7 The *p*-Block Elements

Facts that Matter

- The general valence shell electronic configuration of *p*-block elements is ns^2np^{1-6}.
- **Group 15 Elements**

  Group 15 elements: N, P, As, Sb and Bi

  General electronic configuration; ns^2np^3.

Element	Occurrence
Nitrogen	Comprises 78% by volume of the atmosphere. In the earth's crust as $NaNO_3$ (called Chile saltpetre) and KNO_3 (Indian saltpetre)
Phosphorus	In minerals of the apatite family and as an essential constituent in animal and plant matter.
As, Sb & Bi	As sulphide minerals

Physical Properties

(*i*) Dinitrogen is a diatomic gas while all others are solids.

(*ii*) N & P are non-metals. As and Sb are metalloids and Bi is a metal. This is due to the decrease in ionisation enthalpy and increase in atomic size.

(*iii*) Electronegativity decreases down the group.

Chemical Properties

(*i*) Common oxidation states: –3, +3 and +5.

(*ii*) Due to inert effect, the stability of +5 state decreases down the group and stability of the +3 state increases.

(*iii*) In case of nitrogen, all the oxidation states from +1 to +4 tends to disproportionate in acidic solutions. For example,

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

Anomalous behaviour of nitrogen: Due to its small size, high electronegativity, high ionisation enthalpy and absence of d-orbitals.

N_2 has a unique ability to form pπ-pπ multiple bonds whereas the heavier members of this group do not form pπ-pπ bond because their atomic orbitals are so large and diffused that they cannot have effective overlapping.

Nitrogen exists as a diatomic molecule with triple bond between the two atoms whereas other elements form single bonds in the elemental state. N cannot form dπ-pπ bond due to the non-availability of d-orbitals whereas other elements can.

Trends in Properties

Stability of Hydrides—$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Bond dissociation enthalpy of Hydrides—$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Reducing character of Hydrides—$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
Basic character of Hydrides—$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Acidic character of Oxides—$N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3 > Bi_2O_3$

- **Dinitrogen (N_2)**

Preparation:

(*ii*) **Commercial preparation:** By the liquefaction and fractional distillation of air.

(*ii*) **Laboratory preparation:** By treating an aqueous solution of NH_4Cl with sodium nitrite: $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$

(*iii*) Thermal decomposition of ammonium dichromate will give N_2:
$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + 4H_2O + Cr_2O_3$

(*iv*) Thermal decomposition of barium or sodium azide also gives very pure N_2.

Properties

At high temperature, nitrogen combine with metals to form ionic nitrides (e.g. Mg_3N_2) and with non-metals, it forms covalent nitrides.

- **Ammonia**

Preparation

(*i*) In the laboratory it is prepared by heating ammonium salt with NaOH or lime.
$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$
$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$

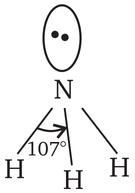
(*ii*) On a large scale it is manufactured by Haber's process.
$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
$\Delta H^0 = -46.1$ kJ/mol

According to Le Chatelier's principle the favourable conditions for the manufacture of NH_3 are

(*i*) Optimum temperature: 700 K, (*ii*) High pressure: 200 atm, (*iii*) Catalyst: iron oxide, (*iv*) Promoters: K_2O and Al_2O_3

Properties:

(*i*) Ammonia is a colourless gas with pungent odour.
(*ii*) Highly soluble in water.
(*iii*) In solid and liquid state it exists as an associated molecule due to hydrogen bonding, which accounts for the high melting and boiling points of NH_3.
(*iv*) NH_3 molecule has Trigonal pyramidal shape.



(*v*) Aqueous solution of ammonia is weakly basic due to the formation of OH^- ions.
(*vi*) It precipitates the hydroxide of many metals from their salt solutions.
Example: $ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$
(*vii*) Ammonia can form coordinate bonds by donating its lone pair on the nitrogen atom, and form complexes:

$$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$
$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$$

- **Oxides of Nitrogen**

Name	Formula	Oxidation State	Chemical Nature
Nitrous oxide or laughing gas	N_2O	+1	Neutral
Nitric oxide	NO	+2	Neutral
Dinitrogen trioxide	N_2O_3	+3	Acidic
Dinitrogen tetraoxide	N_2O_4 or NO_2	+4	Acidic
Dinitrogen pentoxide	N_2O_5	+5	Acidic

Note: As the oxidation state of N_2 increases, acidity of the oxides increases.

- **Nitric Acid**

  Preparation:

  Ostwald's process: It is based upon catalytic oxidation of ammonia by atmospheric oxidation. The main steps involved are—

  1. $4NH_3 + 5O_2 \xrightarrow[\text{9 bar}]{\text{Pt 500 K}} 4NO + 6H_2O$
  2. $2NO + O_2 \longleftrightarrow 2NO_2$
  3. $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

  Properties:

  (*i*) Conc. HNO_3 is a strong oxidizing agent and attacks most metals except noble metals, gold and Pt.

  (*ii*) Cr and Al do not dissolve in conc. HNO_3 because of the formation of a positive film of oxide on the surface.

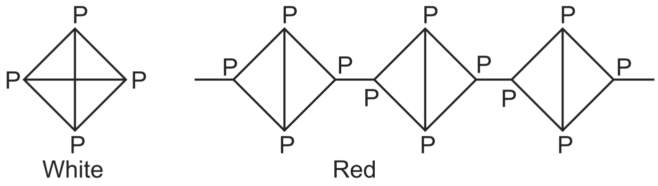
  (*iii*) It oxidises non-metals like I_2 to HIO_3, C to CO_2, S to H_2SO_4.

  (*iv*) Brown ring test is used to detect the presence of NO^-_3 ion. This test is based on the fact that Fe^{2+} ions can reduce nitrates to NO, which reacts with Fe^{2+} ions to form a brown coloured complex, $[Fe(H_2O)_5NO]^{2+}$.

- **Phosphorous**

  Allotropic forms: White, red, α-black and β-black.

  White phosphorous is more reactive than red phosphorous because white phosphorous exists as discrete P_4 molecules. In red phosphorous several P_4 molecules are linked to form a polymeric chain.



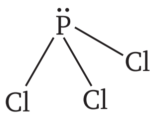
- **Phosphine**

  Preparation: It is prepared in the laboratory by heating white phosphorous with conc. NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \xrightarrow[\text{gas (inert)}]{CO_2} PH_3 + 3NaH_2PO_2$$

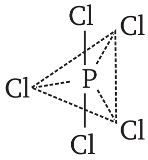
- **Phosphorous halides:** Phosphorous forms two types of halides: PX_3 and PX_5 (X = F, I, Br). Trihalides have pyramidal shape and pentahalides have a trigonal bipyramidal structure.

PCl_3



sp^3 hybridisation
Phosphorous trichloride

PCl_5

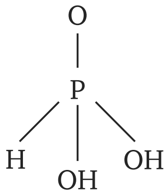


sp^3d hybridisation
Phosphorous pentachloride

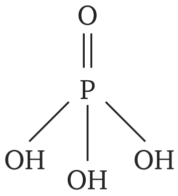
- **Oxoacids of Phosphorous**
  - (*i*) Acids in +3 oxidation state disproportionate to higher and lower oxidation states.

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

  - (*ii*) Acids which contains P — H bond have strong reducing properties.
    Example: H_3PO_2
  - (*iii*) Hydrogen atoms which are attached with oxygen in P—OH form are ionisable and are the cause of basicity.



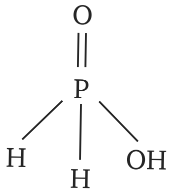
Dibasic



Tribasic

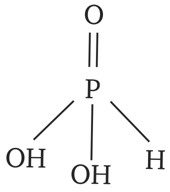
Structures of Some Important Oxoacids of Phosphorous

H_3PO_2



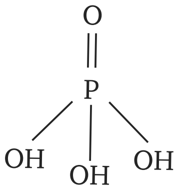
Hypophosphorous
acid or Phosphuric acid
basicity = 1

H_3PO_3



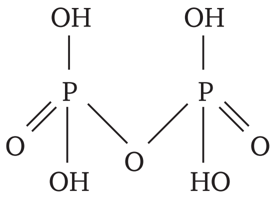
Orthophosphorous acid
or phosphoric acid
basicity = 2

H_3PO_4



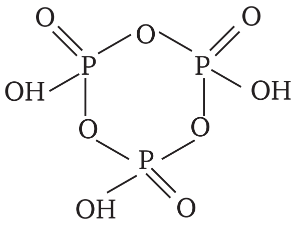
Orthophosphoric acid
basicity = 3

$H_4P_2O_7$



Pyrophosphoric acid
basicity = 4

$(HPO_3)_3$



Trimetaphosphoric acid
basicity = 3

- **Group 16 Elements (Chalcogens)**

  Group 16 elements: O, S, Se, Te, Po

  General electronic configuration: ns^2np^4.

Element	Occurrence
Oxygen	Comprises 20.946% by volume of the atmosphere.
Sulphur	As sulphates such as (gypsum) $CaSO_4.2H_2O$, epsom salt ($MgSO_4.7H_2O$) and sulphides such as (galena) PbS, (zinc blende) ZnS, (copper pyrites) $CuFeS_2$.
Se & Te	As metal selenides and tellurides in sulphide ores.
Polonium	As a decay product of thorium and uranium minerals.

Atomic and Physical Properties

(*i*) Ionisation enthalpy decreases from oxygen to polonium.

(*ii*) Oxygen atom has less negative electron gain enthalpy than sulphur because of the compact nature of the oxygen atom. However, from the sulphur onwards the value again becomes less negative upto polonium.

(*iii*) Eletronegativity gradually decreases from oxygen to polonium, metallic character increases from oxygen to polonium.

(*iv*) Oxygen and sulphur are non-metals, selenium and tellurium are metalloids. Polonium is a radioactive metal.

(*v*) Oxygen is a diatomic gas while S, Se and Te are octa–atomic, S_8, Se_8 and Te_8 molecules, which has a puckered 'ring' structure.

Chemical Properties

(*i*) Common oxidation states: –2, +2, +4 and +6.

(*ii*) Due to inert effect, the stability of +6 state decreases down the group and stability of +4 state increases.

Oxygen exhibits +1 state in O_2F_2 and +2 state in OF_2.

(*iii*) **Anomalous behaviour of oxygen:** Due to its small size, high electronegativity and absence of d-orbitals.

Trends in Properties

Acidic character of Hydrides — $H_2O < H_2S < H_2Se < H_2Te$
Thermal stability of Hydrides — $H_2O > H_2S > H_2Se > H_2Te$
Reducing character of Hydrides — $H_2S < H_2Se < H_2Te$
Boiling point of Hydrides — $H_2S < H_2Se < H_2Te < H_2O$
Reducing property of dioxides — $SO_2 > SeO_2 > TeO_2$
Stability of halides — F > Cl > Br > I

Halides

Dihalides: sp^3 hybridisation but angular structure.
Tetrahalides: sp^3d hybridization – see-saw geometry.
Hexahalides: sp^3d^2 – octahedral (SF_6).

- **Dioxygen**

  Prepared by heating oxygen containing salts like chlorates, nitrates, etc.

  $$2KClO_3 \xrightarrow{\text{electricity}} 2KCl + 3O_2$$

- **Oxides**

  A binary compound of oxygen with another element is called oxide. Oxides can be classified on the basis of nature:

  Acidic oxides: These are non-metallic oxides. Their aqueous solutions are acids. They neutralise bases to form salts. **Example:** SO_2, CO_2, N_2O_5, etc.

  Basic oxides: These are Metallic oxides their aqueous solutions are alkalis. They neutralise acids to form salts. **Example:** Na_2O, K_2O, MgO, etc.

  Amphoteric oxides: Some metallic oxides exhibit a dual behaviour. Neutralises both acids as well as bases to form salts. **Example:** Al_2O_3, Sb_2O_3, SnO, PbO_2, etc.

- **Ozone**

  Preparation:

  Prepared by subjecting cold, dry oxygen to silent electric discharge.

  $$3O_2 \longrightarrow 2O_3$$

  Properties:

  Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \longrightarrow O_2 + O$), it acts as a powerful oxidising agent. For *e.g.*, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

  $$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$
  $$2KI + H_2O + O_3 \longrightarrow 2KOH + I_2 + O_2$$

- **Sulphur Dioxide**

  Preparation:

  By burning of S in air:

  $S + O_2 \longrightarrow SO_2$

  By roasting of sulphide minerals:

  (Iron pyrites) $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

  (Zinc blende) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

  Properties

  (*i*) Highly soluble in water to form solution of sulphurous acid:

  $SO_2 + H_2O \longrightarrow H_2SO_3$

  (*ii*) SO_2 reacts with Cl_2 to form sulphuryl chloride:

  $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$

  (*iii*) It reacts with oxygen to form SO_3 in the presence of V_2O_5 catalyst:

  $2SO_2 + O_2 \longrightarrow 2SO_3$

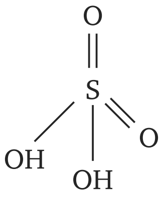
  (*iv*) Moist SO_2 behaves as a reducing agent. It converts Fe(III) ions to Fe(II) ions and decolourises acidified potassium permanganate (VII) solution (It is the test for the SO_2 gas).

  $$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$
  $$5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

- SO_2 molecule is angular.

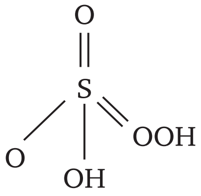
- **Oxoacids of Sulphur**

H_2SO_4



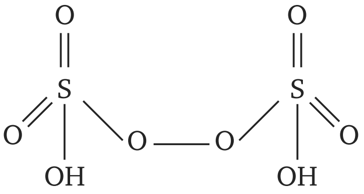
Sulphuric acid

H_2SO_5



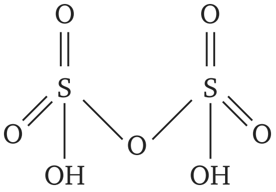
Peroxomonosulphuric acid

$H_2S_2O_8$



Peroxodisulphuric acid

$H_2S_2O_7$



Pyrosulphuric acid (Oleum)

- **Sulphuric Acid**

  Preparation:

  It is manufactured by Contact process which involves 3 steps:

  1. Burning of S or sulphide ores in the presence of air to generate SO_2.
  2. Conversion of SO_2 to SO_3 in presence of V_2O_5 catalyst.
  3. Absorption of SO_3 in H_2SO_4 to give oleum.

  Properties:

  (*i*) In aqueous solution it ionises in 2 steps:

  $H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$

  $HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{2-}$

  (*ii*) It is a strong dehydrating agent, *e.g.* charring action of sugar:

  $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$

  (*iii*) It is a moderately strong oxidising agent:

  $Cu + 2H_2SO_4(conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O$

  $C + 2H_2SO_4(conc.) \longrightarrow CO_2 + 2SO_2 + 2H_2O$

- **Group 17 Elements (halogens)**

  Group 17 elements: F, Cl, Br, I, At

  General electronic configuration: ns^2np^5.

Element	Occurrence
Fluorine	As insoluble fluorides (fluorspar CaF_2, cryolite Na_3AlF_6 and fluoroapatite).
Cl, Br, I	Sea–water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly comprising of sodium chloride solution (2.5% by mass).
Iodine	Certain forms of marine life (various seaweeds).

Atomic and Physical Properties

(*i*) Atomic and ionic radii increase from fluorine to iodine.

(*ii*) Ionisation enthalpy gradually decreases from fluorine to iodine due to increase in atomic size.

(*iii*) Electron gain enthalpy of fluorine is less than that of chlorine. It is due to the small size of fluorine and repulsion between newly added electron and electrons already present in its small 2p orbital.

(*iv*) Electronegativity decreases from fluorine to iodine.
Fluorine is the most electronegative element in the periodic table.

(*v*) The colour of halogens is due to the absorption of radiations in visible region which results in the excitation of outer electrons to the higher energy level.

(*vi*) Bond dissociation enthalpy of fluorine is smaller than that of chlorine is due to electron-electron repulsion among the lone pair of electrons in fluorine molecules where they are much closer to each other than in case of chlorine.
The trend that follow: Cl–Cl > Br–Br > F–F > I–I.

Chemical Properties

(*i*) **Oxidation states:** All halogens exhibit a general oxidation state of–1. However, chlorine, bromine and iodine also exhibit +1, +3, +5 and +7 oxidation states.

(*ii*) Fluorine form two oxides; OF_2 and O_2F_2. These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen.

(*iii*) **Anomalous behaviour of fluorine:** Due to its small size, highest electronegativity, low F-F bond dissociation enthalpy and absence of d-orbitals.

Trends in Properties:

Oxidising property — $F_2 > Cl_2 > Br_2 > I_2$
Acidic strength of Hydrogen halides — HF < HCl < HBr < HI
Stability and bond dissociation enthalpy of Hydrogen halides— HF > HCl > HBr > HI
Stability of oxides of halogens — I > Cl > Br
Ionic character of halides — MF > MCl > MBr > MI

- **Chlorine**

Preparation:

1. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
2. $4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$
3. $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
4. **Deacon's Process:**

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

5. By electrolysis of brine solution (NaCl). Cl_2 is obtained at anode.

Properties:

(*i*) With cold and dilute alkalies, Cl_2 produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$\underset{\text{(cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

$$\underset{\text{(hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

(*ii*) With dry slaked–lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow \underset{\text{(Bleaching powder)}}{Ca(OCl)_2} + CaCl_2 + 2H_2O$$

(*iii*) It is a powerful bleaching agent; bleaching action is due to oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + (O)$$

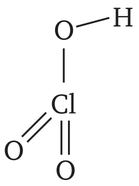
Coloured substance + (O) $\longrightarrow$ Colourless substance

(*iv*) Action of concentrated H_2SO_4 on NaCl give HCl gas:

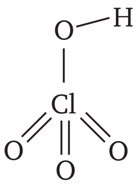
$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$

3 : 1 ratio of concentrated HCl and HNO_3 is known as aqua regia and it is used for dissolving noble metals like Au and Pt.

- **Oxoacids of Halogens**



Chloric acid ($HClO_3$)



Perchloric acid ($HClO_4$)

- **Interhalogen Compounds**

Interhalogen compounds are prepared by the direct combination of halogens.

Example: ClF, ClF_3, BrF_5, IF_7.

They are more reactive than halogens because X–X′ bond is weaker than X–X bonds in halogens (except F-F).

Type	Structure
XX'_3	Bent T–shaped
XX'_5	Square pyramidal
XX'_7	Pentagonal bipyramidal

- **Group 18 elements**

Group 18 elements: He, Ne, Ar, Kr, Xe and Rn

General electronic configuration: ns^2np^6

Atomic radii–Large as compared to other elements in the period since it corresponds to van der Waal radii.

Inert–Due to complete octet of outermost shell, very high ionisation enthalpy and electron gain enthalpy are almost zero.

The first noble compound prepared by Neil Bartlett was $XePtF_6$ by mixing PtF_6 and xenon. $O_2^+PtF_6^-$ led to the discovery of $XePtF_6$ since the first ionisation enthalpy of oxygen molecule (1175 kJ mol^{-1}) was almost identical with that of xenon (1170 kJ mol^{-1}).

Properties:

$$Xe + F_2 \xrightarrow{673\text{ K, 1 bar}} XeF_2$$

$$Xe(g) + 2F_2(g) \xrightarrow{873\text{ K, 7 bar}} XeF_4(s)$$

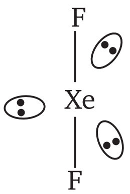
$$Xe(g) + 3F_2(g) \xrightarrow{573\text{ K, 6070 bar}} XeF_6(s)$$

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^-$$

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$

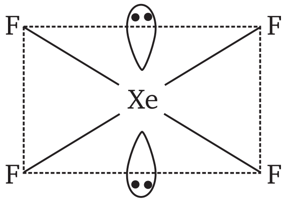
$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF \text{ (partial hydrolysis)}$$
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF \text{ (complete hydrolysis)}$$

XeF_2



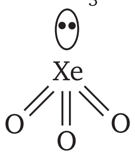
Xenon difluoride (Linear)
sp^3d hybridisation

XeF_4



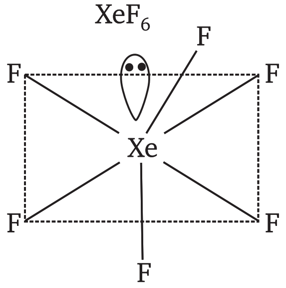
Xenon Tetrafluoride (square planar)
sp^3d^2 hybridisation

XeO_3



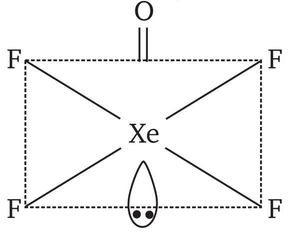
Xenon trioxide (Pyramidal)
sp^3d^3 hybridisation

XeF_6



Xenon hexafluoride
(Distorted octahedral)
sp^3d^3 hybridisation

$XeOF_4$



Xenon oxytetrafluoride
(Square pyramidal)
sp^3d^2 hybridisation

NCERT IN-TEXT QUESTIONS SOLVED

7.1. Why are pentahalides more covalent than trihalides?

Ans. Since elements in the +5 oxidation state have less tendency to lose electrons than in the +3 oxidation state, therefore elements in the +5 oxidation state are more covalent than in the +3 oxidation state. In other words, pentahalides are more covalent than trihalides.

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

Ans. As we move down the group, the size of the element increases and therefore, the lengths of the E–H bond increases and its strength decreases. In other words, as we move down the group the E–H bond can break more easily to evolve H_2 gas which acts as the reducing agent. Since Bi–H bond is the weakest amongst the hydrides of elements of group 15. Hence BiH_3 is the strongest reducing agent.

7.3. Why is N_2 less reactive at room temperature?

Ans. Due to the presence of triple bond between the two nitrogen atoms, the bond dissociation energy of N_2 (941.4 kJ mol^{-}) is very high. Therefore, N_2 is less reactive at room temperature.

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

Ans.
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$\Delta_f H^\ominus = -46.1 \text{ kJ mol}^{-1}$$

To maximise the yield of ammonia pressure should be 200 × 10^5 Pa, a temperature should be 700 K and a catalyst such as iron oxide with small amount of K_2O and Al_2O_3 should be used.

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

Ans. Cu^{2+} ions reacts with excess of ammonia to form a deep blue coloured complex.

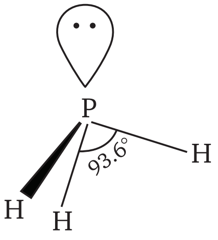
$$Cu^{2+}(aq) + 4NH_4OH(aq) \longrightarrow \underset{\substack{\text{Tetramine copper}\\ \text{(II) ion (Deep blue)}}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$$

7.6. What is the covalence of nitrogen is N_2O_5?

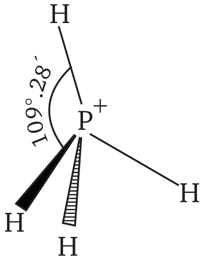
Ans. Covalency depends upon the number of shared pairs of electrons. Now in N_2O_5, each nitrogen atom has four shared pairs of electrons. Therefore, the covalency of N in N_2O_5 is 4.

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

Ans. PH_4^+ ion has four bond pairs and no lone pair. Due to the absence of lone pair-bond pair repulsions and presence of four identical bond pair-bond pair interactions, PH_4^+ assumes tetrahedral geometry with a bond angle of 109°–28′. This explains why bond angle in PH_4^+ is higher than that in PH_3.



PH_3 molecule
pyramidal



PH_4^+ (ion)
tetrahedral

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

Ans. White Phosphorus reacts with NaOH to form phosphine.

$$\underset{\text{Phosphorous}}{P_4} + 3NaOH + 3H_2O \xrightarrow[\text{(CO}_2\text{ atmosphere)}]{\text{heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{2NaHPO_2}$$

7.9. What happens when PCl_5 is heated? [*CBSE Delhi* 2013]

Ans. PCl_5 has less stable axial bonds which break to form PCl_3, when it is heated.

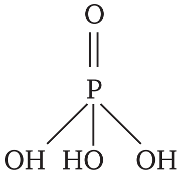
$$PCl_5 \xrightarrow{\text{heat}} PCl_3 + Cl_2$$

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

Ans. $$PCl_5 + 4D_2O \longrightarrow D_3PO_4 + 5DCl$$

7.11. What is the basicity of H_3PO_4?

Ans. The structure of H_3PO_4 is tetrahedral. It has three P–OH and one P = O bond as shown below:



Since it has three ionisable P – OH bonds, therefore, H_3PO_4 is tribasic.

7.12. What happens when H_3PO_3 is heated? [*CBSE Delhi* 2013, 2017]

Ans.
$$\underset{\text{Orthophosphorous acid}}{4H_3PO_3} \xrightarrow{\text{heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Orthophosphoric acid}}{H_3PO_4}$$

7.13. List the important sources of sulphur.

Ans. Sulphur mainly occurs in the earth's crust in the combined state primarily in the form of sulphates and sulphides.

Sulphates: Gypsum ($CaSO_4 . 2H_2O$), epsom salt ($MgSO_4 . 7H_2O$), baryte ($BaSO_4$), *etc.*

Sulphides: Galena (PbS), Zinc blende (ZnS), Copper pyrites ($CuFeS_2$), Iron pyrites (FeS_2).

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

Ans. $H_2O > H_2S > H_2Se > H_2Te > H_2Po$

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

Ans. Due to greater electronegativity of O than S, H_2O undergoes extensive intermolecular H–bonding. As a result H_2O is a liquid at room temperature. In contrast H_2S does not undergo H–bonding. It exists as discrete molecules which are held together by weak van der Waals' forces of attraction. To break these forces of attraction, only a small amount of energy is required. Therefore, H_2S is a gas at room temperature.

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

Zn, Ti, Pt, Fe.

Ans. Pt is a noble metal. Therefore, it does not react with oxygen directly.

7.17. Complete the following reactions:

(*i*) $C_2H_4 + O_2 \longrightarrow$

(*ii*) $4Al + 3O_2 \longrightarrow$

Ans. (*i*) $C_2H_4 + 3O_2 \xrightarrow{\text{heat}} 2CO_2 + 2H_2O$

(*ii*) $4Al + 3O_2 \longrightarrow 2Al_2O_3$

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

Ans. O_3 is an endothermic compound. On heating, it readily decomposes to give dioxygen gas and nascent oxygen.

$$O_3 \xrightarrow{\text{heat}} O_2 + O \text{ (nascent oxygen)}$$

Since nascent oxygen is very reactive, therefore O_3 acts as a powerful oxidising agent.

7.19. How is O_3 estimated quantitatively?

Ans. When O_3 is treated with excess of KI solution buffered with borate buffer (pH 9.2) I_2 is liberated quantitatively.

$$2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

Thus I_2 liberated is titrated against a standard solution of sodium thiosulphate using starch as an indicator.

$$\underset{\text{sod. thiosulphate}}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{\text{sod. tetrationate}}{Na_2S_4O_6} + 2NaI$$

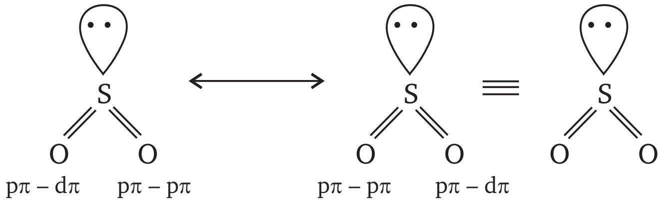
7.20. What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

Ans. It reduces Fe (III) salt to Fe (II) salt.

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

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?

Ans. Yes, two S–O bonds are equal due to resonance.



One S–O bond is pπ – pπ bond and other is pπ – dπ bond

7.22. How is the presence of SO_2 detected?

Ans. SO_2 turns the pink violet coloured $KMnO_4$ solution to colourless due to the reduction of MnO_4^- ions to Mn^{2+} ions.

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

Ans. (*i*) H_2SO_4 is used as an oxidising agent

(*ii*) It is used as an electrolyte in lead storage batteries.

(*iii*) It is used in petroleum refining.

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

Ans.

$$SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$\Delta_f H^\circ = -196.6 \text{ kJ mol}^{-1}$$

To maximize the yield of SO_3 and hence of H_2SO_4 are:

(*i*) Low temperature (720 K) to have optimum rate

(*ii*) Very high pressure (2 bar) and V_2O_5 is used as a catalyst.

7.25. Why is $K_{a_1} << K_{a_2}$ for H_2SO_4 in water?

Ans. H_2SO_4 is a dibasic acid, it ionises in two stages and hence two dissociation constants:

(*i*) $H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$

$K_{a_1} > 10$

(*ii*) $HSO_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$

$K_{a_2} = 1.2 \times 10^{-2}$

K_{a_2} is less than K_{a_1} because negatively charged HSO_4^- ions has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4.

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.

Ans. F_2 has a stronger oxidising power than Cl_2 because it has low bond dissociation energy, lower electron affinity than Cl_2, highest hydration energy and higher standard reduction potential.

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

Ans. The anomalous behaviour of fluorine is due to its:

(*i*) Small size,

(*ii*) highest electronegativity,

(*iii*) low F–F bond dissociation enethalpy,

(*iv*) non-availability of *d*-orbitals in its valence shell.

The two examples are:

(*i*) Due to non-availability of *d*-orbitals in its valence shell, fluorine cannot expand its octet, therefore, shows only –1 oxidation state while all other halogens due to the presence of *d*-orbitals shows positive oxidation states of +1, +3, +5 and +7 besides oxidation state of –1,

(*ii*) Due to its small size, the three lone pair of electrons on each F atom in F – F molecule, repel the bond pair. As a result, F – F bond dissociation energy is lower than that of Cl – Cl bond.

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

Ans. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium but mainly sodium chloride (2.5% by mass). Dried up sea beds contain sodium chloride and carnalite, KCl $MgCl_2 . 6H_2O$. Certain seaweeds contain upto 0.5% of iodine as sodium iodide and Chile saltpetre ($NaNO_3$) contains upto 0.2% of sodium iodate. Thus, sea is the greatest source of halogens.

7.29. Give the reason for bleaching action of Cl_2.

Ans. In the presence of moisture or in aqueous solution, Cl_2 liberates nascent oxygen.

$$Cl_2 + H_2O \longrightarrow 2HCl + \underset{\text{nascent oxygen}}{[O]}$$

This nascent oxygen brings about the oxidation of coloured substances present in organic matter to colourless substances.

$$\text{Coloured substance} + [O] \longrightarrow \text{Colourless substance}$$

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

Ans. (*i*) Phosgene ($COCl_2$)

(*ii*) Mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$)

7.31. Why is ICl more reactive than I_2?

Ans. ICl bond is weaker than I – I bond. Therefore ICl can break easily to form halogen atoms which readily brings about the reaction.

7.32. Why is helium used in diving apparatus?

Ans. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

7.33. Balance the following equation:

$$XeF_6 + H_2O \longrightarrow XeO_2F_2 + HF$$

Ans. $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

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

Ans. Radon is a radioactive element with a very short half life of 3.82 days. This makes the study of chemistry of radon difficult.

NCERT TEXTBOOK QUESTIONS SOLVED

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

Ans. Electronic configuration: ns^2np^3.

Oxidation state: +3, +5, –3. Tendency to show –3 oxidation state decreases down the group.

Atomic size: It goes on increasing down the group due to increase in the number of shells.

Ionisation enthalpy: It goes on decreasing down the group because atomic size goes on increasing down the group.

Electronegativity: It goes on decreasing down the group as the atomic size increases.

7.2. Why does the reactivity of nitrogen differ from Phosphorus?

Ans. Nitrogen exists as a diatomic molecule (N ≡ N). Due to the presence of a triple bond between the two N – atoms the bond dissociation energy is large (941.4 kJ mol^{-1}). As a result nitrogen is said to be chemically inert in its elemental state.

In contrast, P – P single bond is much weaker (213 kJ mol^{-1}) than N ≡ N triple bond Therefore, phosphorus is much more reactive than nitrogen.

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

Ans. Reactivity increases down the group due to increase in the atomic size and decrease in the ionisation energy. *E.g.,* Nitrogen is least reactive at room temperature whereas white phosphorus is more reactive. Among As, Sb and Bi, reactivity also increases due to decrease in ionisation energy and increase in electropositive character.

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

Ans. The electronegativity of N (3.0) is much higher than that of H (2.1). As a result, N—H bond is quite polar and hence NH_3 undergoes intermolecular H–bonding.

In contrast, both P and H have an electronegativity of 2.1. Therefore P – H bond is non–polar and hence PH_3 does not undergo H – bonding.

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

Ans. In the laboratory, nitrogen is prepared by treating the aqueous solution of ammonium chloride with sodium nitrite as per the equation.

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

Small amount of NO and HNO_3 are also formed in this reaction. These impurities can be removed by passing the gas through aqueous sulphuric acid solution containing potassium dichromate.

7.6. How is ammonia manufactured industrially?

Ans. Amnonia is manufactured industry by Haber's process:

N_2 and H_2 gases in the presence of Iron oxide is mixed with K_2O and Al_2O_3 as catalyst at 700 K and at a high pressure of 20×10^6 Pa or 200 atm.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta_f H^\circ = -46.1 \text{ kJ mol}^{-1}$$

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

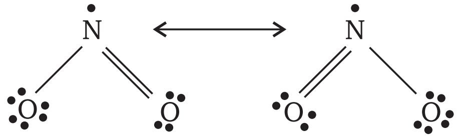
Ans.

$$3Cu + 8HNO_3(dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

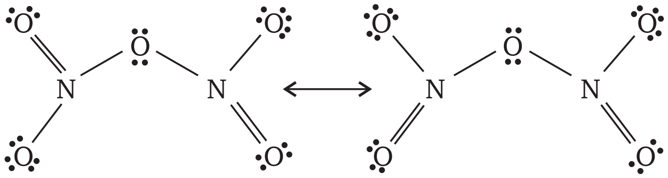
7.8. Give the resonating structures of NO_2 and N_2O_5.

Ans. **NO_2:**



Resonating structures of NO_2

N_2O_5:



Resonating structures of N_2O_5

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

Ans. It is because N – atom is smaller in size and N–H bond is the most polar among N–H, P–H, As –H and Sb–H bonds. The greater polarity of N–H can be accounted on the basis of high electrogrativity of N–atom as compared to P, As and Sb– atoms.

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

Ans. Nitrogen cannot expand its valency beyond 4 due to the absence of *d*-orbitals. It cannot forms five covalent bonds. Therefore, $R_3P = O$ exists, but $R_3N = O$ does not.

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

Ans. Atomic size of N (70 pm) is much smaller than that of Bi (148 pm), therefore electron density on the N–atom is much higher than that on Bi–atom. Consequently the tendency of N in NH_3 to donate its pair of electrons is much higher than that of Bi in BiH_3. Thus, NH_3 is much more basic than BiH_3.

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

Ans. Nitrogen has a triple bond between its two atoms because of its small size and high electronegativity. Phosphorus P_4 has single bond, that is why it is tetra–atomic.

7.13. What is the main difference between the properties of white Phosphorus and red Phosphorus?

Ans. Chemically, red Phosphorus is much less reactive than white Phosphorus.

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

Ans. The single N–N bond is weaker than the single P–P bond because of high interelectronic repulsions of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.

7.15. Give the disproportionation reaction of H_3PO_3.

Ans. H_3PO_3 on heating undergoes self-oxidation reduction as:

$$\underset{\substack{\text{phosphorous}\\ \text{acid}}}{4H_3\overset{+3}{P}O_3} \longrightarrow \underset{\text{Phosphine}}{\overset{-3}{P}H_3} + \underset{\substack{\text{Ortho-phosphoric}\\ \text{acid}}}{3H_3\overset{+5}{P}O_4}$$

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

Ans. Oxidation state of P in PCl_5 is +5. Since P has five valence electrons in its valence shell, therefore it cannot increase its oxidation state beyond +5 by donating its electrons, therefore PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, therefore PCl_5 acts as an oxidising agent. For example, it oxidises Ag to AgCl.

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.

Ans. They have the same general electronic configuration, ns^2np^6. The minimum oxidation state of these elements should be –2, other elements except sulphur and oxygen shows positive oxidation states of +4 and +6.

All of them form hydrides having the general formula EH_2 *i.e.,* H_2O, H_2S, H_2Te, H_2Po. Thus, on the basis of formation of hydrides of the general formula EH_2, these elements are justified to be placed in the same group, *i.e.,* Group 16 of the periodic table.

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

Ans. Due to small size and high electronegativity oxygen forms $p\pi - p\pi$ multiple bonds. As a result, oxygen exists as diatomic (O_2) molecules. These molecules are held together by weak van der Waals' forces of attraction which can be easily overcome by collision of the molecules at room temperature. Therefore, O_2 is a gas at room temperature. Sulphur on the other hand is octa–atomic (S_8) which has high intermolecular forces of attraction, That is why sulphur is a solid at room temperature.

7.19. Knowing the electron gain enthalpy values for $O \longrightarrow O^-$ and $O \longrightarrow O^{2-}$ 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]

Ans. Consider the reaction of a divalent metal (M) with oxygen. The formation of M_2O and MO involves the following steps:

$$M(g) \xrightarrow{\Delta i H_1} M^+(g) \xrightarrow{\Delta i H_2} M^{2+}(g)$$

$$O(g) \xrightarrow{\Delta_{eg} H_1} O^-(g) \xrightarrow{\Delta_{eg} H_2} O^{2-}(g)$$

$$2M^+(g) + O^-(g) \xrightarrow{\text{Lattice energy}} M_2O(s)$$

$$M^{2+}(g) + O^{2-}(g) \xrightarrow{\text{Lattice energy}} MO(s)$$

Although $\Delta_i H_2$ is much more than $\Delta_i H_1$ and $\Delta e_g H_2$ is much higher than that of $\Delta e_g H_1$, yet the lattice energy of formation of MO(s) due to higher charge which is much more than that of $M_2O(s)$. In other words formation of MO is energetically more favourable than M_2O. It is because of this reason that oxygen forms a large number of oxides having O^{2-} species and not O^-.

7.20. Which aerosols deplete ozone?

Ans. Aerosols such as chlorofluorocarbons (CFCs), freon (CCl_2F_2), depletes ozone layer by supplying chlorine free radicals which convert O_3 to O_2.

7.21. Describe the manufacture of H_2SO_4 by contact process.

Ans. **Contact process:** It involves three steps:

(*i*) Burning of sulphur or sulphide ores in the presence of oxygen to produce SO_2.
(*ii*) SO_2 is reacted with O_2 in the presence of V_2O_5 as a catalyst to form SO_3.
(*iii*) SO_3 is absorbed on H_2SO_4 to give oleum which is $H_2S_2O_7$

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \qquad \Delta_r H = -196.6 \text{ kJ mol}^{-1}$$

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The plant is operated at a pressure of 2 bar and a temperature of 720 K.
Dilution of oleum with water gives H_2SO_4 of required concentration.
Sulphuric acid thus, obtained by Contact process is 96 – 98% pure.

7.22. How is SO_2 an air pollutant?

Ans. SO_2 is strongly irritating to the respiratory tract. It causes breathlessness and affects larynx, *i.e.* voice box.

It dissolves in rain water and produces acid rain which damages building materials, especilly marbles. That is why SO_2 is considered an air pollutant.

7.23. Why are halogens strong oxidising agents?

Ans. The easy acceptance of an electron is the reason for the strong oxidising nature of halogens.

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

Ans. Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF. Absence of '*d*' orbitals in fluorine is also the reason of forming only one oxoacid, *i.e.* HOF.

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

Ans. Although O and Cl have about the same electronegativity, yet their atomic size (covalent radii) are quite different O = 66 pm and Cl = 99 pm. As a result, electron density per unit volume on the oxygen atom is much higher than that of chlorine atom. Therefore, oxygen forms hydrogen bond while chlorine does not even though both have approx. the same electronegativity.

7.26. Write two uses of ClO_2.

Ans. (*i*) It acts as a bleaching agent

(*ii*) It is a powerful oxidising agent.

7.27. Why are halogens coloured?

Ans. It is because they absorb light from the visible region and radiate the complementary colour.

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

Ans.

$$2F_2 + \underset{\text{(cold)}}{2H_2O} \longrightarrow 4HF + O_2$$

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\substack{\text{Hypochloric}\\ \text{acid}}}{HClO}$$

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

Ans.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$H_2 + Cl_2 \xrightarrow[\text{light}]{\text{Sun}} 2HCl$$

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

Ans. The ionisation enthalpy of O_2 and Xe are nearly the same.

7.31. Write 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

Ans. (*i*) $H_3PO_3 = +3$ (*ii*) $PCl_3 = +3$ (*iii*) $Ca_3P_2 = -3$

(*iv*) $Na_3PO_4 = +5$ (*v*) $POF_3 = +5$

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 in a solution of NaI in water.

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

(*ii*) $Cl_2(g) + 2NaI(aq) \longrightarrow 2NaCl(aq) + I_2(s)$

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

Ans. All these Xenon fluorides are prepared by direct reaction between Xe and F_2 under different conditions as shown below:

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

$$\underset{1}{Xe(g)} \underset{:}{+} \underset{5}{2F_2(g)} \xrightarrow{\text{873 K, 7 bar}} XeF_4(s)$$

$$\underset{1}{Xe(g)} \underset{:}{+} \underset{20}{3F_2(g)} \xrightarrow{\text{573 K, 60 – 70 bar}} XeF_6(s)$$

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

Ans. ClF. Yes it is a Lewis base due to the presence of lone pair of electrons.

7.35. How is XeO_3 and $XeOF_4$ prepared?

Ans. Complete hydrolysis of XeF_4 and XeF_6 with water gives XeO_3:

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

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

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$:

$$XeF_6 + O_2 \longrightarrow XeOF_4 + 2HF$$

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

Ans. (*i*) $I_2 < F_2 < Br_2 < Cl_2$
(*ii*) $HF < HCl < HBr < HI$
(*iii*) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

7.37. Which of the following does not exist?

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

Ans. (*ii*) 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^-

Ans. (*i*) ICl_4^- is isostructural with XeF_4.
(*ii*) IBr_2^- is isostructural with XeF_2.
(*iii*) BrO_3^- is isostructural with XeO_3.

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

Ans. It is because they do not form covalent bonds and we can measure only van der Waals' radii which are bigger than covalent radii. That is why they have large atomic sizes.

7.40. List the uses of neon and argon gases.

Ans. Use of Argon: It is used to provide inert atmosphere.
Use of Neon: Neon is used in discharge tubes and fluorescent bulbs.

ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

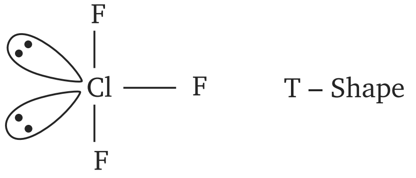
(1 *Mark*)

Q1. Write the balanced equation for complete hydrolysis of XeF_6. [*CBSE* 2009, 2017]

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

Q2. Predict the shape of ClF_3 on the basis of VSEPR theory. [*CBSE* 2009]

Ans.



Q3. In the ring test for identification of nitrate ion, what is the formula of the compound responsible for the brown ring formed at the interface of two liquids? [*CBSE* 2009]

Ans. $[Fe(H_2O)_5NO]^{2+}$

Q4. Why is red Phosphorus less reactive than white Phosphorus? [*AI* 2009, 2017]

Ans. White Phosphorus is more reactive than red Phosphorus under normal conditions because of angular strain in the P_4 molecule where the angles are only 60°.

Q5. Why is Bi(V) a stronger oxidant than Sb(V)? [*AI* 2009]

Ans. Bismuth (Bi) in the pentavalent state can easily accept two electrons and it gets reduced to trivalent state of bismuth.

$$Bi^{5+} + 2e^- \longrightarrow Bi^{3+}$$

Therefore, it acts as a strong oxidising agent.

Q6. Why is dinitrogen very unreactive as compared to phosphorus? [*AI* 2008]

Ans. Due to the presence of a triple bond between the two nitrogen atoms, the bond dissociation enthalpy of N_2 is very high as compared to phosphorus. Therefore, N_2 is less reactive than Phosphorus.

Q7. Nitrogen does not form any pentahalide like Phosphorus. Why? [*CBSE* 2008]

Ans. Nitrogen does not form pentahalide due to non-availability of the *d*-orbitals in its valence shell.

Q8. Which is a stronger acid in aqueous solutions, HF or HCl? [*CBSE* 2008]

Ans. HCl is a stronger acid than HF. The acidic strength of hydrogen halide is HF < HBr < HI.

Q9. Why is the bond angle in PH_3 molecule lesser than that in NH_3 molecule? [*CBSE* 2008]

Ans. The bond angle in PH_3 is much lower (93.6°) than that in NH_3 (107.8°) due to less repulsion between the bond pairs of electrons.

Q10. Why does PCl_3 fume in moisture? Give reason. [*CBSE* 2007]

Ans. PCl_3 hydrolyses in the presence of moisture, giving fumes of HCl.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

Q11. How does ammonia react with a solution of Cu^{2+}? [*CBSE* 2007]

Ans. Ammonia reacts with blue coloured solution of Cu^{2+} ions to form a deep–blue coloured complex.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{Deep blue}}{\left[Cu(NH_3)_4\right]^{2+}}(aq)$$

Q12. Why do nitro compounds have high boiling points in comparison with other compounds of same molecular mass? [*CBSE* 2007]

Ans. Due to polarity, the boiling points of nitro compounds are unusually high in comparison with other compounds of same molecular mass.

Q13. Write two uses of ClO_2. [*CBSE* 2005]

Ans. Uses of ClO_2:

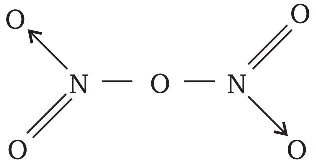
(*i*) Chlorine dioxide (ClO_2) is a powerful oxidising agent.

(*ii*) It is a strong chlorinating agent and its bleaching power is 30 times higher than that of chlorine (Cl_2).

Q14. Why is copper sulphate pentahydrate coloured? [*CBSE* 2004]

Ans. Because Cu(II) possesses unpaired electrons.

Q15. What is the covalency of nitrogen in N_2O_5? [*CBSE* 2003, *Delhi* 2013, *AI* 2014]



Ans. N in N_2O_5 has the covalency of 4.

Q16. What type of hybridisation is associated with N in NH_3? What is the expected bond angle in NH_3? [*AI* 2003]

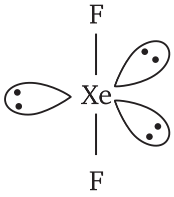
Ans. The N atom in NH_3 is sp^3 hybridised. The expected bond angle is 107°.

Q17. Assign reason for the following:
In solid state PCl_5 behaves as an ionic species. [*AI* 2007]

Ans. In solid state, PCl_5 exists as $[PCl_4]^+[PCl_6]^-$. That is why it behaves as an ionic species.

Q18. Draw the structure of XeF_2 molecule. [*CBSE* 2006, *Delhi* 2013]

Ans. XeF_2 is linear.



(XeF_2 Linear)

Q19. Give reason for the following. Among the noble gases only Xenon is well known to form chemical compounds. [*Foreign* 2006]

Ans. Xe is largest in size and has the highest polarising power.

Q20. Write one chemical reaction to show that chlorine gas can be obtained from bleaching powder? [*CBSE* 2005]

Ans. $CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$

Q21. Write one chemical reaction to show that SO_2 acts as a reducing agent. [*Foreign* 2005]

Ans. $$2H_2S(g) + SO_2(g) \xrightarrow[673\ K]{Fe_2O_3\ \text{catalyst}} 2H_2O(g) + 3S(s)$$

Q22. Write one chemical reaction equation to show that conc. H_2SO_4 is a strong oxidising agent. [*Foreign* 2005]

Ans. $C + 2H_2SO_4\ (conc.) \longrightarrow CO_2 + 2H_2O + 2SO_2$

Q23. Give a chemical equation or name of the reaction to support the following statement: sodium chlorate ($NaClO_3$) is an oxidant. [*Foreign* 2005]

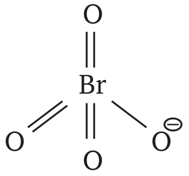
Ans. $I_2 + 2NaClO_3 \longrightarrow 2NaIO_3 + Cl_2$

Q24. Give chemical evidence for the following:
Fluorine is a stronger oxidising agent than chlorine. [*CBSE* 2004]

Ans. $F_2 + 2KCl \longrightarrow 2KF + Cl_2$

Q25. Draw the structure of the following species BrO_4^-. [*AI* 2004]

Ans.

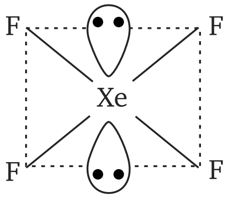


Q26. Write the chemical equation for the reactions which occur when sodium iodate [$NaIO_3$] is reduced with sodium hydrogen sulphite. [*Foreign* 2004]

Ans. $NaIO_3 + 3NaHSO_3 \longrightarrow 3NaHSO_4 + NaI$

Q27. Draw the structure of XeF_4. [*Foreign* 2004]

Ans.



Square planar

Q28. Which is the strongest oxidising agent among ClO_4^-, BrO_4^- and IO_3^-? [*CBSE* 2003, *Delhi* 2013]

Ans. BrO_4^- is the strongest oxidising agent.

Q29. Name one ion whose central atom has the sp^3d^3 type of hybrid orbitals. [*AI* 2003]

Ans. $[XeF_7]^-$

Q30. Why is bond dissociation energy of fluorine molecule less than that of chlorine molecule? [*AI* 2003]

Ans. It is due to inter-electronic repulsion between the valence electrons of two fluorine atoms due to smaller size, lower bond dissociation energy of F_2 molecule than Cl_2 inspite of smaller bond length of Cl_2.

Q31. Account for the following:
Tendency to show – 2 oxidation state diminishes from sulphur to polonium in Group 16. [*AI* 2003]

Ans. It is due to increase in atomic size. So there is a tendency for decrease in electronegativity and tendency to show – 2 oxidation state decreases.

Q32. Why is H_2S more acidic than water?

Ans. It is because bond dissociation energy of S – H bond is less than O – H bond due to longer bond length.

Q33. Why is hydrogen sulphide, with greater molar mass a gas, while water a liquid at room temperature? [*CBSE* 2003 *C*]

Ans. H_2O molecules are associated with intermolecular H–bonding, H_2S is not because oxygen is more electronegative and smaller in size than sulphur. That is why H_2O is a liquid and H_2S is a gas.

Q34. Noble gases are chemically inert. Give reasons. [*CBSE* 2002]

Ans. Noble gases are chemically inert because they have their octet complete except Helium, *i.e.* they have a stable electronic configurations.

Q35. Which compound led to the discovery of the compounds of noble gas?

Ans. $Xe^+[PtF_6]^-$

Q36. Give an example of a compound in which oxidation state of chlorine is +7.

Ans. $HClO_4$

Q37. What is inert pair effect?

Ans. The phenomena by the virtue of which pair of electrons in valence shell is reluctant to take part in bond formation due to poor shielding effect of *d* and *f*-electrons in heavier elements is called inert pair effect. Due to this effect lower oxidation state becomes more stable than higher oxidation state in case of *p*-block elements.

Q38. Why does oxygen not show an oxidation state of +4 and +6 like sulphur?

Ans. It is because oxygen does not have vacant *d*-orbitals.

Q39. Why is N_2 not particularly reactive?

Ans. Nitrogen has triple bond between two nitrogen atoms which has high bond dissociation energy, therefore it is less reactive.

Q40. Why is OF_6 compound not known?

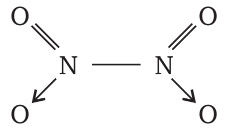
Ans. OF_6 is not known because oxygen does not have vacant *d*-orbitals and thus it cannot expand its octet.

Q41. What are oxoacids?

Ans. Acids containing oxygen are called oxoacids. They are formed by dissolving non-metallic oxides in water, *e.g.* HNO_3, H_2SO_4, H_3PO_4 are oxoacids.

Q42. NO_2 readily forms a dimer. Explain.

Ans. NO_2 has one unpaired electron, therefore it is unstable and forms a dimer, i.e. N_2O_4 whose structure is



Q43. What are chalcogens? Why are group 16 elements called chalcogens?

Ans. Chalcogens are ore forming elements. Most of the ores are oxides and sulphides, therefore oxygen, sulphur and other group 16 elements are called chalcogens.

Q44. Which halogen is radioactive?

Ans. Astatine (At) is radioactive.

Q45. Name the oxides of chlorine that are used as bleaching agents for paper pulp.

Ans. ClO_2 and Cl_2O are used for bleaching paper pulp.

Q46. Among halogen hydrides which has maximum percent of ionic character?

Ans. HF has maximum ionic character because of greater difference in electronegativity.

Q47. What happens when Phosphorus is boiled with caustic alkali?

Ans. $$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Sodium hypophosphate}}{3NaH_2PO_2} + \underset{\text{Phosphite}}{PH_3}$$

Q48. Why do noble gases exist as monoatomic?

Ans. Noble gases have stable electronic configuration, that is why they have no tendency to lose or gain electrons. Therefore they do not form covalent bond.

Q49. Which noble gas is radioactive?

Ans. Radon is the radioactive noble gas.

Q50. Arrange the haloacids in the increasing order of acidic character.

Ans. HF < HCl < HBr < HI

Q51. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Ans. Nitrogen with shell no. $n = 2$ has *s* and *p* orbitals only. It does not have *d*-orbitals to expand its covalence beyond four. That is why it does not form pentahalide.

Q52. PH_3 has lower boiling point than NH_3. Why?

Ans. Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why boiling point of PH_3 is lower than NH_3.

Q53. Write the thermal decomposition reaction of sodium azide.

Ans. Thermal decomposition of sodium azide gives dinitrogen gas as.

$$2NaN_3 \longrightarrow 2Na + 3N_2$$

Q54. Why does NH_3 act as a Lewis base?

Ans. Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

Q55. Why does NO_2 dimerises?

Ans. NO_2 contains odd number of valence electrons. In the valence shell nitrogen (N) has seven electrons and hence is less stable. To become more stable by having even (8) number of electrons in the valence shell, it undergoes dimerisation to form N_2O_4.

Q56. In what way it can be proved that PH_3 is basic in nature?

Ans. PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.

Q57. Why does PCl_3 fume in moisture?

Ans. In the presence of moisture (H_2O), PCl_3 undergoes hydrolysis giving fumes of HCl.

$$PCl_3 + 3H_2O \longrightarrow \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HCl$$

Q58. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Ans. PCl_5 has trigonal bipyramidal structure. It has three equatorial bonds inclined at an angle of 120° and two axial bonds inclined at an angle of 90°. As a result, axial bond pair suffer greater repulsion than the equatorial bond pair. Consequently, axial bonds are longer (240 pm) as compared to equatorial bonds (202 pm). Thus, all the five P–Cl bonds in PCl_5 are not equivalent.

Q59. How do you account for the reducing behaviour of H_3PO_2?

Ans. The structure of H_3PO_2 has two P—H bonds. Due to the presence of these P—H bonds. H_3PO_2 acts as a reducing agent:

$$4AgNO_3 + H_3PO_2 + 2H_2O \longrightarrow 4Ag + H_3PO_4 + 4HNO_3$$

Q60. Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding elements of group 15. Why?

Ans. Due to extra stable half-filled *p*-orbitals electronic configuration of Group 15 elements, large amount of energy is required to remove electrons as compared to Group 16 elements.

Q61. H_2S is less acidic than H_2Te, why?

Ans. Due to the decrease in bond (E—H) dissociation enthalpy down the group, acidic character increases.

Q62. Which form of sulphur shows paramagnetic behaviour?

Ans. In the vapour state, sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding orbitals like O_2 and hence exhibits paramagnetism.

Q63. What happens when

(*i*) Concentrated H_2SO_4 is added to calcium fluoride.

(*ii*) SO_3 is passed through water?

Ans. (*i*) It forms hydrogen fluoride:

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

(*ii*) It dissolves SO_3 to give H_2SO_4:

$SO_3 + H_2O \longrightarrow H_2SO_4$

Q64. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why? [*AI CBSE* 2017]

Ans. Halogens have the smallest size in their respective periods and high effective nuclear charge. As a consequence, they readily accept an electron to acquire noble gas electronic configuration.

Q65. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, yet fluorine is a stronger oxidising agent than chlorine. Why?

Ans. It is due to:

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

(*ii*) high hydration enthalpy of F.

Q66. Fluorine exhibits only –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

Ans. Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d*-orbitals and therefore they can expand their octet and show +1, +3, +5 and +7 oxidation states also.

Q67. Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify.

Ans. $$3Cl_2 + \underset{\text{(hot and conc.)}}{6NaOH} \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

Yes, chlorine from zero oxidation state is changed into –1 and +5 oxidation states simultaneously.

Q68. When HCl reacts with finely divided iron, it forms ferrous chloride and not ferric chloride. Why?

Ans. Its reaction with iron produces H_2:

$Fe + 2HCl \longrightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

Q69. Why are the elements of Group 18 known as noble gases?

Ans. The elements present in Group 18 have their valence shell orbitals completely filled and therefore, react with a few elements only under certain harsh conditions. Therefore, they are now known as noble gases.

Q70. Noble gases have very low boiling points. Why?

Ans. Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquified at very low temperature. Hence, they have low boiling points.

Q71. Does the hydrolysis of XeF_6 lead to a redox reaction?

Ans. No the products of hydrolysis are $XeOF_4$ and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reactants.

II. Short Answer Type Questions

(2 *or* 3 *Marks*)

Q1. Account for the following observations:

(*i*) Among the halogens, F_2 is the strongest oxidising agent?

(*ii*) Fluorine exhibits only –1 oxidation state whereas other halogens exhibit higher positive oxidation states also.

(*iii*) Acidity of oxoacids of chlorine are:
$HOCl < HOClO < HOClO_2 < HOClO_3$

[*CBSE* 2009]

Ans. (*i*) Low bond dissociation enthalpy and high hydration (solvation) enthalpy or highest S.R.P value of F_2 among halogens.

(*ii*) Due to its high electronegativity.

(*iii*) Higher the oxidation state of chlorine in the oxoacid, stronger is the acid.

Q2. Account for the following:

(*a*) Chlorine water has both oxidising and bleaching properties.

(*b*) H_3PO_2 and H_3PO_3 act as a good reducing agents while H_3PO_4 does not.

(*c*) On addition of ozone gas to KI solution, violet vapours are obtained.

Ans. (*a*) Chlorine water produces nascent oxygen which is responsible for bleaching action and oxidation.

$Cl_2 + H_2O \longrightarrow 2HCl + [O]$

(*b*) Both H_3PO_2 and H_3PO_3 have P–H bonds, so they act as reducing agents. while H_3PO_4, does not have P–H bond but has O–H bond, so it cannot act as a reducing agent.

(*c*) Ozone gas acts as a strong oxidising agent, so it oxidises iodide ions to iodine:

$$2I^{\ominus}(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^{\ominus}(aq) + I_2(g) + O_2(g)$$

I_2 vapours so evolved have violet colour.

Q3. Give reasons for the following:

(*a*) CN^- ion is known but CP^- ion is not known

(*b*) NO_2 dimerises to form N_2O_4.

(*c*) ICl is more reactive than I_2.

[*CBSE* 2009]

Ans. (*a*) Nitrogen being smaller in size forms pπ–pπ multiple bond with carbon, so CN^- ion is known, but Phosphorus does not form pπ–pπ bond due to its bigger size.

(*b*) NO_2 is an odd electron molecule and therefore it gets dimerised to stable N_2O_4.

(*c*) Because ICl has less bond dissociation enthalpy than I_2.

Q4. (*a*) What is the covalency of nitrogen in N_2O_5?

(*b*) Explain why both N and Bi do not form pentahalides while Phosphorus does. [*CBSE* 2009]

Ans. (*a*) 4

(*b*) Unlike P, N does not have *d*-orbitals in its valence shell. Bi prefers +3 oxidation state due to inert pair effect.

Q5. When conc. H_2SO_4 was added into an unknown salt present in a test tube, a brown gas (A) was evolved. This gas can be identified when copper turnings were also added into this test-tube. On cooling, the gas (A) changed into a colourless gas (B).

(*a*) Identify the gases (A) and (B)

(*b*) Write equations for the reactions involved. [*CBSE* 2009]

Ans. (*a*) A is NO_2 gas.
B is N_2O_4 gas.

(*b*) $MNO_3 + H_2SO_4 \longrightarrow MHSO_4 + HNO_3$

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

$$\underset{\text{Brown gas}}{2NO} \rightleftharpoons \underset{\text{Colourless}}{N_2O_4}$$

Q6. (*a*) Why does chlorine water lose its yellow colour on standing?

(*b*) What happens when Cl_2 reacts with cold dilute solution of sodium hydroxide? Write equation only. [*CBSE* 2009]

Ans. (*a*) Chlorine water loses its yellow colour on standing due to the formation of HCl and HClO

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

(*b*) $Cl_2 + \underset{\text{(cold and dilute)}}{2NaOH} \longrightarrow NaCl + NaClO + H_2O$

Q7. Write down the equations for hydrolysis of XeF_4 and XeF_6. Which of these two reactions is Redox reaction? [*CBSE* 2009]

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

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

Hydrolysis of XeF_4 is a Redox reaction. Here Xe^{4+} is changing into Xe and Xe^{6+}.

$$Xe^{4+} \longrightarrow Xe^0 + Xe^{6+}$$

Q8. Account for the following:

(*i*) NH_3 is a stronger base than PH_3.

(*ii*) Sulphur has a greater tendency for catenation than oxygen.

(*iii*) Bond dissociation energy of F_2 is less than that of Cl_2.

[*CBSE* 2009, *CBSE* (*Delhi*) 2013]

Ans. (*i*) Due to the presence of lone pair of electrons on the central atom both NH_3 and PH_3 can act as Lewis bases. When NH_3 or PH_3 accepts a proton, an additional N–H or P – H bond is formed.

$H_3N{:} + H^+ \longrightarrow NH_4^+$

$H_3P{:} + H^+ \longrightarrow PH_4^+$

Due to smaller size of N than P, N–H bond thus formed is much stronger than P–H bond. As a result NH_3 has more tendency than PH_3 to accept a proton. Therefore, NH_3 is a stronger base than PH_3.

(*ii*) Sulphur has a stronger tendency for catenation than oxygen because of stronger S – S bonds as compared to O – O bonds.

(*iii*) Due to smaller size, the lone pair of electrons on the F – atom repels the bond pair electrons of the F – F bond to a greater extent as compared to the large sized Cl atoms. Hence F – F bond dissociation energy is lower than that of Cl – Cl bond dissociation energy.

Q9. Explain the following situation:

(*i*) In the structure of HNO_3 molecule the N–O bond (121 pm) is shorter than N–OH bond (140 pm).

(*ii*) SF_4 is easily hydrolysed whereas SF_6 is not easily hydrolysed.

(*iii*) XeF_2 has a straight linear structure and not a bent angular structure.

[*CBSE* 2009]

Ans. (*i*) There is a double bond character in N–O bond due to resonance, but there is no double bond character in N–OH. This explains that N–O bond is shorter than N–OH bond in HNO_3.

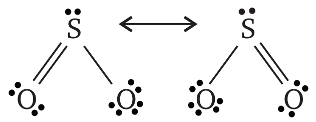
(*ii*) SF_6 does not undergo hydrolysis because the six F atoms protects the sulphur atom from the attack by water due to steric hindrance. SF_4 readily undergoes hydrolysis because the four F atoms cannot protect the *s* atoms from the attack by water.

(*iii*) As XeF_2 has 5 pair (10 electrons) around Xe forming a sp^3d hybridisation. Therefore, its geometry is linear.

Q10. (*i*) Draw the structure of SO_2 molecule. Comment on the nature of two S–O bonds formed in it. Are the two S–O bonds in this molecule equal?

(*ii*) What happens when white Phosphorus is heated with conc. NaOH solution in an inert gas atmosphere? [*CBSE* 2008]

Ans. (*i*) Structure of SO_2:



In SO_2 one electron from *p*-orbital jumps to vacant *d*-orbital and S-atom is sp^2-hybridised. The two of the three sp^2-orbitals form bonds with two O while the third contains the lone pair of electrons. Now S has one half filled *p*-orbital and one half filled *d*-orbital. These form one $p\pi$–$p\pi$ and one $p\pi$–$d\pi$ (*i.e.* double bond) with oxygen atom. Due to resonance, the two π bonds are equal in length.

(*ii*) When white phosphorus is heated with conc. NaOH solution in inert gas atmosphere, phosphine gas is produced.

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2 + PO_2$$

Q11. (*a*) How does xenon atom form compounds even though xenon atom has a closed shell electronic configuration?

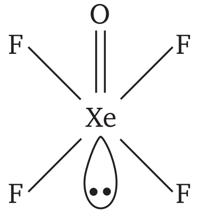
(*b*) Draw the structure of $XeOF_4$.

(*c*) Complete and balance the following equation: $XeF_4 + H_2O \longrightarrow$

[*AI* 2014] [*CBSE* 2008 *C*]

Ans. (*a*) The ionisation energy of xenon (1170 kJ mol^{-1}) is nearly equal to that of oxygen (1175 kJ mol^{-1}). While the ionisation energies of other noble gases are very high. Due to this reason, only xenon (Xe) form real chemical compounds.

(*b*) Structure of $XeOF_4$



(Square Pyramidal)

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

Q12. Give reasons for the following:

(*a*) Oxygen molecule has the formula O_2 while sulphur is S_8.

(*b*) H_2S is less acidic than H_2Te.

[*CBSE* 2008 *C*]

Ans. (*a*) Due to small size and high electronegativity oxygen forms $p\pi$–$p\pi$ multiple bonds. As a result oxygen exists as a diatomic (O_2) molecule. Due to its bigger size and lower electronegativity; sulphur does not form $p\pi$–$p\pi$ multiple bonds. Consequently, sulphur has high tendency of catenation and by the virtue of it forms octa–atomic (S_8) molecules having eight membered puckered ring structure.

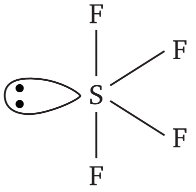
(*b*) As the atomic size increases down the group, the bond length increases. Hence the bond strength decreases on moving down the group. Consequently the cleavage of X–H bond (X = O, S, Se, Te *etc.*) becomes easier. Thus, H_2S is less acidic than H_2Te.

Q13. Draw the structure of the following molecules:

(*i*) SF_4

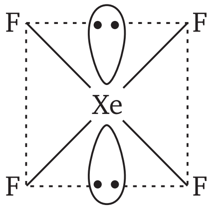
(*ii*) XeF_4 [*Delhi* 2013, 2016]

Ans. (*i*)



(SF_4)

(*ii*)



(XeF_4)
Square planar

Q14. (*a*) PH_3 has lower boiling point than NH_3, why?

(*b*) Write the balanced equation when ammonia is dissolved in water. [*CBSE* 2007]

Ans. (*a*) Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. Therefore, the boiling point of PH_3 is lower than NH_3.

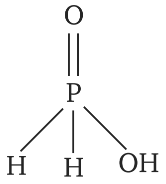
(*b*) $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+ (aq) + OH^-(aq)$

Q15. Draw the structure of the following species:

(*i*) H_3PO_2

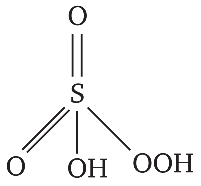
(*ii*) H_2SO_5 [*CBSE* 2007][*AI* 2017]

Ans. (*i*)



(hypophosphorous acid H_3PO_2)

(*ii*)



(peroxomonosulphuric acid)
H_2SO_5

Q16. What happens when

(*i*) Tin dissolves in a hot alkali solution?

(*ii*) XeO_3 reacts with an aqueous alkali solution?

Write the complete chemical equation in each case. [*CBSE* 2006 *C*]

Ans. (*i*) Tin dissolves in hot alkali solution to form a stannate.

$$Sn(s) + 2KOH(aq) + 4H_2O(l) \longrightarrow K_2[Sn(OH)_6](aq) + 2H_2(g)$$

(*ii*) XeO_3 reacts with aqueous alkali to form hydrogen Xenate ions, $HXeO_4^-$ which slowly disproportionates to give Xenon and perxenate ion, XeO_6^{4-}:

$$XeO_3 + OH^- \longrightarrow HXeO_4^-$$

$$2HXeO_4 + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

Q17. What happens when:

(*i*) Chlorine is passed through a hot concentrated solution of an alkali like $Ba(OH)_2$?

(*ii*) XeF_4 undergo hydrolysis?

Write the chemical equation in each case. [*CBSE* 2006]

Ans. (*i*) When chlorine is passed through a hot concentrated solution of $Ba(OH)_2$, barium trioxochlorate salts are obtained as:

$$6Cl_2(g)+6Ba(OH)_2(aq) \longrightarrow Ba(ClO_3)_2\ (aq) + 5BaCl_2(aq) + 6H_2O(l)$$

(*ii*) Hydrolysis of XeF_4 gives XeO_3:

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

Q18. (*a*) What prompted Bartlett to the discovery of noble gas compounds?

(*b*) State two important uses of noble gases. [*CBSE* 2006]

Ans. (*a*) Bartlett (1962) prepared a red compound of formula $O_2^+(PtF_6)^-$, dioxygenyl hexafluoroplatinate (V). He argued that the first ionisation energy of oxygen O_2 [= 1175 kJ mol^{-1}] was almost identical with that of xenon (1170 kJ mol^{-1}). He thought that if oxygen could form such compounds, xenon should also forms similar compounds. He prepared Xe^+PtF_6 (a red compound) by mixing PtF_6 with xenon:

$$Xe + PtF_6 \longrightarrow Xe+\ [PtF_6]^-$$

(*b*) **Uses of noble gases**

(*i*) Xenon is used in photographic flash tubes.

(*ii*) Liquid helium is used as a cryogenic agent for carrying out experiments at low temperature.

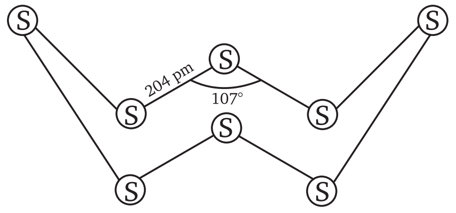
Q19. What are the allotropes of sulphur? Draw structures of S_8 and S_6. [*CBSE* 2005 *C*]

Ans. **Allotropes of sulphur:**

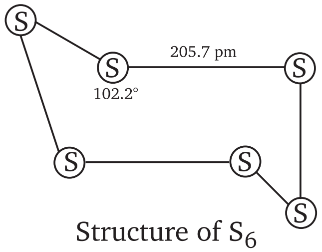
(*i*) The stable form of sulphur at room temperature is orthorhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

(*ii*) Both orthorhombic and monoclinic sulphur are molecular solids. The S_8 ring in both, the form is puckered and has a crown shape.

(*iii*) Several other modifications having 6-20 S-atoms are also there. In cyclo-S_6-form, the ring is having chair form.



Structure of S_8



Structure of S_6

Q20. Give reasons for the following:

(*a*) Nitric oxide becomes brown when released in air.

(*b*) PCl_5 is ionic in nature in the solid state. [*CBSE* 2006]

Ans. (*a*) It is because Nitric oxide reacts with oxygen to form nitrogen dioxide which is brown in colour.

$2NO + O_2 \longrightarrow 2NO_2$ (brown)

(*b*) PCl_5 is ionic in nature in solid state because it exists as $[PCl_4]^+ [PCl_6]^-$

Q21. Give reasons for the following:

(*a*) Ammonia acts as a ligand.

(*b*) Sulphur disappears when boiled with an aqueous solution of Sodium sulphite. [*CBSE* 2006]

Ans. (*a*) NH_3 has lone pair of electrons, therefore it acts as ligand.

(*b*) It is due to the formation of sodium thiosulphate:

$$Na_2SO_3 + S \longrightarrow \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

Q22. Account for the following:

(*i*) Thermal stability of water is much higher than that of H_2S.

(*ii*) White Phosphorus is more reactive than red Phosphorus. [*AI* 2006, 2017]

Ans. (*i*) It is because bond dissociation energy of H–O bond is higher as compared to H–S bond.

(*ii*) White Phosphorus is less stable and therefore, more reactive than the red Phosphorus because of angular strain in the P_4 molecule where the angles are only 60°. It readily catches fire in air to give dense white fumes of P_4O_{10}.

Q23. Write the chemical equations involved in the preparation of the following:

(*a*) XeF_4 (*b*) H_3PO_3

Ans. (*a*) $Xe + 2F_2 \xrightarrow[\text{1 bar}]{\text{873 K}} XeF_4$

(*b*) $P_4O_6 + 6H_2O \longrightarrow \underset{\text{Phosphorous acid}}{4H_3PO_3}$

Q24. Give reasons for the following:

(*a*) Sugar gets charred on addition of concentrated sulphuric acid.

(*b*) All five bonds in PCl_5 molecule are not equivalent. [*Foreign* 2006]

Ans. (*a*) It is because concentrated sulphuric acid is a strong dehydrating agent.

(*b*) It is because all the bonds are not in the same plane. Axial bonds are longer than equatorial bonds due to more repulsion.

Q25. Give reason.

(*a*) HF is least volatile, whereas HCl is the most volatile.

(*b*) Concentrated nitric acid turns yellow on exposure to sunlight.

[*Foreign* 2006]

Ans. (*a*) HF is least volatile because of extensive intermolecular hydrogen bonding.

Whereas HCl has least van der Waals' forces of attraction, therefore it is most volatile.

(*b*) It is because nitric acid decomposes to form NO_2 which is brown in colour.

Q26. Find the oxidation states of halogens in the following:

(*i*) Cl_2O (*ii*) $KBrO_3$

(*iii*) $NaClO_4$ (*iv*) ClO_2 [*AI* 2006 *C*]

Ans. (*i*) Cl_2O

$$2x - 2 = 0$$
$$2x = 2$$
$$x = +1$$

(*ii*) $KBrO_3$

$$1 + x - 6 = 0$$
$$x = +5$$

(*iii*) $NaClO_4$

$$1 + x - 8 = 0$$
$$x = +7$$

(*iv*) ClO_2

$$x - 4 = 0$$
$$x = +4$$

Q27. How would you account for the following:

(*i*) Enthalpy of dissociation for F_2 is much less than that of Cl_2?

(*ii*) Sulphur in vapour state exhibits paramagnetism? [*AI* 2006 *C*]

Ans. (*i*) It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2*p* orbitals of fluorine.

(*ii*) In vapour state, sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π-orbitals like O_2 and hence exhibits paramagnetism.

Q28. Explain the following observations.

(*i*) Bismuth oxide is not acidic in any of its reaction.

(*ii*) HF is a weaker acid than HI in aqueous solution. [*AI* 2006 *C*]

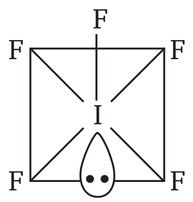
Ans. (*i*) Bismuth is metal. That is why its oxide is not acidic.

(*ii*) HF has higher bond dissociation energy than HI due to smaller bond length. So HF is a weaker acid than HI in aqueous solution.

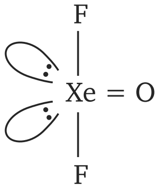
Q29. Write the structural formulae for the following: [*CBSE* 2005]

(*i*) IF_5 (*ii*) $XeOF_2$

Ans. (*i*)



(*ii*)



Q30. Assign an appropriate reason for each of the following statements:

(*i*) More metal fluorides are ionic in nature than metal chlorides.

(*ii*) SCl_6 is not known but SF_6 is known. [*CBSE* 2005]

Ans. (*i*) It is due to greater difference in electronegativity in fluorides than in chlorides.

(*ii*) In SCl_6 there is more interelectronic repulsion than in SF_6.

Q31. Assign a reason for each of the following:

(*i*) In group 15 the bond angle H – M – H decreases in the following order $NH_3(107.8)^\circ$, PH_3 $(93.6)^\circ$, AsH_3 $(91.8)^\circ$

(*ii*) Sulphur hexafluoride is used as a gaseous electric insulator. [*CBSE* 2005]

Ans. (*i*) It is due to increase in size of group 15 elements down the group. The bond angle decreases as bond length increases and bond pair-bond pair repulsion decreases.

(*ii*) It is because it is chemically inert.

Q32. Complete the following reaction equations:

(*i*) $Ca(OCl)_2 + HCl \longrightarrow$

(*ii*) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow$

[*AI* 2005]

Ans. (*i*) $Ca(OCl)_2 + 4HCl \longrightarrow CaCl_2 + 2H_2O + 2Cl_2$

(*ii*) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 6CaSiO_3 + 10CO$

Q33. Assign a reason for each of the following statements:

(*i*) SF_6 is not easily hydrolysed.

(*ii*) Hydrogen fluoride has a much higher boiling point than hydrogen chloride.

Ans. (*i*) It is because SF_6 is stable and inert.

(*ii*) HF molecules are associated with intermolecular H-bonding whereas HCl molecules are not.

Q34. Complete the following chemical equations:

$U(s) + ClF_3(l) \longrightarrow$

Ans. $U(s) + 3ClF_3(l) \longrightarrow UF_6(g) + 3ClF(g)$

Q35. Assign reason for each of the following:

(*a*) Noble gases are mostly chemically inert.

(*b*) Bismuth is a strong oxidising agent in pentavalent state. [*CBSE* 2005 *C*]

Ans. (*a*) It is due to stable electronic configuration.

(*b*) Bi^{3+} is more stable than Bi^{5+} due to inert pair effect. That is why Bi^{5+} gains 2 electron to form Bi^{3+} ions and acts as an oxidising agent.

$\therefore\ Bi^{5+} + 2e^- \longrightarrow Bi^{3+}$

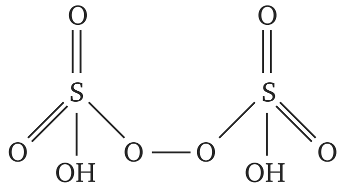
Q36. Draw the structures of the following:

(*i*) Peroxodisulphuric acid

(*ii*) Bromine trifluoride

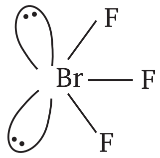
[*CBSE* 2005 *C*, *Delhi* 2013]

Ans. (*i*)



peroxodisulphuric acid ($H_2S_2O_8$)

(*ii*)



Bent-T-shaped (BrF_3)

Q37. Give reasons for the following:

(*i*) Bleaching of flowers by Cl_2 is permanent, while that of SO_2 is temporary.

(*ii*) Nitric oxide becomes brown when released in air. [*CBSE* 2005 *C*]

Ans. (*i*) Chlorine bleaches by oxidation, so its bleaching action is permanent. SO_2 bleaches by reduction, therefore bleached substance regains colour on exposure to O_2.

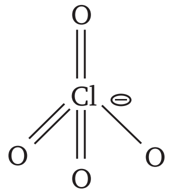
(*ii*) NO combines with O_2 to form NO_2 which is brown in colour.

Q38. (*i*) Draw the structure of ClO_4^-.

(*ii*) Give reasons: Xenon does not form fluorides such as XeF_3 and XeF_5.

[*AI* 2004 *C*]

Ans. (*i*)



(*ii*) Xe(54): $6s^2\ 6p^6$

On excitation it will have unpaired electron in even numbers and not in odd, therefore it shows +2, +4, +6 oxidation states and not +1, +3, +5.

Q39. Account for the following:

(*a*) Deep sea divers use a mixture of He(80%) and O_2(20%) instead of air for breathing.

(*b*) Among the hydrogen halides HF is least volatile, whereas HCl is most volatile. [*CBSE* 2003 *C*]

Ans. (*a*) It is because 'He' has very low solubility in blood even under high pressure.

(*b*) HF is associated with intermolecular H-bonding. HCl has least van der Waals' forces of attraction, therefore it is most volatile.

Q40. Give the chemical reaction in support of the following observations:

(*i*) The +5 oxidation state of Bi is less stable than its +3 oxidation state.

(*ii*) Sulphur exhibits greater tendency for catenation than selenium. [*AI* 2004]

Ans. (*i*) Bi^{5+} is less stable than Bi^{3+} due to inert pair effect.

(*ii*) Sulphur is small in size than selenium, therefore it forms more stable covalent bond with sulphur atom as compared to Se–Se bond. S–S bond has higher bond dissociation energy than Se–Se bond.

Q41. Write the chemical equation for the reactions which occur when.

(*i*) SO_2 reacts with hydrogen sulphide (H_2S). [*Foreign* 2004]

(*ii*) Sulphur dioxide reacts with sodium chlorate in strongly acidic solution. [*Foreign* 2004]

Ans. (*i*) $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$

(*ii*) $2NaClO_3 + SO_2 \xrightarrow{\text{acid}} 2ClO_2 + Na_2SO_4$

Q42. Write balanced equations for the following reactions and name the main product formed in each case.

(*i*) $O_2^- + H_2O \longrightarrow$

(*ii*) $P_4 + KOH + H_2O \longrightarrow$ [*Foreign* 2003]

Ans. (*i*) $4O_2^- + 2H_2O \longrightarrow 4OH^- + \underset{\text{Oxygen gas is formed}}{3O_2}$

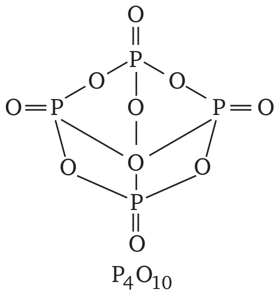
(*ii*) $P_4 + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$

Potassium hypophosphate and phosphine gas will be formed.

Q43. Draw the structural formulae of the following molecules:

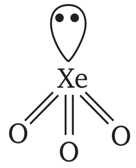
(*i*) P_4O_{10}(s) (*ii*) XeO_3(s) [*CBSE* 2006 *C*]

Ans. (*i*)



P_4O_{10}

(*ii*)



XeO_3

Q44. Give reasons for the following:

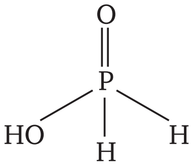
(*a*) Addition of Cl_2 to KI solution gives it a brown colour but excess of Cl_2 turns it colourless. [*CBSE* 2005 *C*]

(*b*) Phosphinic acid behaves as monoprotic acid. [*CBSE* 2004]

Ans. (*a*) $Cl_2 + 2KI \longrightarrow 2KCl + \underset{\text{(Brown)}}{I_2}$

$3Cl_2 + I_2 \longrightarrow \underset{\text{(Colourless)}}{2ICl_3}$

(*b*) Phosphinic acid behaves as a monoprotic acid due to one replaceable hydrogen atom.



Q45. Explain the following observations:

(*a*) ClF_3 exists but FCl_3 does not.

(*b*) (*i*) Among the hydrides of elements of group 16, water shows unusual physical properties. [*CBSE* 2003]

(*ii*) Justifying the order of your choice, arrange the following in decreasing order of property indicated.
$HClO_4$, $HClO_3$, $HClO_2$, HClO: oxidising power.

Ans. (*a*) It is because 'Cl' has vacant *d*-orbitals whereas 'F' does not have *d*-orbitals.
So, Cl can show higher oxidation state, F cannot. Also, F is the most electronegative element and it can only exhibit an oxidation state of –1.

(*b*) (*i*) Water is a liquid and other hydrides are gases. Water is thermally most stable among the hydrides of group 16 elements.
(*ii*) $HClO > HClO_2 > HClO_3 > HClO_4$
HClO is unstable and it breaks down

to form HCl and [O] due to which it is a strong oxidising agent.

Q46. Account for the following:

(*a*) PH_3 is a weaker base than NH_3.

(*b*) SF_6 exists but SH_6 does not.

(*c*) Sulphur exhibits tendency for catention but oxygen does not.

(*d*) The electron affinity of fluorine is less than that of chlorine.

[*AI* 2003 *C*]

Ans. (*a*) In PH_3, lone pair is available but due to its bigger size than nitrogen it is a weaker base as compared to nitrogen.

(*b*) SF_6 exists because F_2 is a stronger oxidising agent. SH_6 does not exist because H_2 is a weaker oxidising agent.

(*c*) Oxygen can form multiple bonds, whereas sulphur form only single bonds with other sulphur atoms. Therefore, sulphur shows catenation to more extent than oxygen.

(*d*) In 'F' there is more interelectronic repulsion due to smaller size as compared to 'Cl', therefore it has a lower electron affinity.

Q47. Complete the following equations:

(*i*) $P_4 + H_2O \rightarrow$

(*ii*) $XeF_4 + O_2F_2 \rightarrow$ [*CBSE* 2014]

Ans. (*i*) $P_4 + 6H_2O \rightarrow PH_3 + 3H_3PO_2$

(*ii*) XeF_6 can be prepared by the interaction of XeF_4 and O_2F_2 at 143 K

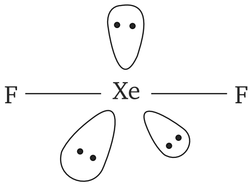
$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

Q48. Draw the structures of the following:

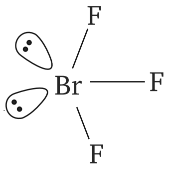
(*i*) XeF_2

(*ii*) BrF_3 [*CBSE* 2014, 2016]

Ans. (*i*) XeF_2 (linear)



(*ii*) BrF_3 (bent T-shaped)



Q49. (*a*) Account for the following:

(*i*) Interhalogens are more reactive than pure halogens.

(*ii*) N_2 is less reactive at room temperature.

(*iii*) Reducing character increases from NH_3 to BiH_3.

(*b*) Draw the structures of the following:

(*i*) $H_4P_2O_7$ (Pyrophosphoric acid)

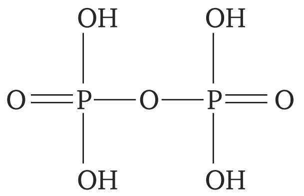
(*ii*) XeF_4 [*CBSE* 2015]

Ans. (*a*) (*i*) This is because the covalent bond between dissimilar atoms (X – X') in interhalogen compounds is weaker than that between similar atoms (X – X or X' – X') in halogens, except the F–F bond.

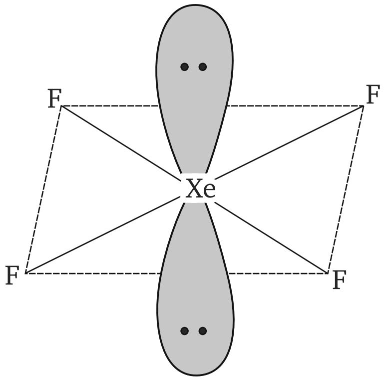
(*ii*) N_2 is less reactive at room temperature because its molecule is very small on the account of triple bond between two N-atoms and the bond dissociation enthalpy of the molecule very high.

(*iii*) The reducing character depends on the stability of the hydride. The greater the instability of a hydride, the greater is its reducing character. Because the stability decreases from NH_3 to BiH_3, so the reducing character increases in the same order.

(*b*)



$$O{=}\underset{OH}{\overset{OH}{P}}{-}O{-}\underset{OH}{\overset{OH}{P}}{=}O$$



XeF_4

Q50. Give reasons:

(*i*) SO_2 is reducing while TeO_2 is an oxidising agent.

(*ii*) Nitrogen does not form pentahalide.

(*iii*) ICl is more reactive than I_2.

[*CBSE* 2016]

Ans. (*i*) In case of sulphur, because of the presence of empty d-orbitals, it can expand its octet and raises its oxidation state from the +4 to +6. Hence, it acts as a reducing agent.

TeO_2 being a heavy element due to the inert pair effect, prefers lower oxidation state. Hence, acts as an oxidising agent.

(*ii*) Nitrogen does not form a pentahalide because of the non-availability of the d–orbitals in its valence shell.

(*iii*) The I-Cl bond in ICl is weaker than the I–I bond in I_2. Therefore, ICl is more reactive than I_2.

Q51. What happens when:

(*i*) SO_2 gas is passed through an aqueous solution Fe^{3+} salt?

(*ii*) XeF_4 reacts with SbF_5? [*CBSE* 2016]

Ans. (*i*) SO_2 is a reducing agent, and it reduces Fe^{3+} to Fe^{2+} and changes the solution from brown-red to green colour.

(*ii*) Xenon fluorides react with fluoride ion acceptors to form cationic species:

$XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$

III. Long Answer Type Questions

(5 *Marks*)

Q1. A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous KOH liberates a highly poisonous gas (C) having rotten fish smell. With excess of chlorine it forms (D) which hydrolyses to compound (E). Identify compounds (A) to (E).

[*CBSE* 2009]

Ans. (A) White Phosphorus

(B) Red Phosphorus

(C) Phosphine or (PH_3)

(D) Phosphorus pentachloride or (PCl_5)

(E) Phosphoric acid or (H_3PO_4)

Q2. Conc. H_2SO_4 is added followed by heating to each of the following test tubes labelled (I) to (IV). Identify in which of the above test tube the following change will be observed. Support your answer with the help of chemical equation:

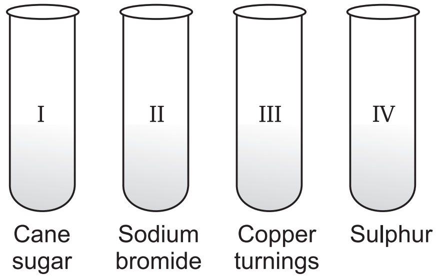
(*a*) formation of black substance

(*b*) evolution of brown gas

(*c*) evolution of colourless gas

(*d*) formation of a brown substance which on dilution becomes blue.

(*e*) disappearance of yellow powder along with evolution of colourless gas.



Ans. (*a*) $\underset{\text{white}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Black substance}}{12C} + 11H_2O$

(*b*) $2NaBr + 2H_2SO_4 \longrightarrow \underset{\text{Brown gas}}{Br_2\uparrow} + Na_2SO_4 + SO_2 + 2H_2O$

(*c*) $2KCl + H_2SO_4 \longrightarrow \underset{\text{(Colourless gas)}}{2HCl\uparrow} + K_2SO_4$

(*d*) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

(*e*) $3S + 2H_2SO_4 \longrightarrow \underset{\text{Colourless gas}}{3SO_2\uparrow} + 2H_2O$

Q3. (*a*) Draw the structures of the following:

(*i*) $H_2S_2O_8$

(*ii*) $HClO_4$

[*Delhi* 2013]

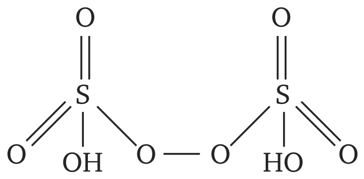
(*b*) How would you account for the following:

(*i*) NH_3 is a stronger base than PH_3.

(*ii*) Sulphur has a greater tendency for catenation than oxygen.

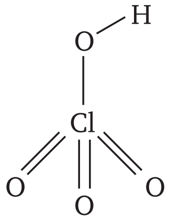
(*iii*) F_2 is a stronger oxidising agent than Cl_2. [*AI* 2009]

Ans. (*a*) (*i*)



($H_2S_2O_8$)
(Peroxodisulphuric acid)

(*ii*)



($HClO_4$) perchloric acid

(*b*) (*i*) Due to the presence of lone pair of electrons on the central atom, both NH_3 and PH_3 acts as Lewis bases. When NH_3 or PH_3 accepts a proton, an additional N – H or P – H bond is formed.

$H_3N + H^+ \longrightarrow NH_4^+$, $H_3P + H^+ \longrightarrow PH_4^+$

Due to smaller size of N-atom than P-atom, N – H bond thus formed is much stronger than P – H bond. As a result NH_3 has more tendency than PH_3 to accepta proton. Therefore, NH_3 is a stronger base than PH_3.

(*ii*) The property of catenation depends upon the strength of the element–element bond. Since sulphur S–S bond strength is much more than O – O bond strength. So sulphur has greater tendency for catenation than oxygen.

(*iii*) Since F_2 has smaller size than Cl_2 and there is absence of *d*-orbitals in fluorine, that is why F_2 is a stronger oxidising agent than Cl_2.

Q4. (*a*) Arrange $HClO_3$, $HClO_2$, HOCl and $HClO_4$ in order of increasing acidic strength. Give reason for your answer.

(*b*) Write the balanced chemical equation for the reaction of Cl_2 with hot and conc. NaOH solution. Justify that this reaction is a disproportionation reaction.

(*c*) Give one use of ClF_3. [*CBSE* 2008]

Ans. (*a*) Acidic strength of oxoacids of the same halogen increases with increase in oxidation number of the halogen.

Thus, the increasing order of acidic strength is

$\underset{+1}{HOCl} < \underset{+3}{HClO_2} < \underset{+5}{HClO_3} < \underset{+7}{HClO_4}$

(*b*) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

This reaction is a disproportionation reaction as oxidation state of chlorine is changed from zero to –1 and +5 simultaneously.

(*c*) ClF_3 is used for the production of UF_6 in the enrichment of ^{235}U.

$U(s) + 3ClF_3(l) \longrightarrow UF_6(g) + 3ClF(g)$

Q5. (*a*) Why do some noble gases form compounds with fluorine and oxygen only?

(*b*) How are the following compounds prepared from XeF_6?

(*i*) $XeOF_4$ and (*ii*) XeO_3

(*c*) Draw the structure of BrF_3 [*CBSE* 2008]

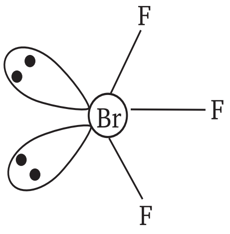
Ans. (*a*) Fluorine and oxygen are most electronegative elements and hence they are very reactive. Therefore, they form compounds with noble gases particularly xenon.

(*b*) Partial Hydrolysis of XeF_6 with water and it complete hydrolysis gives $XeOF_4$ and XeO_3 respectively:

(*i*) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

(*ii*) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

(*c*) Structure of BrF_3.



(Bent T shaped)

Q6. (*a*) How is sulphur dioxide prepared in

(*i*) Laboratory (*ii*) Industries

(*b*) What happens when sulphur dioxide is passed through water and reacts with sodium hydroxide? Write balanced equation.

(*c*) Write its any two uses. [*CBSE* 2007]

Ans. (*a*) Sulphur dioxide

(*i*) **Laboratory preparation:** It is prepared in the laboratory by treating a sulphite solution with dilute sulphuric acid:

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

(*ii*) **Industrial preparation:** It is produced industrially as a by-product of the rusting of the sulphide ores.

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(g) + 8SO_2(g)$$

(*b*) When sulphur dioxide is passed through water, it forms a solution of sulphurous acid.

$$SO_2(g) + H_2O(l) \rightleftharpoons \underset{\text{Sulphurous acid}}{H_2SO_3(aq)}$$

When sulphur dioxide reacts with sodium hydroxide solution, sodium sulphite is formed.

$$2NaOH + SO_2 \longrightarrow \underset{\text{Sod. sulphite}}{Na_2SO_3} + H_2O$$

(*c*) **Uses:**

(*i*) In refining of petroleum and sugar

(*ii*) In bleaching wool and silk.

Q7. Account for the following:

(*i*) All the bonds in PCl_5 are not equivalent.

(*ii*) Sulphur in vapour state exhibits paramagnetism.

(*iii*) Among the noble gases, only xenon is known to form true chemical compounds.

(*iv*) PbO_2 is a stronger oxidising agent than SnO_2. [*CBSE* 2006 *C*]

Ans. (*i*) As a result of sp^3d hybridisation, there are two axial bonds and three equatorial bonds in PCl_5 molecule. As the axial bond pair suffer more repulsive interactions from the equatorial bond pairs, therefore, the axial bonds are slightly elongated and slightly weaker than equatorial bonds.

(*ii*) In vapour state, sulphur partly exists as S_2 molecule and S_2 molecule has two unpaired electrons in antibonding π orbital and hence exhibits paramagnetism.

(*iii*) Xenon has the lowest ionisation energy among the noble gases except radon which is however radioactive.

(*iv*) Due to inert pair effect the lower oxidation state gets more stabilised with the increase in atomic number in the same group of *p*-block elements. Hence, PbO_2 is a stronger oxidising agent than SnO_2.

Q8. (*a*) Explain the Ostwald's process to manufacture nitric acid.

(*b*) Write the balanced reaction when nitric acid react with

(*i*) I_2 (*ii*) C (*iii*) S_8 (*iv*) P_4

(c) Give any two uses of HNO_3.

[*CBSE* 2006]

Ans. (*a*) **Ostwald's process:** This method is based upon catalytic oxidation of NH_3 by atomospheric oxygen:

$$4NH_3(g) + 5O_2(g) \xrightarrow[\text{500 K, 9 bar}]{\text{Pt}} 4NO(g) + 6H_2O(g)$$

Nitric oxide thus formed combine with oxygen to give NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons \underset{\substack{\text{Nitrogen}\\\text{dioxide}}}{2NO_2(g)}$$

Nitrogen dioxide so formed, dissolves in water to give nitric acid, HNO_3:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

(*b*) **Balanced Reactions:**

(*i*) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(*ii*) $C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$

(*iii*) $S_8 + 48HNO_3\ (conc.) \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

(*iv*) $P_4 + 20HNO_3\ (conc.) \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(*c*) **Uses:**

(*i*) Nitric acid is used to manufacture ammonium nitrate for making fertilisers.

(*ii*) It is used for the preparation of trinitrotoluene used in making explosives and other organic nitro compounds.

Q9. Give reasons for each of the following:

(*a*) Bleaching of flowers by Cl_2 is permanent while by SO_2 is temporary.

(*b*) Molten aluminium bromide is a poor conductor of electricity.

(*c*) Nitric oxide becomes brown when released in air.

(*d*) PCl_5 is ionic in nature in the solid state.

(*e*) Ammonia is a good complexing agent. [*CBSE* 2006]

Ans. (*a*) Cl_2 bleaches by oxidation, while SO_2 does it by reduction. The reduced product gets oxidise again and the colour is regained back.

(*b*) Aluminium bromide exists as a dimer, Al_2Br_6. In this structure, each aluminium atom forms one coordinate bond by accepting a lone pair of electrons from the bromine atom of another aluminium bromide molecule and thus complete the octet of electrons. Due to lack of free electrons, molten aluminium bromide is a poor conductor of electricity.

(*c*) Nitric oxide reacts with air and oxidised into NO_2 which is brown in colour.

$$2NO + O_2 \longrightarrow 2NO_2$$

(*d*) In solid state PCl_5 exists as $[PCl_4]^+ [PCl_6]^-$ and hence it is ionic in nature. Due to its ionic nature, it conducts current on fusion.

(*e*) N atom in ammonia has lone pair of electrons which can coordinate with other atoms or cations required for the stability of electron pair.

Q10. (*a*) How is nitric acid prepared in laboratory?

(*b*) Draw its structure.

(*c*) What happens when it reacts with

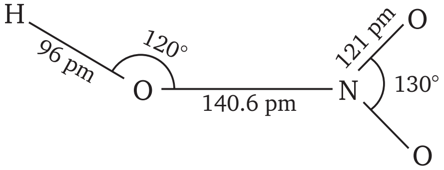
(*i*) Copper (*ii*) Zinc?

[*CBSE* 2005, *AI* 2014]

Ans. (*a*) **Laboratory preparation of nitric acid:** In laboratory, nitric acid is prepared by heating $NaNO_3$ and *conc.* H_2SO_4 in a glass retort.

$$\underset{\text{Sod. Nitrate}}{NaNO_3} + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow NaHSO_4 + \underset{\text{Nitric acid}}{HNO_3}$$

(*b*) **Structure of HNO_3:**



(*c*) (*i*) Copper reacts with dilute HNO_3 to give NO and it reacts with concentrated HNO_3 to give NO_2.

$$3Cu + 8HNO_3\ (dil.) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 8HNO_3\ (conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(*ii*) Zn reacts with dilute nitric acid to give N_2O and with concentrated acid it forms NO_2:

$$4Zn + 10HNO_3\ (dil.) \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3\ (conc.) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

Q11. (*a*) With the help of chemical equations, explain in brief the principle of contact process for the manufacture of sulphuric acid.

(*b*) How are the following isolated from their compounds?

Phosphorus from calcium phosphate.

Ans. (*a*) **Contact process:** It involves three steps:

(*i*) Burning of sulphur or sulphide ores in the presence of oxygen to produce SO_2.

(*ii*) SO_2 is treated with O_2 in the presence of V_2O_5 as a catalyst to form SO_3.

(*iii*) SO_3 is absorbed in H_2SO_4 to give oleum, $H_2S_2O_7$

$$S + O_2 \longrightarrow SO_2$$

The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.

The key step is the catalytic oxidation of SO_2 with O_2 to form SO_3 in the presence of V_2O_5 as catalyst.

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$
$\Delta_r H = -196.6 \text{ kJ mol}^{-1}$
The plant is operated at a pressure of 2 bar and a temperature 720 K. The SO_3 gas from catalytic converter is absorbed by concentrated H_2SO_4 to produce oleum.
$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$
Dilution of oleum with water gives H_2SO_4 of required concentration.
The sulphuric acid thus obtained by Contact process is generally 96 – 98% pure.

(*b*) $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$
$P_4O_{10} + 10C \longrightarrow P_4 + 10CO$

Q12. (*a*) Which poisonous gas is evolved when white phosphorus is heated with conc. NaOH
(*b*) Which noble gas has the lowest boiling point?
(*c*) Fluorine is a stronger oxidising agent than chlorine. Why?
(*d*) What happens when H_3PO_3 is heated?
(*e*) Complete the equation:
$PbS + O_3 \longrightarrow$ [*Delhi CBSE* 2017]

Ans. (*a*) On heating with caustic soda solution, white phosphorus forms a poisonous gas, phosphine.
$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + NaH_2PO_2$
(*b*) Helium has the lowest boiling point.
(*c*) The oxidising power of halogens decreases as we go down the group. The electrode potential of F_2 is +2.87 V, while that of Cl_2 is +1.36 V. This means that fluorine can be reduced more easily than chlorine. Therefore, fluorine is the strongest oxidising agent.
(*d*) On heating, H_3PO_3 decomposes to form phosphoric acid and phosphine.
$4H_3PO_3 \text{ 457 K} \longrightarrow 3H_3PO_4 + PH_3$
(*e*) $PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$

IV. Value-Based Questions

Q1. At an exhibition a Fortune Teller predicts your future. Ram and Shyam ran to get their fortune read. The fortune teller asked them to take a blank paper from the lot. He put the paper into a trough of water. Both the children read what was written on it.
(*a*) When the blank paper is dipped into a trough of water some written text become visible. Give a plausible explanation for this.
(*b*) What value do you get from this?

Ans. (*a*) The writing was done using the solution of lead acetate. This had become invisible after drying. The trough contained an aqueous solution of H_2S. Reaction of H_2S with lead acetate black precipitate of lead sulphide. Hence the writing visible becomes.
(*b*) Knowledge is the antidote to fear and blind belief.

Q2. Chlorine gas is a very useful gas. At the same time it can be used for the manufacture of certain poisonous gases.
(*a*) Name two poisonous gases manufactured from chlorine.
(*b*) The teacher while teaching made the student aware of both merits and demerits of chemicals. What value based education she tried to impart?

Ans. (*a*) Phosgene gas ($COCl_2$), and tear gas (CCl_3NO_2)
(*b*) Self awareness, Critical thinking.

Q3. Mohan while diluting concentrated acid added water to it. This caused splashes and he suffered from minor burns on his hands. Dinesh came to his help, took him to the medical room for first aid and also explained the right way to dilute sulphuric acid.
(*a*) Explain why Mohan's method of dilution caused splashes?

(*b*) What moral value is highlighted by Dinesh's action?

Ans. (*a*) While diluting acid one should always add acid to the water, not water to the acid because dilution of acid is an exothermic reaction.

(*b*) Social responsibility and Scientific attitude.

V. HOTS Questions

Q1. Both Cl and O have the same electronegativity but only O can form H–bond?

Ans. ∵ Their sizes are different, so the electron density on oxygen atom is much higher than on Cl. Due to this reason Cl is unable to form H-bonding.

Atomic Sizes : O = 66 pm,
Cl = 99 pm.

Q2. Why ICl bonds are weaker than Cl_2?

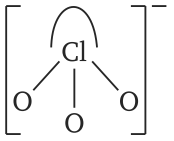
Ans. In Cl_2, overlapping has to be taken place between Cl – Cl atom, their sizes are equal, therefore overlapping is effective, But in case of ICl, the sizes of I and Cl are different. This result in **"ineffective overlapping"** and hence weaker bond.

Q3. (*a*) $HClO_4$ is more acidic than $HClO_3$.

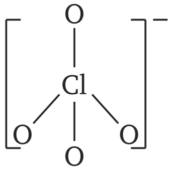
Or

pK_a of $HClO_3$ is more than $HClO_4$.

Ans.



Conjugate anion of $HClO_3$



Conjugate anion of $HClO_4$

Greater number of oxygen atoms, greater is the dispersal of negative (–) charge and greater is stability of anion.

$$HClO_4 > HClO_3$$