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 P4 molecule. 	it exists as a chain of tetrahedral P4 units. 

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

Solution:
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.

Q 15: Give the disproportionation reaction of H_3PO_3.

Solution:
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.

$4H_3P^{+3}O_3 \rightarrow 3H_3P^{+5}O_4 + P^{-3}H_3$

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

Solution:
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.

Q 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:
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^2np^4, where n varies from 2 to 6

(ii) Oxidation state:

As these elements have six valence electrons (ns^2np^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.

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

Solution:
Oxygen is smaller in size when compared to sulphur. Since its size is small, it can form pπ−pπ 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.

Q 19: Knowing the electron gain enthalpy values for $O \rightarrow O^{-1}$ 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).

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

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^{-} ion. Hence, we can say that formation of O^{2-} is energetically more favourable than formation of O^{-}.

Q 20. Which aerosols deplete ozone?

Solution:
The aerosol which is responsible for the depletion of ozone is: Freons or chlorofluorocarbons (CFCs).

The molecules of CFS break down when there is presence of ultraviolet radiations and forms chlorine free radicals which then combines with ozone to form oxygen.

Q 21. Describe the manufacture of H_2SO_4 by contact process.

Solution:

The steps which are required in the production of Sulphuric Acid by the contact process

Step (1)

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

Step (2)

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 (3)

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

$$SO_3 + H_2S_4 \rightarrow H_2S_2O_7$$

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.

Q 22: How is SO_2 an air pollutant?

Solution:

The environment is harmed by sulphur dioxide in many ways:

1. Sulphuric acid is formed, when it is combined with water vapour present in the atmosphere. This causes acid that damages plants, soil, buildings (those made of marble are more prone), etc.

2. SO_2 causes irritation in respiratory tract, throat, eyes and can also affect the larynx to cause breathlessness.

3. The colour of the leaves of the plant gets faded when it is exposed to sulphur dioxide for a long time. This defect is known as chlorosis. The formation of chlorophyll is affected by the presence of sulphur dioxide.

Q 23: Why are halogens strong oxidising agents?

Solution:

Halogens have an electronic configuration of np^5, where n =2 to 6. Thus, halogens require only one more electron to complete their octet and to attain the stable noble gas configuration. Moreover, halogens have high negative electron gain enthalpies and are highly electronegative with low dissociation energies. As a result, they have a high tendency to gain an electron. Hence, they act as strong oxidising agents.

Q 24: Explain why fluorine forms only one oxoacid, HOF.

Solution:

Fluorine has high electronegativity and small size, hence it forms only one oxoacid i.e., HOF.

Q 25: Explain why inspite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

Solution:

Oxygen has a smaller size and due to which a higher electron density per unit volume. Hence, oxygen forms hydrogen bonds while chlorine does not despite having similar electronegative values.

Q 26. Write two uses of ClO_2.

Solution:

Applications of ClO_2
(a) Used for purification of water.
(b) Used for bleaching.

Q 27. Why are halogens coloured?

Solution:

Halogens are coloured because they take in radiations from the visible spectrum. This excites the valence electrons to a higher energy level. The amount of energy required for excitation differs from halogen to halogen, thus they exhibit different colours.

Q28. Write the reactions of F_2 and Cl_2 with water.

Solution:

(i) $Cl_2 + H_2O \rightarrow HCL + HOCL$

(ii) $2\,F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$

Q29. How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only

Solution:

(i) HCl is prepared from $Cl_2$by reacting it with water.
$Cl_2 + H_2O \rightarrow HCL + HOCL$

(ii) Cl_2 is prepared by Deacon's process from HCL
$4HCL + O_2 \rightarrow 2Cl_2 + 2H_2O$

Q30. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?

Solution:

N. Barlett observed that PtF_6 and O_2 react to produce a compound $O_2^+[PtF_6]^-$.
As the first ionization enthalpy of Xe (1170 kJ/mol) is very close to that of O_2 , he figured that PtF_6 could also oxidize Xe to Xe^+. Thus, he reacted PtF_6 and Xe to form a red coloured compound $Xe^+[PtF_6]^-$.

Q31. What are the oxidation states of phosphorus in the following:
(a) H_3PO_3
(b) PCl_3
(c) Ca_3P_2
(d) Na_3PO_4
(e) POF_3?

Solution:

Let the oxidation state of phosphorous be x
(a) H_3PO_3
3 + x + 3(-2) = 0
x -3 = 0
x =3

(b) PCl_3
x + 3(-1) = 0
x = 3

(c) Ca_3P_2
3 (2) + 2 (x) = 0
2x = -6
x = -3

(d) Na_3PO_4
3 (1) + x + 4 (-2) = 0
x -5 =0
x =5

(e)POF_3
x + (-2) + 3 (-1) = 0
x -5 = 0
x = 5

Q 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:

(a) $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

(b) $Cl_2 + NaI \rightarrow 2NaCl + I_2$

Q33. How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

Solution:

XeF_2, XeF_4 and XeF_6 are obtained through direction reactions between Xe and F_2. The product depends upon the conditions of the reaction :

$Xe + F_2 \rightarrow XeF_2$
(excess)

When Xe reacts with F_2 under the condition of 673K and 1 bar XeF_2 is produced.

$Xe + 2F_2 \rightarrow XeF_4$
(1:5 ratio)

When Xe reacts with F_2 in the ratio of 1:5 under the condition of 873K and 7 bar XeF_4 is produced.

$Xe + 3F_2 \rightarrow XeF_6$
(1 : 20 ratio)

When Xe reacts with F_2 in the ratio of 1:20 under the condition of 573K and 60-70 bar XeF_6 is produced.

Q34. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Solution:

ClO^- is isoelectronic with ClF.
Total electrons in ClO^- = 17 + 8 + 1 =26
Total electrons in ClF = 17 + 9 = 26
As ClF accepts electrons from F to form ClF_3, ClF behaves like a Lewis base.

Q35. How are XeO_3 and $XeOF_4$ prepared?

Solution:

XeO_3 can be obtained using two methods :
(1) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
(2) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$
$XeOF_4$ is obtained using XeF_6
$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

Q36. 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:

(1) Bond dissociation energy normally lowers on moving down a group because of increase in the atomic size. However, F_2has a lower bond dissociation energy than Cl_2 and Br_2. This is because the atomic size of fluorine is very small.
Therefore, the increasing order for bond dissociation enthalpy is:
$I_2 < F_2 < Br_2 < Cl_2$
(2) Bond dissociation energy of a H-X molecule (where X = F, Cl, Br, I) lowers with an increase in the size of an atom. As, H-I bond is the weakest it will be the strongest acid.
Therefore, the increasing order acidic strength is :
HF <HCl<HBr< HI

(3) $BiH_3 \leq SbH_3 < AsH_3 < PH_3 < NH_3$
On moving from nitrogen to bismuth, the atomic size increases but the electron density of the atom decreases. Hence, the basic strength lowers.

Q37. Which one of the following does not exist?
(i) $XeOF_4$ (ii) NeF_2 (iii) XeF_2 (iv) XeF_6

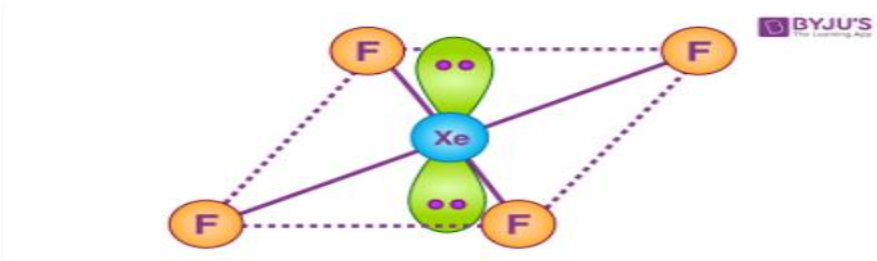
Solution:

The one that does not exist is NeF_2.

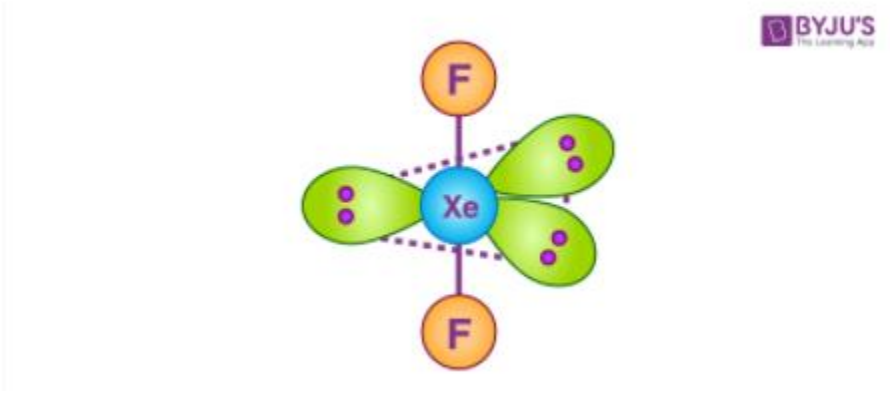
Q38. Give the formula and describe the structure of a noble gas species which is isostructural with:
(a) ICl_4^-
(b) IBr_2^-
(c) BrO_3^-

Solution:

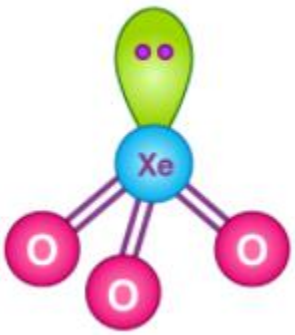
(a) XeF_4 is isoelectronic to ICl_4^- . And it is square planar in geometry:



(b) XeF_2 is isoelectronic with IBr_2^- . It has a linear structure.



(c)XeO_3 is isoelectric and isostructural to BrO_3^-. It has a pyramidal structure.



Q39. Why do noble gases have comparatively large atomic sizes?

Solution:

Noble gases have atomic radii that correspond to van der Waal's radii. Whereas, other elements have a covalent radius. Now, by definition, van der Waal's radii are bigger than covalent radii. This is the reason why noble gases have relatively bigger atomic sizes.

Q40. List the uses of neon and argon gases.

Solution:

Uses of Argon gas:
(a) Argon is used to keep an inert atmosphere in high temperature metallurgical operations like arc welding.
(b) It is used in fluorescent and incandescent lamps where it is required to check the sublimation of the

filament. Thereby, increasing the life of the lamp.
(c) Argon is used in laboratories to handle substances that are air-sensitive.

Uses of neon gas:
(a) Neon is filled in discharge tubes for advertising or decoration.
(b) Neon is used for making beacon lights.
(c) It is used alongside helium to protect electrical equipment against high voltage.