Chapter–7

The *p*-Block Elements

basic concepts

1. **p-Block Elements:** The elements of Group 13 (Boron family–B, Al, Ga, In, Tl); Group 14 (Carbon family–C, Si, Ge, Sn, Pb); Group 15 (Nitrogen family–N, P, As, Sb, Bi, Mc); Group 16 (Oxygen family–O, S, Se, Te, Po, Lv); Group 17 (Halogen family–F, Cl, Br, I, At, Ts) and Group 18 (Noble gases–He, Ne, Ar, Kr, Xe, Rn, Og) receive their last electron in their *np* orbitals. All these elements are therefore, called *p*-block elements. They are represented by general outer electronic configuration $ns^2\ np^{1-6}$.

   Common characteristics of *p*-block elements

   (*i*) *p*–Block elements exist in all the three physical states and may be metals, non-metals or metalloids.

   (*ii*) Ionisation energy increases across a period and decreases down the group.

   (*iii*) They have high value of electronegativity which decreases down the group but increases across a period. Fluorine has the highest value of electronegativity.

   (*iv*) They have high electron affinity. Generally, electron affinity increases from left to right in a period and decreases from top to bottom in a particular group.

   (*v*) The atomic and ionic radii of *p*-block elements decreases on moving across in a period and increases down a group.

   (*vi*) Except oxygen, fluorine and zero group elements, all other elements exhibit positive and negative oxidation states. Due to inert pair effect some of the *p*-block elements exhibit variable oxidation states, *e.g.*, Sn (II) and Sn (IV); Pb (II) and Pb (IV); Tl (I) and Tl (III), etc.

   (*vii*) P, O, S and halogens are very reactive while other elements of *p*-block are less reactive.

   (*viii*) As we move from Group 13 to 17 in the *p*-block, the reducing character decreases and the oxidising character increases. Thus, halogens are the best oxidising agents.

2. **Inert Pair Effect:** In the *p*-block elements as we go down a group, the intervening *d* and *f* orbitals, due to their poor screening effect result in the greater attraction on the ns^2 electrons. This pair of electrons cannot, therefore, take part in the bonding. This effect is called "inert pair effect".

3. **General Characteristics of *p*-Block Elements (Groups 15–18)**

Group 15

(A) General Information

1. **Name:** Nitrogen family
2. **Elements:** $_7$N, $_{15}$P, $_{33}$As, $_{51}$Sb, $_{83}$Bi
3. **Electronic Configuration:**

$_7\text{N} = [\text{He}]\ 2s^2\ 2p^3$; $_{15}\text{P} = [\text{Ne}]\ 3s^2\ 3p^3$;

$_{33}\text{As} = [\text{Ar}]\ 3d^{10}\ 4s^2\ 4p^3$; $_{51}\text{Sb} = [\text{Kr}]\ 4d^{10}\ 5s^2\ 5p^3$;

$_{83}\text{Bi} = [\text{Xe}]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$; $_{115}\text{Mc} = [\text{Rn}]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^3$.

(B) Atomic and Physical Properties

1. **Atomic Radii:** They are smaller than the corresponding elements of Group 14 because of increase in nuclear charge. Down the group they show an increase mainly due to addition of a new shell.
2. **Oxidation States:** Because of small size, N and P can gain three electrons to complete their octets and hence show an oxidation state of – 3. In addition to – 3 oxidation state, the elements of Group 15 also show +3 and +5 oxidation states. Nitrogen exhibits all the oxidation states from – 3 to +5.
3. **Ionisation Enthalpy (IE):** IEs of these elements are much higher than the corresponding elements of Group 14 because of increase in nuclear charge and greater stability of exactly half-filled orbitals. Down the group the values decrease due to increase in atomic size.
4. **Metallic Character:** Metallic character increases down the group due to decrease in ionisation enthalpy and increase in atomic size. Thus, N and P are non-metals, As and Sb are metalloids while Bi is a typical metal.
5. **Electronegativity:** These are more electronegative than Group 14 elements because of further decrease in size. It decreases down the group because of increase in atomic size.
6. **Melting Points and Boiling Points:** Melting points first increase from N to As due to increase in nuclear charge and then decrease from Sb to Bi. The decrease is due to increase in size and weakening of interatomic forces and also due to inert pair effect resulting in the formation of 3 bonds instead of 5.
7. **Density:** The densities increase regularly down the group as usual.

(C) Chemical Properties

1. **Hydrides:** They form covalent hydrides with the formula EH_3.

   Properties of Hydrides

   (*i*) **Thermal stability:** It decreases down the group because the size of the atom increases and hence the bond dissociation enthalpy decreases.

   (*ii*) **Reducing character:** It increases down the group due to decrease in bond dissociation enthalpy. Except NH_3, all are strong reducing agents.

   (*iii*) **Basic character:** It decreases down the group because as atomic size increases, electron density decreases on central atom E, *i.e.*, the order is $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

   (*iv*) **Boiling points:** Boiling point of NH_3 is greater than PH_3 because of intermolecular hydrogen bonding. Boiling points increase from PH_3 onwards because of increase of molecular mass and hence van der Waals forces.

2. **Halides**

   Trihalides: All of these elements directly combine with halogens to form trihalides of the type EX_3. Except NBr_3 and NI_3, all are stable and have pyramidal shape. They are easily hydrolysed by water.

   Pentahalides: P, As and Sb form pentahalides of the formula EX_5. N does not form pentahalide because of non-availability of *d*-orbital in its valence shell. Bi does not form pentachloride due to inert pair effect. Pentahalides involve sp^3d hybridisation and have trigonal bipyramidal shape.

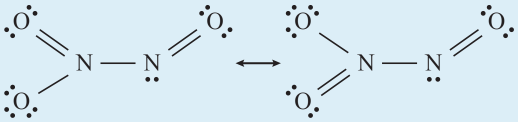
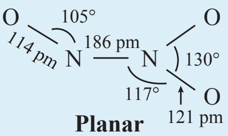
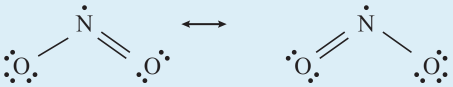
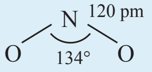
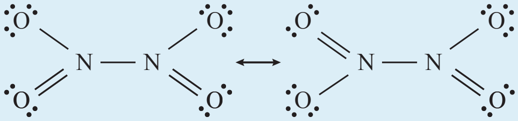
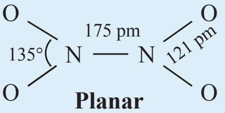
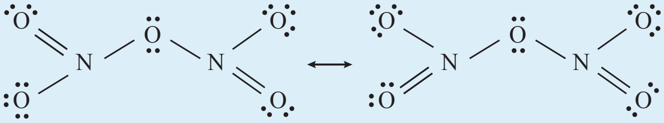
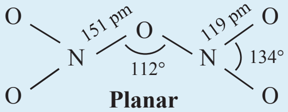
3. **Oxides:** All these elements form two types of oxides—E_2O_3 and E_2O_5. The oxide in the higher oxidation state is more acidic than that of lower oxidation state. Their acidic character decreases down the group.

Table 7.1: Oxides of Nitrogen

Name	Formula	Oxidation State of Nitrogen	Common Methods of Preparation	Physical Appearance and Chemical Nature
Dinitrogen oxide [Nitrogen (I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral

Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$	Blue solid, acidic
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673\,K} 4NO_2 + 2PbO + O_2$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen (V) oxide]	N_2O_5	+ 5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

Table 7.2: Structures of Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O		N — N — O 113 pm 119 pm **Linear**
NO		N — O 115 pm
N_2O_3		 **Planar**
NO_2		 **Angular**
N_2O_4		 **Planar**
N_2O_5		 **Planar**

Oxides of phosphorus: Two important oxides of phosphorus are P_4O_6 (a dimer of P_2O_3) and P_4O_{10} (a dimer of P_2O_5). These are obtained as follows:

$$P_4 + 3O_2(\text{limited}) \xrightarrow{\Delta} P_4O_6$$

$$P_4 + 5O_2(\text{excess}) \xrightarrow{\Delta} P_4O_{10}$$

Oxides of other elements: As_4O_6 , As_2O_5 , Sb_4O_6 , Sb_2O_5 , Bi_2O_3 and Bi_2O_5.

Properties: Trioxides of N, P and As are acidic. The acidic character decreases down the group. Oxide of Sb is amphoteric while that of Bi is basic. All pentoxides are acidic. Acidic character decreases down the group. N_2O_5 is the strongest acidic oxide while Bi_2O_5 is the weakest.

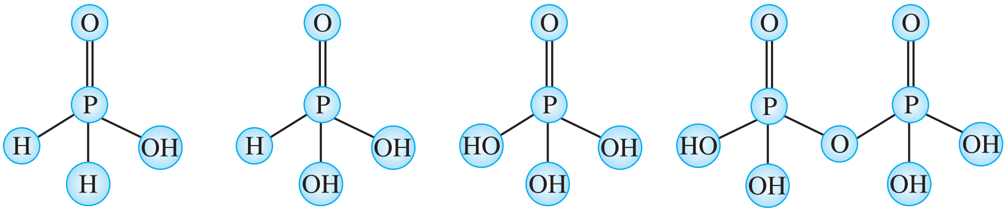
4. **Oxo-acids:** The elements of this group form a number of oxo-acids out of which those of nitrogen and phosphorus are more common.

Oxo-acids of Nitrogen:

Formula (Name)	Oxidation state of N
$H_2N_2O_2$ (Hyponitrous acid)	+ 1
HNO_2 (Nitrous acid)	+ 3
HNO_3 (Nitric acid)	+ 5

Oxo-acids of Phosphorus:

Formula (Name)	Oxidation state	Basicity
H_3PO_2 (Hypophosphorous acid)	+ 1	1
H_3PO_3 (Orthophosphorous acid)	+ 3	2
H_3PO_4 (Orthophosphoric acid)	+ 5	3
$H_4P_2O_7$ (Pyrophosphoric acid)	+ 5	4



Hypophosphorous acid (H_3PO_2) Orthophosphorous acid (H_3PO_3) Orthophosphoric acid (H_3PO_4) Pyrophosphoric acid ($H_4P_2O_7$)

Fig. 7.1: Structure of oxoacids of phosphorus

Preparation of H_3PO_3 and H_3PO_4

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

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

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Acids in +3 oxidation state of phosphorus tend to disproportionate, *e.g.*,

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

The acids which contain P–H bonds have strong reducing properties. Thus, hypophosphorus acid is a good reducing agent as it contains two P–H bonds and reduces $AgNO_3$ to metallic silver.

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

H atoms which are attached with oxygen in P–OH are ionisable and cause the basicity. Thus, H_3PO_4 and H_3PO_3 are tribasic and dibasic, respectively, as the structure of H_3PO_4 has three P–OH bonds and H_3PO_3 has two.

5. **Dinitrogen (N_2)**

In the laboratory, it is prepared by heating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l) + NaCl(aq)$$

It can also be prepared by heating ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

Properties of dinitrogen: N_2 has very little reactivity at ordinary temperature. The chemical inertness of dinitrogen is attributed to high bond enthalpy of $N \equiv N$ bond (946 kcal/mol).

It forms nitrides with highly electropositive metals like lithium, calcium and magnesium, etc.

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

It combines with dioxygen at about 2000 K to form nitric oxide, NO.

$$N_2 + O_2(g) \xrightleftharpoons{\text{Heat}} 2NO(g)$$

Uses:

1. It is used in the manufacture of ammonia.
2. Liquid nitrogen is used as a refrigerant to preserve biological materials.

6. Ammonia (NH_3)

In the laboratory, it is prepared by heating a mixture of slaked lime and ammonium chloride. Ammonia is obtained on small scale by heating ammonium salts with bases.

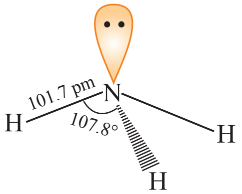
$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\text{Heat}} 2NH_3 + CaCl_2 + 2H_2O$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

Manufacture of ammonia:

Ammonia is generally manufactured by Haber's process which involves the direct combination of nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[773\text{ K}]{\text{Fe/Mo}} 2NH_3(g); \quad \Delta H = -46.1\text{ kJ/mol}$$



Properties of ammonia: It has trigonal pyramidal structure with three bond pairs and one lone pair of electrons.

It is extremely soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions.

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

It forms salts with acids, *e.g.*, NH_4Cl, $(NH_4)_2SO_4$, etc.

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{(White ppt.)}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

$$2FeCl_3(aq) + 3NH_4OH(aq) \longrightarrow \underset{\text{(Brown ppt.)}}{Fe_2O_3.xH_2O(s)} + 3NH_4Cl(aq)$$

Ammonia acts as Lewis base due to the presence of a lone pair of electrons on nitrogen and hence forms a number of complexes with metal ions.

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

$$\underset{\text{White ppt.}}{AgCl(s)} + 2NH_3(aq) \longrightarrow \underset{\text{Colourless}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses:

1. It is used to produce various nitrogenous fertilizers.
2. It is used in the manufacture of some inorganic nitrogen compounds like nitric acid.

7. Nitric Acid (HNO_3)

Laboratory preparation: In the laboratory, it can be prepared by heating $NaNO_3$ or KNO_3 with concentrated H_2SO_4 in a glass retort.

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

Manufacture of HNO_3 (Ostwald's process):

The reaction involving manufacture of HNO_3 are as follows:

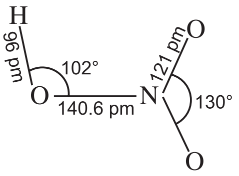
$$4NH_3(g) + \underset{\text{(From air)}}{5O_2(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt/Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

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

Properties of HNO_3: When pure, it is a colourless liquid. The impure acid is generally yellow due to the presence of NO_2 as impurity. Nitric acid containing dissolved nitrogen dioxide is known as fuming nitric acid.

In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown alongside.



In an aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Oxidising agent: Nitric acid is very strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of acid, temperature and the nature of the material undergoing oxidation.

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

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

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

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

Metals such as Cr, Al do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Oxidation of non-metals:

Sulphur is oxidised to sulphuric acid.

$$\begin{array}{l} 2HNO_3 \longrightarrow H_2O + 2NO_2 + (O)] \times 24 \\ S_8 + 24(O) + 8H_2O \longrightarrow 8H_2SO_4 \\ \hline S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O \\ \hline \end{array}$$

Carbon is oxidised to carbon dioxide.

$$\begin{array}{l} 2HNO_3 \longrightarrow H_2O + 2NO_2 + (O)] \times 2 \\ C + 2(O) + H_2O \longrightarrow CO_2 + H_2O \\ \hline C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2 \\ \hline \end{array}$$

Iodine is oxidised to iodic acid (HIO_3).

$$\begin{array}{l} 2HNO_3 \longrightarrow H_2O + 2NO_2 + (O)] \times 5 \\ I_2 + 5(O) \longrightarrow I_2O_5 \\ I_2O_5 + H_2O \longrightarrow 2HIO_3 \\ \hline I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O \\ \hline \end{array}$$

Phosphorus is oxidised to phosphoric acid.

$$\begin{array}{l} 2HNO_3 \longrightarrow H_2O + 2NO_2 + (O)] \times 10 \\ P_4 + 10(O) \longrightarrow P_4O_{10} \\ P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4 \\ \hline P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O \\ \hline \end{array}$$

Brown Ring test for NO_3^- ion:

The brown ring test for nitrates depend on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown-coloured complex.

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

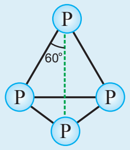
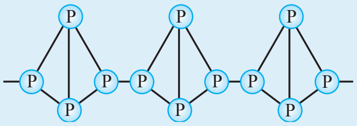
$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

8. Phosphorus

Allotropic forms of phosphorus are:

1. White or yellow phosphorus
2. Black phosphorus
3. Red phosphorus

Table 7.3: Differences between the Properties of White and Red Phosphorus

Property	White Phosphorus	Red Phosphorus
1. State	Translucent white waxy solid.	Iron grey lustrous powder.
2. Odour	Garlic smell.	Odourless.
3. Physiological action	Poisonous.	Non-poisonous.
4. Solubility	Insoluble in water but soluble in CS_2.	Insoluble in water as well as CS_2.
5. Stability	Less stable, due to angular strain in the molecule where the bond angles are only 60°.	More stable than white phosphorus.
6. Action of air	Readily catches fire in air with a greenish glow which is visible in dark.	Does not glow in dark.
7. Action of alkali	PH_3 is formed. $P_4 + 3NaOH + 3H_2O \xrightarrow{\Delta,\ CO_2} PH_3 + 3NaH_2PO_2$	No reaction.
8. Effect of heat	Changes to β-black phosphorus when heated at 473 K under high pressure and changes to red phosphorus when heated at 573 K.	Changes to α-black phosphorus when heated at 803 K in a solid tube.
9. Structure	Consists of discrete tetrahedral P_4 molecules. 	Tetrahedral units of P_4 joined together through covalent bonds to give polymeric structure. 

9. Phosphine (PH_3)

Preparation: In the laboratory, phosphine is prepared by heating white phosphorous with concentrated sodium hydroxide solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \xrightarrow{\Delta,\ CO_2} PH_3 + 3NaH_2PO_2$$

In order to purify it from the impurities, it is absorbed in HI to form PH_4I which on treating with KOH gives off phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

It can also be prepared by the reaction of calcium phosphide with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

Properties

Phosphine is a colourless gas with rotten fish smell and is highly poisonous. It is slightly soluble in water. When it is absorbed in copper sulphate or mercuric chloride solution, corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

Phosphine is weakly basic and gives phosphonium compounds with acids, *e.g.*,

$$PH_3 + HBr \longrightarrow PH_4Br$$

Uses:

The spontaneous combustion of phosphine is technically used in Holme's signal.

It is also used in smoke screens.

10. Phosphorus Halides: Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

Phosphorus Trichloride: It is obtained by passing dry chlorine over heated white phosphorous.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

It can also be obtained by the action of thionyl chloride on white phosphorus.

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties: It is a colourless, oily liquid and hydrolyses in the presence of moisture.

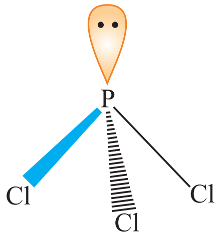
$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

It reacts with organic compounds containing —OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

It has a pyramidal shape as shown in figure alongside, in which phosphorus is sp^3 hybridised.



Phosphorus Pentachloride: It is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

Properties: PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

When heated, it sublimes but decomposes on stronger heating.

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

Finely divided metals on heating with PCl_5 give corresponding chlorides.

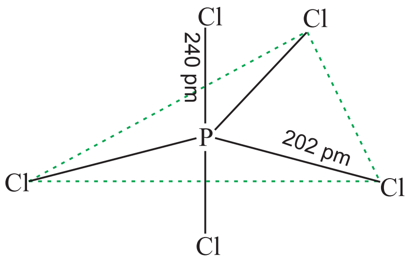
$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

It is used in the synthesis of some organic compounds, *e.g.*, C_2H_5Cl, CH_3COCl.

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown in figure alongside.

The three equatorial P—Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion from equatorial bond pairs.



In the solid state, it exists as an ionic solid, $[PCl_4]^+ [PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

Group 16

(A) General Information

1. **Name:** Oxygen family or Chalcogens
2. **Elements:** ${}_{8}O$, ${}_{16}S$, ${}_{34}Se$, ${}_{52}Te$, ${}_{84}Po$, ${}_{116}Lv$
3. **Electronic Configuration:** ${}_{8}O = [He]\ 2s^2\ 2p^4$; ${}_{16}S = [Ne]\ 3s^2\ 3p^4$
   ${}_{34}Se = [Ar]\ 3d^{10}\ 4s^2\ 4p^4$; ${}_{52}Te = [Kr]\ 4d^{10}\ 5s^2\ 5p^4$; ${}_{84}Po = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
   ${}_{116}Lv = [Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^4$.

(B) Atomic and Physical Properties

1. **Atomic Radii:** They are smaller than the corresponding elements of Group 15 because of increase in nuclear charge. Down the group they increase mainly due to addition of a new shell.
2. **Oxidation States:** Because of high electronegativity and tendency to gain two electrons oxygen shows an oxidation state of –2 only (except in OF_2 where it has +2, and H_2O_2 where it is –1). All other elements show oxidation states of +2, +4 and +6 because of different excitations possible to empty *d*-orbitals.
3. **Ionisation Enthalpy:** First IE of these elements are lower than those of corresponding elements of Group 15 despite their smaller atomic radii. This is due to greater stability of half-filled orbitals of Group 15 elements. IE_2 values are higher than those of Group 15 because of smaller size of the ions and greater effective nuclear charge. IE decreases down the group.
4. **Electron Gain Enthalpy:** Because of small size of atom, oxygen has less negative electron gain enthalpy than sulphur. However, from sulphur onwards positive value again becomes less negative up to polonium.
5. **Metallic Character:** These elements have very little metallic character because of high IE. Down the group, the metallic character increases due to decrease in IE. Thus, O and S are non-metals, Se and Te have very little metallic character while Po is metallic.
6. **Electronegativity:** These are more electronegative than Group 15 elements because of further decrease in size. It decreases down the group because of increase in atomic size. Oxygen is the second most electronegative element.
7. **Melting and Boiling Points:** Melting and boiling points increase regularly from O to Te due to increase in size and hence greater van der Waals' forces. The element Po, has lower melting and boiling point than Te because of the maximum inert pair effect.

(C) Chemical Properties

Anomalous Behaviour of Oxygen

The anomalous behaviour of oxygen is due to its small size, high electronegativity and absence of *d*-orbitals. The absence of *d*-orbitals in oxygen limits its covalency to four.

1. **Hydrides:** They form hydrides of the formula H_2E.

   Properties of Hydrides:

   (*i*) Thermal stability: It decreases down the group because as the size of the atom increases the bond dissociation enthalpy decreases.

   (*ii*) Acidic character: It increases down the group because they can dissociate more easily to give H^+ ions.

$$H_2E + aq \rightleftharpoons H^+ + HE^-$$

$$HE^- + aq \rightleftharpoons H^+ + E^{2-}$$

   (*iii*) Reducing nature: Except H_2O, all are reducing agents. The reducing character increases down the group.

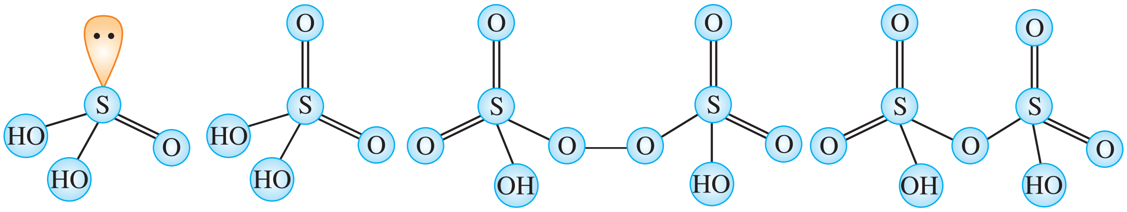
   (*iv*) Boiling point/volatility: H_2O has the highest boiling point because of H-bonding. After a sudden drop from H_2O to H_2S, boiling point gradually increases from H_2S to H_2Te because of increase of molecular mass and hence van der Waals' forces.

2. **Halides:** These elements form a large number of halides of the type, EX_2, EX_4 and EX_6 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order F^-, Cl^-, Br^-, I^-. Amongst hexahalides, hexafluorides are the only stable halides. SF_6 is exceptionally stable for steric reasons. It has sp^3d^2 hybridisation and thus, has octahedral structure.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 is a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structures in which one of equatorial position is occupied by a lone pair (see-saw shape). All elements except selenium form dichlorides and dibromides. These dihalides have sp^3 hybridisation and thus, have tetrahedral structure. The well known monohalides S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2, Se_2Br_2 are dimeric in nature and undergo disproportionation as given below.

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

3. **Oxides:** All these elements form oxides of the type, EO_2 and EO_3 where E is the element of the group. Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent. Both EO_2 and EO_3 types of oxides are acidic in nature.
4. **Oxo-acids:** In this family, sulphur forms a number of oxo-acids. Out of these, sulphuric acid, H_2SO_4, is the most important and is called the King of Chemicals. A few important oxo-acids of sulphur are:



Sulphurous acid (H_2SO_3) Sulphuric acid (H_2SO_4) Peroxodisulphuric acid ($H_2S_2O_8$) Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Fig. 7.2: Structure of some oxoacids of sulphur

Sulphuric Acid (H_2SO_4)

Manufacture of H_2SO_4: Sulphuric acid is manufactured by the Contact process which involves the following equations:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

$$SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7(l)}$$

Oleum is diluted with water to get H_2SO_4 of desired concentration.

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$$

Properties of Sulphuric Acid:

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. Because of its low volatility, concentrated H_2SO_4 can be used to manufacture more volatile acids from their salts.

$$2MX + H_2SO_4 \longrightarrow \underset{\text{(Conc.)}}{2HX} + M_2SO_4 \qquad (M = \text{metal}, X = F, Cl, NO_3)$$

Concentrated sulphuric acid is a powerful dehydrating agent.

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

Hot concentrated H_2SO_4 is a moderately strong oxidising agent.

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

$$3S + 2H_2SO_4(\text{conc.}) \longrightarrow 3SO_2 + 2H_2O$$

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

5. **Dioxygen (O_2)**

Preparation of O_2: Dioxygen can be prepared by the following ways:

1. By decomposition of oxygen rich compounds.

$$2KMnO_4(s) \longrightarrow K_2MnO_4(s) + MnO_2(s) + O_2(g)$$

$$2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$$

$$2KClO_3(s) \xrightarrow[420\text{ K}]{MnO_2} 2KCl(s) + 3O_2(g) \qquad \text{(Laboratory preparation)}$$

2. By thermal decomposition of oxides of metals which are low in electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g); \qquad 2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

$$2Pb_3O_4(s) \longrightarrow 6PbO(s) + O_2(g) \qquad 2PbO_2(s) \longrightarrow 2PbO(s) + O_2(g)$$

3. By decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Industrially, dioxygen is obtained by liquefaction of air followed by fractional distillation.

Properties of Dioxygen:

Dioxygen is a colourless and odourless gas. It liquefies at 90 K and freezes at 55 K. Some of the reactions of dioxygen with metals, non-metals and other compounds are given below.

$$2Ca + O_2 \longrightarrow 2CaO; \qquad 4Al + 3O_2 \longrightarrow 2Al_2O_3$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}; \qquad 4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

A binary compound of oxygen with another element is called oxide. Oxides can be simple (*e.g.*, MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). Simple oxides are further classified as acidic, basic, amphoteric and neutral oxides. An oxide which combines with water to form an acid is called an acidic oxide.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

As a general rule only non-metal oxides (*e.g.*, CO_2, SO_2, N_2O_5, Cl_2O_7) are acidic but oxides of some metals in higher oxidation state also have acidic character (*e.g.*, Mn_2O_7, CrO_3, V_2O_5). The oxide which combines with water to form a base is called a basic oxide. In general, metallic oxides (*e.g.*, Na_2O, CaO, BaO) are basic.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The oxides which show characteristics of both acidic as well as of basic oxides are called amphoteric oxides. For example, Al_2O_3, ZnO, SnO_2, PbO. They react with acids as well as bases.

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \longrightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[Al(OH)_6](aq)$$

The oxides which are neither acidic nor basic are called neutral oxides. For example, CO, NO, N_2O, H_2O.

Uses:

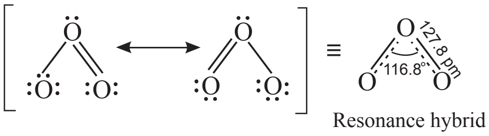
1. It is used oxyacetylene welding.
2. Oxygen cylinders are widely used in hospitals.

6. Ozone (O_3)

Preparation of Ozone: Ozone is prepared by subjecting pure and dry oxygen to silent electric discharge.

$$3O_2(g) \longrightarrow 2O_3(g); \quad \Delta H^\circ(298\text{ K}) = 142\text{ kJ mol}^{-1}$$

Structure of Ozone



Resonance hybrid

Ozone is a pale blue gas having a strong characteristic smell. 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.

$$PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$$

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

Uses: Ozone is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc.

7. Sulphur (S)

Sulphur forms numerous allotropes of which the yellow rhombic (α-sulphur) and monoclinic (β-form) are the most important. Both rhombic and monoclinic sulphur have S_8 molecules. In cyclo-S_6 form, the ring adopts the chair form as shown below:

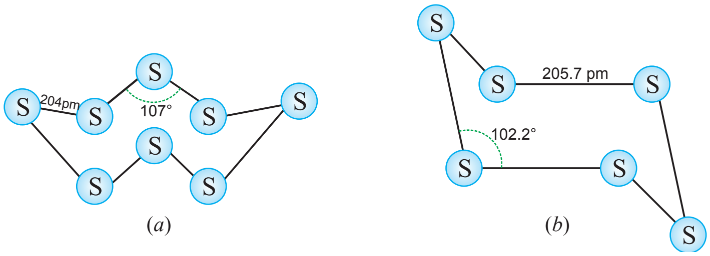


Fig. 7.3: The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

8. Sulphur Dioxide (SO_2)

Preparation of SO_2: Sulphur dioxide is formed together with a little (6–8%) sulphur trioxide when sulphur is burnt in air or oxygen.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

In the laboratory, it is prepared by treating a sulphite with dilute sulphuric acid.

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

Industrially, it is obtained as a by-product of roasting of sulphide ores.

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

Properties of Sulphur Dioxide:

Sulphur dioxide is colourless gas with pungent smell and is highly soluble in water. Its aqueous solution is acidic and turns blue litmus red. It reacts readily with sodium hydroxide solution to form sodium sulphite and sodium hydrogen sulphite.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

Sulphur dioxide reacts with chlorine in the presence of charcoal as a catalyst to form sulphuryl chloride. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium pentaoxide catalyst.

$$SO_2(g) + Cl_2(g) \xrightarrow{\text{Charcoal}} SO_2Cl_2(l)$$

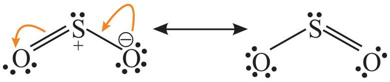
$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

In the presence of moisture, it liberates nascent hydrogen and thus acts as reducing agent.

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

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

The molecule of SO_2 is angular.



Structure of SO_2

Uses: Sulphur dioxide is used

(*i*) in refining petroleum and sugar,

(*ii*) in the manufacture of sulphuric acid, calcium hydrogen sulphite and sodium metabisulphite,

(*iii*) as an anti-chlor, disinfectant and preservative,

(*iv*) in bleaching wool and silk.

Group 17

(A) General Information

1. **Name:** Halogen family
2. **Elements:** $_{9}F$, $_{17}Cl$, $_{35}Br$, $_{53}I$, $_{85}At$, $_{117}Ts$

3. **Electronic Configuration:** ${}_{9}F = [He]\ 2s^2\ 2p^5$; ${}_{17}Cl = [Ne]\ 3s^2\ 3p^5$; ${}_{35}Br = [Ar]\ 3d^{10}\ 4s^2\ 4p^5$; ${}_{53}I = [Kr]\ 4d^{10}\ 5s^2\ 5p^5$; ${}_{85}At = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$; ${}_{117}Ts = [Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$.

(B) Atomic and Physical Properties

1. **Atomic Radii:** Halogens are the smallest in their respective periods due to increase in nuclear charge. Down the group, their size increases regularly due to addition of a new shell.
2. **Oxidation States:** All the halogens show –1 oxidation state. Because of highest electronegativity, fluorine shows an oxidation state of –1 only. Other elements also show oxidation states of +1, +3, +5 and +7, because of the different excitations possible due to empty *d*-orbitals.
3. **Ionisation Enthalpy:** This is higher than the corresponding members of Group 16 because of increase in nuclear charge. They are so high that these elements have little tendency to lose electrons. Down the group, the IE decreases so that I can lose electrons to form I^+.
4. **Electron Gain Enthalpy:** Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small orbitals of fluorine and thus, the incoming electron does not experience much attraction.
5. **Metallic Nature**: The elements are non-metals because of very high ionisation enthalpies. The element, I, shows some metallic character (lustre, etc.) as it can form I^+ by loss of electron.
6. **Electronegativity:** These are the most electronegative elements in their respective periods. Down the group electronegativity decreases. Thus, fluorine is the most electronegative element in the periodic table.
7. **Melting Points and Boiling Points:** Increase regularly down the group because of increase in size and nuclear charge resulting in greater van der Waals' forces of attraction. Thus, F_2 and Cl_2 are gases, Br_2 is a liquid while I_2 is a solid.
8. **Colour:** All halogens are coloured. This is due to the absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level while the remaining light is transmitted. The colour of the halogen is the colour of the transmitted light. The amount of energy required for the excitation decreases progressively from fluorine to iodine as the size of the atom increases. The energy of the transmitted light therefore goes on increasing from fluorine to iodine. For example, fluorine absorbs violet light and hence appears pale yellow while iodine absorbs yellow and green light and hence appears deep violet.
9. **Bond Dissociation Enthalpy:** Bond dissociation enthalpy decreases from Cl_2 to I_2. This is due to increase in the size of halogen atom on moving down the group from chlorine to iodine. Bond dissociation enthalpy of fluorine is smaller than chlorine or bromine. This is due to small size of fluorine which results large electron–electron repulsion among the lone pairs in F_2 molecule. Thus, the bond dissociation enthalpy decreases in the order $Cl_2 > Br_2 > F_2 > I_2$.

(C) Chemical Properties

All halogens are highly reactive. This is due to their low bond dissociation enthalpy and high negative electron gain enthalpy values. The reactivity of halogen decreases down the group. Fluorine is the strongest oxidising halogen. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \qquad (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \qquad (X = Br \text{ or } I)$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hypohalic and hypohalous acids. I^- ion is oxidised by oxygen in acidic medium to iodine.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq) \qquad (X = Cl \text{ or } Br)$$

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(l)$$

Anomalous behaviour of fluorine:

The anomalous behaviour of fluorine is due to its small size, low F–F bond dissociation enthalpy, highest electronegativity and absence of *d*-orbitals in valence shell.

Most of the reactions of fluorine are exothermic. This is due to its small size and strong bond formed by it with other elements.

1. **Hydrides:** All elements of Group 17 form hydrides of the type HX (X = F, Cl, Br, I). The reactivity of halogen towards hydrogen decreases from fluorine to iodine.
   - (*i*) **Physical state:** Except HF which is a liquid due to H-bonding, all are gases.
   - (*ii*) **Thermal stability:** It decreases down the group because of decrease in bond dissociation enthalpy.
   - (*iii*) **Reducing character:** It increases from HF to HI because of decrease of stability.
   - (*iv*) **Acidic strength:** HF < HCl < HBr < HI. This is because bond dissociation enthalpies are in the order HF > HCl > HBr > HI.
2. **Halides:** Halogens react with metals to form metal halides. For example,

$$Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$$

Halides of metals.

(*i*) With a particular metal, ionic character is

M–F > M–Cl > M–Br > M–I.

(*ii*) With metals of low IE, halides are all ionic.

(*iii*) With metals of high IE, halides are covalent.

(*iv*) With metals showing more than one oxidation states, halides in higher oxidation state are more covalent i.e., $SnCl_4$ and $PbCl_4$ are more covalent than $SnCl_2$ and $PbCl_2$ respectively.

3. **Oxides:** Halogens form many binary compounds with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. They are called fluorine oxides because fluorine is more electronegative than oxygen. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used to remove plutonium as PuF_6 from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which oxidation states of halogens range from +1 to +7. The higher oxides of halogens tend to be more stable than the lower ones. The stability of the oxides of halogen decreases in the order, I > Cl > Br. This is because iodine–oxygen bond is stable due to greater polarity of iodine–oxygen bond. The stability of chlorine–oxygen bond is due to multiple bond formation involving *d*-orbitals of the chlorine atoms. Bromine being in between lacks both of these characteristics.

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides. They are very powerful oxidising agents. The iodine oxides, I_2O_4, I_2O_5 and I_2O_7 are insoluble solids. I_2O_5 is a very good oxidising agent and is used in estimation of carbon monoxide.

4. **Oxo-acids:** Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as hypofluorous acid. The other halogens form acid of the type HOX—hypohalous acid, HOXO—halous acid, $HOXO_2$—halic acid and $HOXO_3$—perhalic acid.

Table 7.4: Oxoacids of Halogens

F	Cl	Br	I
HOF	HOCl	HOBr	HOI
—	HOClO	—	—
—	$HOClO_2$	$HOBrO_2$	$HOIO_2$
—	$HOClO_3$	$HOBrO_3$	$HOIO_3$

The acidic strength of oxo-acids of different halogens having same oxidation state decreases in the order:

HClO > HBrO > HIO

This is because electronegativity follows the order, Cl > Br > I.

Acidic strength of oxo-acids containing the same halogen are in the order:

$$HClO < HClO_2 < HClO_3 < HClO_4$$

This is because in solution, ClO_4^- is the most stable due to dispersal of –ve charge on four O-atoms.

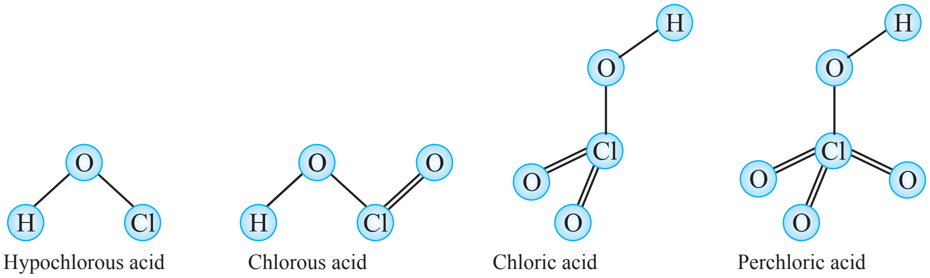


Fig. 7.4: Structures of oxoacids of chlorine

5. **Interhalogen Compounds:** Halogens combine amongst themselves to form a number of compounds known as interhalogen compounds. They can be assigned general composition as XX′, XX'_3, XX'_5, and XX'_7 where X is halogen of larger size and X′ of smaller size and X is more electropositive than X′.

$$\underset{\text{(Equal volumes)}}{Cl_2 + F_2} \xrightarrow{437\text{ K}} 2ClF; \qquad Cl_2 + \underset{\text{(Excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3$$

$$\underset{\text{(Equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl; \qquad I_2 + \underset{\text{(Excess)}}{3Cl_2} \longrightarrow 2ICl_3$$

$$\underset{\text{(Diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3; \qquad Br_2 + \underset{\text{(Excess)}}{5F_2} \longrightarrow 2BrF_5$$

Properties: All interhalogen compounds are covalent compounds and are diamagnetic in nature. In general, interhalogen compounds are more reactive than halogens (except F_2). This is because X–X′ bond in interhalogens is weaker than X–X bond in halogens except F–F bond. All of these compounds undergo hydrolysis.

$$XX' + H_2O \longrightarrow HX' + HOX$$

The molecular structures of interhalogen compounds can be explained on the basis of VSEPR theory. The XX'_3 compounds have bent ‘T’ shape, XX'_5 compounds have square pyramidal and IF_7 has pentagonal bipyramidal structures.

Uses:

Interhalogen compounds can be used as non-aqueous solvents. They are very useful fluorinating agents. ClF_3 and and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

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

6. **Chlorine (Cl_2)**

Preparation of Cl_2: Chlorine can be prepared by heating concentrated hydrochloric acid with an oxidising agent such as manganese dioxide, potassium permanganate.

$$MnO_2 + \underset{\text{(conc.)}}{4HCl} \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In laboratory, it is prepared by heating a mixture of sodium chloride, manganese dioxide and concentrated H_2SO_4.

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

Manufacture of Chlorine:

(*i*) **Deacon’s process:** In this process, hydrogen chloride gas is oxidised by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

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

(*ii*) **Electrolytic process:** Chlorine is obtained by the electrolysis of brine. Reactions involved in the process are:

At cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$; $Na^+ + OH^- \longrightarrow NaOH$

At anode: $Cl^- \longrightarrow Cl + e^-$; $Cl + Cl \longrightarrow Cl_2$

Overall reaction: $2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + Cl_2(g) + H_2$

Properties of Chlorine:

Chlorine is a greenish-yellow gas with pungent and suffocating odour. It is about 2.5 times heavier than air. It is soluble in water.

Chlorine reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$; $2Na + Cl_2 \longrightarrow 2NaCl$

$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$; $S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$; $H_2 + Cl_2 \longrightarrow 2HCl$

It reacts with compounds containing hydrogen to form HCl.

$H_2S + Cl_2 \longrightarrow 2HCl + S$; $C_{10}H_{16} + 8Cl_2 \longrightarrow 16HCl + 10C$

$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow \underset{\text{(explosive)}}{NCl_3} + 3HCl$; $\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

With cold and dilute alkalies, chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies, it gives chloride and chlorate.

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

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

With dry slaked lime, it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$. Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. HOCl so formed gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl; \quad HOCl \longrightarrow HCl + \underset{\text{Nascent oxygen}}{[O]}$$

It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10HCl$$

It is a powerful bleaching agent and the bleaching action is due to oxidation.

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

Coloured substance + O $\longrightarrow$ Colourless substance

Uses of Chlorine: Chlorine is used

(*i*) for bleaching cotton and textiles.

(*ii*) in sterilising drinking water.

(*iii*) in the extraction of gold and platinum.

(*iv*) in the manufacture of dyes, drugs and organic compounds such as $CHCl_3$, CCl_4, DDT, refrigerants, etc.

7. **Hydrogen Chloride (HCl)**

Preparation of HCl: In laboratory, it is prepared by heating sodium chloride with concentrated H_2SO_4.

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

$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing through concentrated H_2SO_4.

Properties of Hydrogen Chloride: It is a colourless and pungent smelling gas. It is extremely soluble in water.

➡ When three parts of conc. HCl and one part of conc. HNO_3 are mixed, aqua regia is formed, which is used for dissolving noble metals such as gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

➡ It reacts with NH_3 and gives white fumes of NH_4Cl.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

➡ It decomposes salts of weaker acids.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2\uparrow$$

Uses of Hydrogen Chloride: Hydrochloric acid is used

(*i*) in the manufacture of chlorine, glucose and NH_4Cl.

(*ii*) for extracting glue from bones and purifying bone black.

Group 18 (Noble Gases)

(A) General Information

1. **Names:** *Rare gases* – because they are present in very small amounts in the air.
   Inert gases – old name when they were considered to be chemically unreactive (inert).
   Noble gases – this name is preferred because they do react to form compounds though to a small extent.
2. **Elements:** He, Ne, Ar, Kr, Xe, Rn and Og.
3. **Electronic Configuration:** Outer shell configuration is $ns^2\ np^6$ (except He having $1s^2$).

(B) Atomic and Physical Properties

1. **Atomic Radii:** Atomic radii increase down the group with increase in atomic number.
2. **Ionisation Enthalpy:** They have the highest IEs in their respective periods because of fully-filled orbitals and hence greatest stability. Down the group, it decreases due to increase in atomic size.
3. **Electron Gain Enthalpy:** Since noble gases have stable electronic configuration, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.
4. **Melting and Boiling Points:** They have low melting points and boiling points because of weak van der Waals' forces present between their atoms. Down the group, melting and boiling point increase because of increase in atomic size and hence increase of van der Waals' forces. Helium has the lowest boiling point (4.2 K) of any known substance.
5. **Liquefaction:** Because of weak van der Waals' forces present in them, it is difficult to liquefy them. Down the group, the ease of liquefaction increases because of increase of atomic size and hence increase of van der Waals' forces.

(C) Chemical Properties

In general, noble gases are the least reactive. Their inertness to chemical reactivity is due to following reasons:

(*i*) The noble gases except helium have completely filled ns^2np^6 electronic configuration in their valence shell.

(*ii*) They have high ionisation enthalpy and more positive electron gain enthalpy.

Chemistry of Compounds of Noble Gases: In 1962, Bartlett studied the following reaction:

$$O_2 + PtF_6 \longrightarrow \underset{\text{Dioxygenyl hexafluoro platinate}}{O_2^+[PtF_6]^-}$$

As IE of molecular oxygen was almost the same as that of xenon, the following reaction was also found to occur:

$$Xe + PtF_6 \xrightarrow{298\text{ K}} Xe^+[PtF_6]^-$$

Preparation of Xenon Fluorides: Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

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

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

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

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143 K.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

Xenon fluorides are readily hydrolysed even by traces of water.

$$2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$$

Xenon fluorides react with fluoride ion acceptor to form cationic species and fluoride ion donors to form fluoro anions.

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

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

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^- \qquad [M = Na, K, Rb, Cs]$$

Xenon–Oxygen Compounds: Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

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

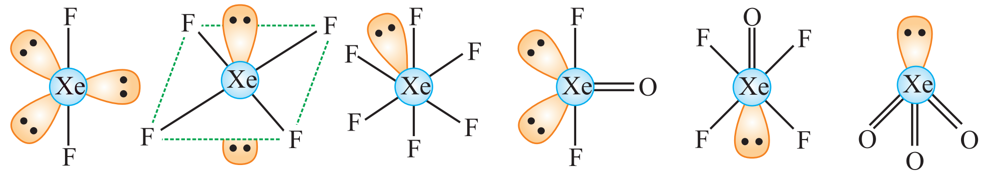
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \longrightarrow \underset{\substack{\text{Xenon}\\\text{oxytetrafluoride}}}{XeOF_4} + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow \underset{\substack{\text{Xenon}\\\text{dioxydifluoride}}}{XeO_2F_2} + 4HF$$

Structures of Xenon Compounds: The shapes of xenon fluoride and oxyfluorides can be explained on the basis of hybridisation and these are shown in figure given below.



$XeF_2(sp^3d)$ Linear

$XeF_4(sp^3d^2)$ Square Planar

$XeF_6(sp^3d^3)$ Distorted Octahedral

$XeOF_2(sp^3d)$ T-shaped

$XeOF_4(sp^3d^2)$ Square Pyramidal

$XeO_3(sp^3)$ Trigonal Pyramidal

Fig. 7.5: Structures of some xenon compounds

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Why are pentahalides of P, As, Sb and Bi more covalent than their trihalides?

Ans. Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.

As, in pentahalides, the central atom is in +5 oxidation state while in trihalides it is in +3 oxidation state. Therefore, pentahalides are more covalent than trihalides.

Q. 2. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements?

Ans. This is because BiH_3 is the least stable among the hydrides of Group 15.

Q. 3. Why is N_2 less reactive at room temperature?

Ans. N_2 is less reactive at room temperature because of strong $p\pi - p\pi$ overlap resulting into the triple bond ($N \equiv N$), consequently high bond enthalpy.

Q. 4. Mention the conditions to maximise the yield of ammonia.

Ans. Ammonia is prepared by the Haber's process.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{Iron oxide} + K_2O + Al_2O_3\ (\text{catalyst})]{700\ \text{K},\ 200 \times 10^5\ \text{Pa}} 2NH_3(g);\quad \Delta_f H^\circ = -92.2\ \text{kJ mol}^{-1}$$

In accordance with Le Chatelier's principle, a high pressure of 200×10^5 Pa, low temperature (optimum temperature of ~ 700 K) along with catalyst iron oxide with small amounts of K_2O and Al_2O_3 are used to maximise the yield of ammonia.

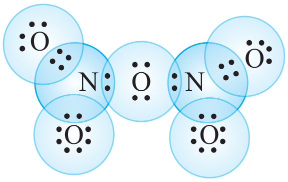
Q. 5. How does ammonia react with a solution of Cu^{2+}?

Ans. Ammonia reacts with a solution of Cu^{2+} by donating a lone pair of electron.

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

Q. 6. What is the covalence of nitrogen in N_2O_5?

Ans. Covalency depends upon the number of shared pair of electrons. In N_2O_5 each nitrogen atom has four shared pairs of electrons as shown below:

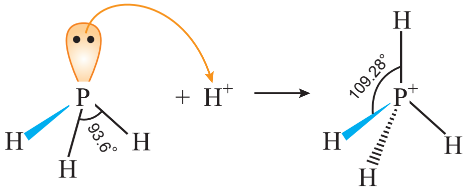


Therefore, the covalency of N in N_2O_5 is 4.

Q. 7. (*a*) Bond angle in PH_4^+ is higher than in PH_3. Why?

(*b*) What is formed when PH_3 reacts with an acid?

Ans. (*a*) Both are sp^3 hybridised. In PH_4^+ all the four orbitals are bonded whereas in PH_3 there is a lone pair of electrons on P, which is responsible for lone pair–bond pair repulsion in PH_3, reducing the bond angle to less than 109°28′.



PH_3 molecule (Pyramidal)

PH_4^+ ion (Tetrahedral)

(*b*) PH_3 reacts with acids like HI to form PH_4I.

Q. 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 (PH_3).

$$\underset{\text{Phosphorus}}{P_4} + 3NaOH + 3H_2O \xrightarrow[CO_2\ \text{atmosphere}]{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

Q. 9. What happens when PCl_5 is heated?

Ans. PCl_5 has three equatorial (202 pm) and two axial (240 pm) bonds. Since axial bonds are weaker than equatorial bonds, therefore, when PCl_5 is heated, the less stable axial bonds break to form PCl_3.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2.$$

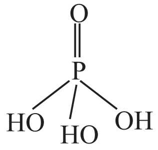
Q. 10. Write a balanced equation for the reaction of PCl_5 with water.

Ans. It reacts with heavy water to form phosphorus oxychloride $POCl_3$ and deuterium chloride (DCl).

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

Q. 11. What is the basicity of H_3PO_4?

Ans.



Three P—OH groups are present in the molecule of H_3PO_4. Therefore, its basicity is three.

Q. 12. What happens when H_3PO_3 is heated?

Ans. Orthophosphorous acid on heating disproportionates to give orthophosphoric acid and phosphine.

$$\underset{\substack{\text{Orthophosphorous}\\\text{acid}}}{4H_3PO_3} \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\substack{\text{Orthophosphoric}\\\text{acid}}}{3H_3PO_4}$$

Q. 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 $MgSO_4.7H_2O$, etc.

Sulphides: Galena PbS, zinc blende ZnS, copper pyrite $CuFeS_2$.

Traces of sulphur occur as H_2S in volcanoes. Organic materials such as eggs, garlic, onion, mustard, hair and wool also contain sulphur.

Q. 14. Write the order of thermal stability of the hydrides of Group 16 elements.

Or

Arrange the following hydrides of group 16 element in the increasing order of their thermal stability

H_2O, H_2S, H_2Po, H_2Se, H_2Te *[CBSE (F) 2017]*

Ans. Since the size of the element increases down the group, the E—H bond dissociation enthalpy decreases and hence E—H bond breaks more easily. Therefore, the thermal stability of the hydrides of group 16 elements decreases down the group.

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

Q. 15. Why is H_2O a liquid and H_2S a gas?

Ans. Due to small size and high electronegativity of oxygen, molecules of water are associated through hydrogen bonding, resulting in its liquid state. On the other hand, H_2S molecules are not associated through H-bonding. Hence, it is a gas.

Q. 16. Which of the following does not react with oxygen directly?

Zn, Ti, Pt, Fe

Ans. Platinum is a noble metal. The sum of its first four ionisation enthalpies is very large. Hence, it does not react with oxygen directly. On the other hand, Zn, Ti and Fe are active metals and hence directly react with oxygen to form their respective oxides.

Q. 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*) $4Al + 3O_2 \xrightarrow{\text{Heat}} 2Al_2O_3$

Q. 18. Why does O_3 act as a powerful oxidising agent?

Ans. Due to the ease with which it liberates atoms of nascent oxygen, it acts as a powerful oxidising agent.

$$O_3 \longrightarrow O_2 + \underset{\text{(nascent oxygen)}}{O}$$

Q. 19. How is O_3 estimated quantitatively?

Ans. When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating ozone gas.

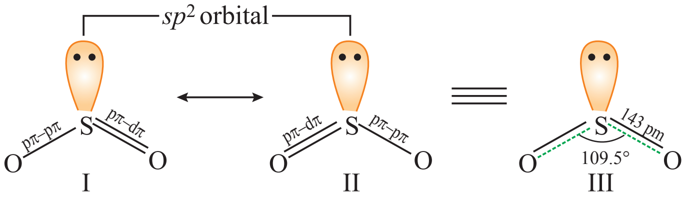
Q. 20. What happens when sulphur dioxide is passed through an aqueous solution of Fe (III) salt?
[CBSE Delhi 2019 (56/2/1)]

Ans. SO_2 acts as a reducing agent and hence reduces an aqueous solution of Fe (III) salt to Fe (II) salt.

$$\begin{array}{rcl} SO_2 + 2H_2O & \longrightarrow & SO_4^{2-} + 4H^+ + 2e^- \\ 2Fe^{3+} + 2e^- & \longrightarrow & 2Fe^{2+} \\ \hline 2Fe^{3+} + SO_2 + 2H_2O & \longrightarrow & 2Fe^{2+} + SO_4^{2-} + 4H^+ \\ \hline \end{array}$$

Q. 21. Comment upon the nature of two S—O bonds formed in SO_2 molecule. Are the two S—O bonds in this molecule equal?

Ans.



Resonating structures of SO_2

In SO_2, S is sp^2 hybridised. Two of the three sp^2 orbitals form two σ - bonds with oxygen atoms while the third contains the lone pair of electrons. Thus, S is now left with one half filled p orbital and one half filled d orbital. These orbitals form one $p\pi - p\pi$ and one $p\pi - d\pi$ double bond with oxygen atom. Due to the resonance, the two S – O bonds are equal (bond length = 143 pm).

Q. 22. How is the presence of SO_2 detected?

Ans. SO_2 is a pungent smelling gas. It can be detected by the following two tests:

(*i*) SO_2 turns acidified $K_2Cr_2O_7$ green due to reduction of $Cr_2O_7^{2-}$ to Cr^{3+} ions.

$$\begin{array}{rcl} SO_2 + 2H_2O & \longrightarrow & SO_4^{2-} + 4H^+ + 2e^-] \times 3 \\ Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ \hline \underset{\text{(orange)}}{Cr_2O_7^{2-}} + 3SO_2 + 2H^+ & \longrightarrow & \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O \end{array}$$

(*ii*) SO_2 turns the pink violet colour of $KMnO_4$ colourless due to reduction of MnO_4^- to Mn^{2+} ions.

$$\begin{array}{rcl} SO_2 + 2H_2O & \longrightarrow & SO_4^{2-} + 4H^+ + 2e^-] \times 5 \\ MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ \hline \underset{\text{(pink violet)}}{2MnO_4^-} + 5SO_2 + 2H_2O & \longrightarrow & \underset{\text{(colourless)}}{2Mn^{2+}} + 5SO_4^{2-} + 4H^+ \end{array}$$

Q. 23. Mention three areas in which H_2SO_4 plays an important role.

Ans. (*i*) H_2SO_4 is used in the manufacture of fertilisers, *e.g.*, ammonium sulphate, superphosphate.

(*ii*) It is used in storage batteries.

(*iii*) It is used in detergent industry.

Q. 24. Write the conditions to maximise the yield of H_2SO_4 by contact process.

Ans. The key step in the manufacture of H_2SO_4 by contact process is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta_r H^\circ = -196.6 \text{ kJ mol}^{-1}$$

The forward reaction is exothermic and proceed with decrease in number of moles. Therefore, low temperature (optimum temperature 720 K), high pressure (in practice 2 bar) and use of catalyst V_2O_5 to increase the rate of reaction at low temperature are the favourable conditions for maximum yield of H_2SO_4.

Q. 25. Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

Ans. $$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

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

H_2SO_4 is a very strong acid in water mainly because its first ionisation to H_3O^+ and HSO_4^- is large. The ionisation HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. This explains why $K_{a_2} << K_{a_1}$.

Q. 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. [*CBSE Sample Paper 2016*]

Ans. The electrode potential depends upon the parameters indicated below:

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\Delta_{\text{diss}}H^+} X(g) \xrightarrow{\Delta_{eg}H^-} X^-(g) \xrightarrow{\Delta_{\text{hyd}}H^-} X^-(aq)$$

(Values in kJ mol^{-1})	$\Delta_{\text{diss}}H$	$\Delta_{\text{eg}}H$	$\Delta_{\text{hyd}}H$
Fluorine	158.8	– 333	515
Chlorine	242.6	– 349	381

The two factors, high hydration enthalpy of F^- ion (515 kJ mol^{-1}) and low F—F bond dissociation enthalpy compensate more than the less negative electron gain enthalpy of fluorine. Due to this, electrode potential of F_2 (+ 2.87 V) is much higher than that of Cl_2 (+1.36 V) and hence F_2 is a stronger oxidising agent than Cl_2.

Q. 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 enthalpy, and (*iv*) non-availability of *d*-orbitals in its valence shell.

The two examples are:

(*i*) Fluorine forms only one oxo-acid while other halogens form a number of oxo-acids.

(*ii*) HF is a liquid due to strong H-bonding while other hydrogen halides are gases.

Q. 28. Sea is the greatest source of halogens. Comment.

Ans. Sea water contains chlorides, bromides and iodides of Na, K, Mg and Ca, but mainly sodium chloride solution (2.5% by mass). Certain forms of marine life contain iodine in their systems. For example, seaweeds contain up to 0.5% of iodine as sodium iodide.

Q. 29. Give the reason for bleaching action of Cl_2.

Ans. In 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 vegetable and organic matter to colourless substances.

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

Thus, the bleaching action of Cl_2 is due to oxidation.

Q. 30. Name two poisonous gases which can be prepared from chlorine gas. [*CBSE Delhi 2019 (56/2/1)*]

Ans. Two poisonous gases which can be prepared from chlorine gas are:

(*i*) Phosgene gas ($COCl_2$)

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

Q. 31. Why is ICl more reactive than I_2?

Ans. ICl is more reactive than I_2 because I—Cl bond is weaker than I—I bond. Consequently, ICl breaks easily to form halogen atoms which readily bring about the reactions.

Q. 32. Why is helium used in diving apparatus?

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

Q. 33. Balance the following equation:

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

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

Q. 34. Why has it been difficult to study the chemistry of radon?

Ans. Radon is radioactive with very short half-life (3.82 days) which makes the study of chemistry of radon difficult.

NCERT Textbook Exercises

Q. 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:** The valence shell electronic configuration of these elements is ns^2np^3. The *s*-orbital in these elements is completely filled and *p*-orbitals are half-filled, making their electronic configuration extra stable.

Oxidation state: The common oxidation states of these elements are –3, +3, and +5. The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. In fact, last member of the group, bismuth hardly forms any compound in –3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi(V) compound is BiF_5. The stability of +5 oxidation state decreases and that of +3 oxidation state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxo-acids.

Atomic size: Covalent and ionic (in a particular state) radii increase down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled *d* and/or *f* orbitals in heavier members.

Ionisation enthalpy: IE decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled *p*-orbitals electronic configuration and smaller size, the ionisation enthalpy of the Group 15 elements is much greater than that of Group 14 elements in the corresponding periods. The order of successive ionisation enthalpies as expected is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$.

Electronegativity: The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that pronounced.

Q. 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 enthalpy is large (941.4 kJ mol^{-1}). Thus, nitrogen is inert and unreactive in its elemental state.

In contrast, white or yellow phosphorus exists as a tetraatomic molecule P_4. Since the P–P single bond is much weaker (213 kJ mol^{-1}) than N≡N triple bond (941.4 kJ mol^{-1}), therefore, phosphorus is much more reactive than nitrogen.

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

Ans. Refer to Basic Concepts Point C (Group 15).

Q. 4. Why does NH_3 form hydrogen bonds but PH_3 does not?

Ans. The electronegativity of N (3.0) is much higher than that of H (2.1). Due to this, N–H bond is quite polar and hence NH_3 undergoes intermolecular H-bonding.

On the other hand, both P and H have an electronegativity of 2.1. Therefore, P–H bond is not polar and hence PH_3 does not undergo H-bonding.

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

Ans. Nitrogen is prepared in the laboratory by heating an equimolar aqueous solution of ammonium chloride with sodium nitrite. The ammonium nitrite formed as a result of double displacement reaction, being unstable decompose to form dinitrogen gas.

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow NH_4NO_2(aq) + NaCl(aq)$$

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2(aq)} \xrightarrow{\text{Heat}} \underset{\text{Dinitrogen}}{N_2(g)} + 2H_2O(l)$$

Q. 6. How is ammonia manufactured industrially?

Ans. Refer to Basic Concepts Point (C) 6 (Group 15).

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

Ans. On heating with dil. HNO_3, copper gives copper nitrate and nitric oxide.

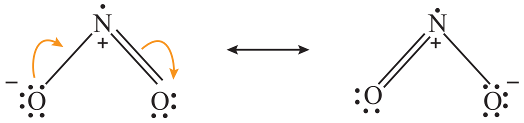
$$3Cu + 8HNO_3(\text{dil.}) \xrightarrow{\text{Heat}} 3Cu(NO_3)_2 + 4H_2O + 2NO$$

With concentrated HNO_3, instead of NO, NO_2 is evolved.

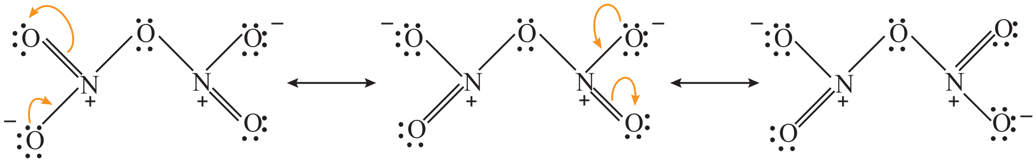
$$Cu + 4HNO_3(\text{conc.}) \xrightarrow{\text{Heat}} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Q. 8. Give the resonating structures of NO_2 and N_2O_5.

Ans. Resonating structures of NO_2 are:



Resonating structures of N_2O_5 are:



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

[**Hint:** Can be explained on the basis of sp^3 hybridisation in NH_3 and only *s–p* bonding between hydrogen and other elements of the group].

Ans. As we move from N to P to As to Sb, the electronegativity of the central atom goes on decreasing. Bond pairs of electrons, lie much away from the central atom. In other words, force of repulsion between the adjacent bond pairs goes on decreasing and hence the bond angles keep on decreasing from NH_3 to SbH_3.

Q. 10. Why does $R_3P{=}O$ exist but $R_3N{=}O$ does not (R = alkyl group)?

Ans. N due to the absence of *d*-orbitals, cannot form $p\pi - d\pi$ multiple bonds. Thus, N cannot expand its covalency beyond four but in $R_3N{=}O$, N has a covalency of 5. So, the compound $R_3N{=}O$ does not exist. On the other hand, P due to the presence of *d*-orbitals forms $p\pi - d\pi$ multiple bonds and hence can expand its covalency beyond 4. Therefore, P forms $R_3P{=}O$ in which the covalency of P is 5.

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

Ans. Since the atomic size of N (70 pm) is much smaller than that of Bi (148 pm), electron density on the N-atom is much higher than that on Bi-atom. As a result, the tendency of N in NH_3 to donate its lone pair of electrons is much higher than that of Bi in BiH_3. Thus, NH_3 is much more basic than BiH_3.

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

Ans. Nitrogen because of its small size and high electronegativity forms $p\pi - p\pi$ multiple bonds. Thus, it exists as a diatomic molecule having a triple bond between the two N-atoms. Phosphorus due to its larger size and lower electronegativity usually does not form $p\pi - p\pi$ multiple bonds with itself. Instead it prefers to form P–P single bonds and hence it exists as tetrahedral P_4 molecules.

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

Ans. Refer to Basic Concepts Point 8 (Group 15).

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

Ans. The property of catenation depends upon the E—E bond strength of the element. Since the N—N (159 kJ mol^{-1}) bond strength is much weaker than P—P (213 kJ mol^{-1}) bond strength, hence, nitrogen shows less catenation properties than phosphorus.

Q. 15. Give the disproportionation reaction of H_3PO_3.

Ans. H_3PO_3, on heating, disproportionates to give PH_3 in which P is reduced and H_3PO_3 in which P is oxidised.

$$\underset{\text{Phosphorous acid}}{4H_3\overset{+3}{P}O_3} \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{\overset{-3}{P}H_3} + \underset{\text{Orthophosphoric acid}}{3H_3\overset{+4}{P}O_4}$$

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

Ans. The oxidation state of P in PCl_5 is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating 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. So, PCl_5 acts as an oxidising agent. For example, it oxidises Ag to AgCl and Sn to $SnCl_4$.

Q. 17. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

Ans. (*i*) **Electronic configuration:**

$_{8}O = [He]\ 2s^2\ 2p^4$;

$_{16}S = [Ne]\ 3s^2\ 3p^4$;

$_{34}Se = [Ar]\ 3d^{10}\ 4s^2\ 4p^4$

$_{52}Te = [Kr]\ 4d^{10}\ 5s^2\ 5p^4$ and $_{84}Po = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$

All these elements have same (ns^2np^4) valence shell electronic configuration and hence are justified to be placed in Group 16 of the periodic table.

(*ii*) **Oxidation states:** They need two more electrons to form dinegative ions to acquire the nearest noble gas configuration. So, the minimum oxidation state of these elements should be –2. Oxygen predominantly and sulphur to some extent being electronegative show an oxidation state of –2. Since these elements have six electrons in the valence shell, therefore, at the maximum they can show an oxidation state of +6. Other positive oxidation states shown by these elements are +2 and +4. Although, oxygen due to the absence of *d*-orbitals does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group, *i.e.*, Group 16 of the periodic table.

(*iii*) **Formation of hydrides:** All the elements complete their respective octets by sharing two of their valence electrons with 1s-orbital of hydrogen to form hydrides of the general formula EH_2, *i.e.*, H_2O, H_2S, H_2Se, H_2Te and H_2Po. Therefore, on the basis of formation of hydrides of the general formula, EH_2, these elements are justified to be placed in Group 16 of the periodic table.

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

Ans. Because of its small size, oxygen is capable of forming pπ – pπ bond and exists as diatomic O_2 molecule. The intermolecular forces in oxygen are weak van der Waals force, due to which it is a gas at room temperature. On the other hand, sulphur, due to its larger size prefers to form S–S single bond and exist as octaatomic S_8 molecule having puckered ring structure. Because of larger size the force of attraction holding the S_8 molecules together are much stronger. Hence sulphur is a solid at room temperature.

Q. 19. Knowing the electron gain enthalpy values of $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-? **[*HOTS*]**

[**Hint:** Consider lattice energy factor in the formation of compounds.]

Ans. Let us 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 $\Delta_{eg} H_2$ is much higher than $\Delta_{eg} H_1$ yet the lattice energy of the formation of MO(*s*) due to higher charges is much more than that of $M_2O(s)$. Thus, formation of MO is energetically more favourable than M_2O. Due to this, oxygen forms a large number of oxides having the O^{2-} species and not O^-.

Q. 20. Which aerosols deplete ozone?

Ans. Aerosols such as chlorofluorocarbons (CFCs), *i.e.*, freon (CCl_2F_2) depletes the O_3 layer by supplying Cl free radicals which convert O_3 to O_2 as shown below:

$$\underset{\text{Freon}}{Cl_2CF_2(g)} \longrightarrow \bullet Cl(g) + \bullet CClF_2(g)$$

$$\bullet Cl(g) + O_3(g) \longrightarrow ClO\bullet(g) + O_2(g)$$

$$ClO\bullet(g) + \bullet O(g) \longrightarrow \bullet Cl(g) + O_2(g)$$

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

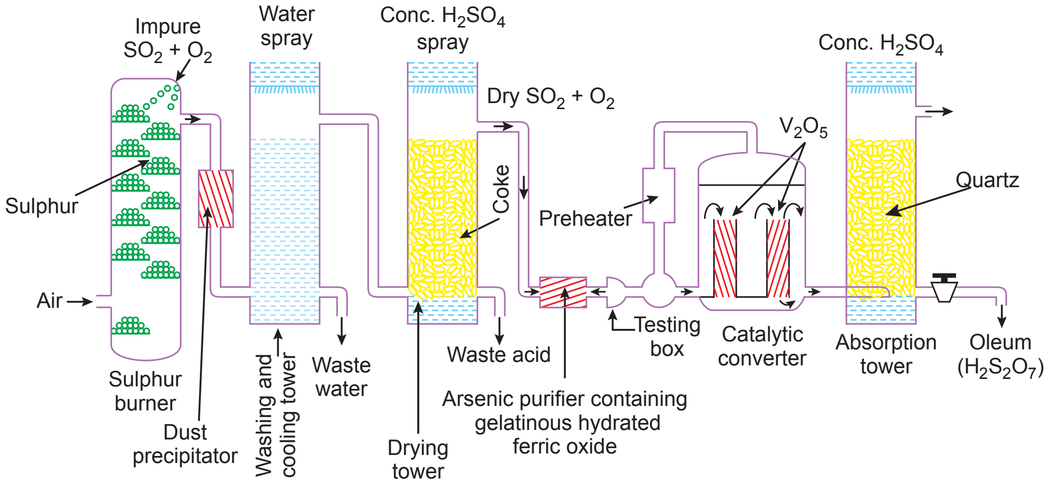
Ans. Sulphuric acid is manufactured by the contact process which involves three steps:

(*i*) Burning of sulphur or sulphide ores in air to produce SO_2.

(*ii*) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(*iii*) Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$).

A flow diagram for the manufacture of sulphuric acid is shown in figure given below. The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.



Flow diagram for the manufacture of sulphuric acid

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g); \ \Delta_r H° = -196.6 \text{ kJ mol}^{-1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise the rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives H_2SO_4 of the desired concentration.

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

The sulphuric acid obtained by contact process is 96-98% pure.

Q. 22. How is SO_2 an air pollutant?

Ans. (*i*) SO_2 dissolves in moisture present in air to form H_2SO_3 which damages building materials especially marble.

$$CaCO_3 + H_2SO_3 \longrightarrow CaSO_3 + H_2O + CO_2$$

(*ii*) Even at a low concentration of 0.03 ppm, SO_2 has a damaging effect on plants. If exposed for a long time, it slows down the formation of chlorophyll resulting in injury to the leaves including loss of green colour. This is called **chlorosis**.

(*iii*) SO_2 is strongly irritating to the respiratory tract. SO_2 at a concentration of 5 ppm causes throat and eye irritation resulting in cough, tears and redness in eyes. It causes breathlessness and affects voice box.

Q. 23. Why are halogens strong oxidising agents?

Ans. Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.

$$X + e^- \longrightarrow X^-$$

Thus, halogens act as strong oxidising agents. Their oxidising power, however, decreases from F_2 to I_2.

Q. 24. Explain why fluorine forms only one oxo acid, HOF.

Ans. Due to high electronegativity, small size and absence of *d*-orbitals, F does not form oxo-acids such as HOFO, $HOFO_2$ and $HOFO_3$ in which the oxidation state of F would be +3, +5 and +7. It just forms one oxo-acid, *i.e.*, HOF in which the oxidation state of F is +1.

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

Ans. Although N and Cl have about the same electronegativity, yet their atomic size (covalent radii) are much different: N = 70 pm and Cl = 99 pm. Thus, electron density per unit volume on nitrogen atom is much higher than that on chlorine atom. Hence, nitrogen forms hydrogen bonds while chlorine does not though both have nearly the same electronegativity.

Q. 26. Write two uses of ClO_2.

Ans. (*a*) ClO_2 is a powerful oxidising agent and chlorinating agent. It is used for bleaching wood pulp and cellulose and for purifying drinking water.

(*b*) It is an excellent bleaching agent. Its bleaching power is about 30 times higher than that of Cl_2 and is used for bleaching flour to make white bread.

Q. 27. Why are halogens coloured?

Ans. All halogens are coloured. This is due to absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level while the remaining light is transmitted. The colour of the halogen is the colour of transmitted light.

Q. 28. Write the reactions of F_2 and Cl_2 with water.

Ans. F_2 being a strong oxidising agent oxidises H_2O to O_2 or O_3

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$3F_2(g) + 3H_2O(l) \longrightarrow 6H^+(aq) + 6F^-(aq) + O_3(g)$$

Cl_2 reacts with H_2O to form hydrochloric acid and hypochlorous acid.

$$Cl_2(g) + H_2O(l) \longrightarrow \underset{\text{Hydrochloric acid}}{HCl(aq)} + \underset{\text{Hypochlorous acid}}{HOCl(aq)}$$

Q. 29. How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only. ***[CBSE 2019 (56/4/1)]***

Ans. HCl can be oxidised to Cl_2 by a number of oxidising agents like MnO_2, $KMnO_4$.

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

Cl_2 can be reduced to HCl by reacting with H_2 in the presence of diffused sunlight.

$$H_2 + Cl_2 \xrightarrow{\text{Diffused sunlight}} 2HCl$$

Q. 30. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6? ***[CBSE Delhi 2013]***

Ans. Neil Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid, $O_2^+ PtF_6^-$

$$O_2(g) + PtF_6(g) \longrightarrow O_2^+[PtF_6]^-$$

Here, O_2 gets oxidised to O_2^+ by PtF_6.

Since the first ionisation enthalpy of Xe (1170 kJ mol^{-1}) is fairly close to that of O_2 molecules (1175 kJ mol^{-1}), Bartlett thought that PtF_6 should also oxidise Xe to Xe^+. This inspired Bartlett to carry out the reaction between Xe and PtF_6. When Xe and PtF_6 were mixed, a rapid reaction occurred and a red solid with the formula, $Xe^+[PtF_6]^-$ was obtained.

$$Xe + PtF_6 \xrightarrow{278\text{ K}} Xe^+[PtF_6]^-$$

Q. 31. What are the oxidation states of phosphorus in the following:

(*i*) H_3PO_3 **(*ii*) PCl_3**

(*iii*) Ca_3P_2 **(*iv*) Na_3PO_4** **(*v*) POF_3**

Ans. Let the oxidation state of P be *x*.

(*i*) $\overset{+1}{H_3}\overset{x}{P}\overset{-2}{O_3}$ $\quad\therefore\ 3(1)+x+3(-2)=0$ or $x=+3$

(*ii*) $\overset{x}{P}\overset{-1}{Cl_3}$ $\quad\therefore\ x+3(-1)=0$ or $x=+3$

(*iii*) $\overset{+2}{Ca_3}\overset{x}{P_2}$ $\quad\therefore\ 3(2)+2\times x=0$ or $x=-3$

(*iv*) $\overset{+1}{Na_3}\overset{x}{P}\overset{-2}{O_4}$ $\quad\therefore\ 3(1)+x+4(-2)=0$ or $x=+5$

(*v*) $\overset{x}{P}\overset{-2}{O}\overset{-1}{F_3}$ $\quad\therefore\ x+1(-2)+3(-1)=0$ or $x=+5$

Q. 32. Write balanced equations for the following:

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

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

Ans. (*i*) Cl_2 is produced.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\,] \times 4$$
$$4HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$\overline{\underline{4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O}}$$

(*ii*) Cl_2 being an oxidising agent oxidises NaI to I_2

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

Q. 33. How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

Ans. Refer to Basic Concepts Point C (Group 18).

Q. 34. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Ans. Replace O^- (9 electrons) in ClO^- by F (9 electrons). The resulting neutral molecule is ClF. Since ClF can combine further with F to form ClF_3 so, ClF is a Lewis base.

Q. 35. How are XeO_3 and $XeOF_4$ prepared?

Ans. Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

In contrast, partial hydrolysis of XeF_6 gives $XeOF_4$.

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

Q. 36. Arrange the following in 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. ***[CBSE Delhi 2019 (56/2/1)]***

Ans. (*i*) $I_2 < F_2 < Br_2 < Cl_2$

Bond dissociation enthalpy decreases with increase in the size of the atom as we move from Cl to I. The low F—F bond dissociation enthalpy is due to the fact that F atom is very small in size and hence the three lone pair of electrons on each F atom repel the bond pair of F—F bond very strongly.

(*ii*) As the size of atom increases from F to I, the bond dissociation enthalpy of H—X bond decreases from H—F to H—I. Therefore, the acid strength increases in the opposite order:

$HF < HCl < HBr < HI$.

(*iii*) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

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

Q. 37. Which one of the following does not exist?

(*i*) $XeOF_4$

(*ii*) NeF_2

(*iii*) XeF_2

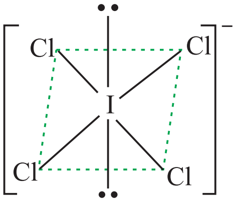
(*iv*) XeF_6

Ans. The sum of first and second ionisation enthalpies of Ne are much higher than those of Xe. Thus, F_2 can oxidise Xe to Xe^{2+} but cannot oxidise Ne to Ne^{2+}. In other words, NeF_2 does not exist and all the xenon fluorides (XeF_2 and XeF_6) and xenon oxyfluoride ($XeOF_4$) do exist.

Q. 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*) **Structure of ICl_4^-:** I in ICl_4^- has four bond pairs and two lone pairs of electrons. Therefore, according to VSEPR theory, it should be square planar.

ICl_4^- has $(7 + 1 \times 4 + 1) = 12$ valence electrons. A noble gas species having 12 valence electrons is XeF_4 ($8 + 1 \times 4 = 12$). Therefore, like ICl_4^-, XeF_4 is also square planar.

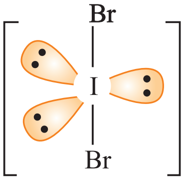


Square planar

(*ii*) **Structure of IBr_2^-:** I in IBr_2^- has two bond pairs and three lone pairs of electrons. So, according to VSEPR theory, it should be linear.

Here, IBr_2^- has 10($7 + 1 \times 2 + 1$) valence electrons. A noble gas species having 10 valence electrons is XeF_2 ($8 + 1 \times 2 = 10$).

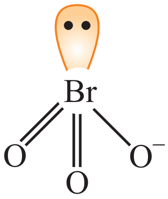
Thus, like IBr_2^-, XeF_2 is also linear.



Linear

(*iii*) **Structure of BrO_3^-:** The central atom Br has seven electrons. Four of these electrons form two double bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion. The remaining two electrons form one lone pair. Hence, in all, there are three bond pairs and one lone pair of electrons around Br atom in BrO_3^-. Therefore, according to VSEPR theory, BrO_3^- should be pyramidal.

Here, BrO_3^- has 8 ($7 + 0 \times 3 + 1$) valence electrons. A noble gas species having 8 valence electrons is XeO_3 ($8 + 0 \times 3 = 8$). Thus, like BrO_3^-, XeO_3 is also pyramidal.



Pyramidal

Q. 39. Why do noble gases have comparatively large atomic sizes?

Ans. Noble gases have only van der Waals' radii while others have covalent radii. As van der Waals' radii are larger than covalent radii. Hence, noble gases have comparatively large atomic sizes.

Q. 40. List the uses of neon and argon gases.

Ans. **Uses of Neon:**

(*i*) Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

(*ii*) Neon bulbs are used in botanical gardens and in green houses.

(*iii*) Neon is used in voltage regulators and indicators.

Uses of Argon:

(*i*) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.

(*ii*) It is used in the laboratory for handling substances that are air-sensitive.

(*iii*) Argon is used in radio valves and rectifiers.

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Out of the following halides of group 16, which does not possess reducing property?

(*a*) H_2Te (*b*) H_2Se (*c*) H_2S (*d*) H_2O

2. SO_2 acts as a/an

(*a*) Oxidising agent (*b*) Reducing agent (*c*) Bleaching agent (*d*) All of these

3. Which of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species?

(*a*) $S < O < Cl < F$ (*b*) $F < Cl < O < S$ (*c*) $Cl < F < S < O$ (*d*) $O < S < F < Cl$

4. Which of the following is not tetrahedral in shape? [*NCERT Exemplar*]

(*a*) NH_4^+ (*b*) $SiCl_4$ (*c*) SF_4 (*d*) SO_4^{2-}

5. Which of the following are peroxoacids of sulphur? [*NCERT Exemplar*]

(*a*) H_2SO_5 and $H_2S_2O_8$ (*b*) H_2SO_5 and $H_2S_2O_7$

(*c*) $H_2S_2O_7$ and $H_2S_2O_8$ (*d*) $H_2S_2O_6$ and $H_2S_2O_7$

6. Hot conc. H_2SO_4 acts as moderately strong oxidising agent. It oxidises both metals and nonmetals. Which of the following element is oxidised by conc. H_2SO_4 into two gaseous products? [*NCERT Exemplar*]

(*a*) Cu (*b*) S (*c*) C (*d*) Zn

7. In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black precipitate is obtained. On boiling the precipitate with dil. HNO_3, it forms a solution of blue colour. Addition of excess of aqueous solution of ammonia to this solution gives ______________. [*NCERT Exemplar*]

(*a*) deep blue precipitate of $Cu(OH)_2$ (*b*) deep blue solution of $[Cu(NH_3)_4]^{2+}$

(*c*) deep blue solution of $Cu(NO_3)_2$ (*d*) deep blue solution of $Cu(OH)_2.Cu(NO_3)_2$

8. Which of the following options are not in accordance with the property mentioned against them? [*NCERT Exemplar*]

(*a*) $F_2 > Cl_2 > Br_2 > I_2$ Oxidising power.

(*b*) $MI > MBr > MCl > MF$ Ionic character of metal halide.

(*c*) $F_2 > Cl_2 > Br_2 > I_2$ Bond dissociation enthalpy.

(*d*) $HI < HBr < HCl < HF$ Hydrogen-halogen bond strength.

9. When chlorine reacts with hot and conc. NaOH, the product(s) formed are

(*a*) chloride (*b*) hypochlorite

(*c*) chlorate (*d*) mixture of chloride and chlorate

10. If chlorine gas is passed through hot NaOH solution, two changes are observed in the oxidation number of chlorine during the reaction. These are _________ and __________. [*NCERT Exemplar*]

(*a*) 0 to +5 (*b*) 0 to +3 (*c*) 0 to –1 (*d*) 0 to +1

11. On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because: [*NCERT Exemplar*]

(*a*) H_2SO_4 reduces HI to I_2 (*b*) HI is of violet colour

(*c*) HI gets oxidised to I_2 (*d*) HI changes to HIO_3

12. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power. [*NCERT Exemplar*]

Ion	**ClO_4^-**	**IO_4^-**	**BrO_4^-**
Reduction potential E^o/V	**$E^o = 1.19$ V**	**$E^o = 1.65$ V**	**$E^o = 1.74$ V**

(*a*) $ClO_4^- > IO_4^- > BrO_4^-$ (*b*) $IO_4^- > BrO_4^- > ClO_4^-$

(*c*) $BrO_4^- > IO_4^- > ClO_4^-$ (*d*) $BrO_4^- > ClO_4^- > IO_4^-$

13. The correct order of increasing bond angles in the following species is:

(*a*) $Cl_2O < ClO_2^- < ClO_2$ (*b*) $ClO_2^- < Cl_2O < ClO_2$

(*c*) $Cl_2O < ClO_2 < ClO_2^-$ (*d*) $Cl_2O < ClO_2 < ClO_2^-$

14. Which of the following is isoelectronic pair? **[*NCERT Exemplar*]**

(*a*) ICl_2, ClO_2 (*b*) BrO_2^-, BrF_2^+ (*c*) ClO_2, BrF (*d*) CN^-, O_3

15. The set with correct order of acidity:

(*a*) $HClO < HClO_2 < HClO_3 < HClO_4$ (*b*) $HClO_4 < HClO_3 < HClO_2 < HClO$

(*c*) $HClO < HClO_4 < HClO_3 < HClO_2$ (*d*) $HClO_4 < HClO_2 < HClO_3 < HClO$

16. In which case, order of acidic strength is not correct?

(*a*) $HClO_4 > HClO_3 > HClO_2$ (*b*) $HI > HBr > HCl$

(*c*) $HF > H_2O > NH_3$ (*d*) $HIO_4 > HBrO_4 > HClO_4$

17. Which of the statement given below is incorrect?

(*a*) ONF is isoelectronic with O_2N^- (*b*) O_3 molecule is bent

(*c*) OF_2 is an oxide of fluorine (*d*) Cl_2O_7 is an anhydride of perchloric acid

18. In the preparation of compounds of Xe, Bartlett had taken $O_2^+PtF_6^-$ as a base compound. This is because: **[*NCERT Exemplar*]**

(*a*) both O_2 and Xe have same size.

(*b*) both O_2 and Xe have same electron gain enthalpy.

(*c*) both O_2 and Xe have almost same ionisation enthalpy.

(*d*) both Xe and O_2 are gases.

19. Two types of F × F angles are present in which of the following molecule (X = S, Xe, C):

(*a*) SF_6 (*b*) CF_4 (*c*) XeF_4 (*d*) SF_4

20. The structure of XeF_6 is

(*a*) distorted octahedral (*b*) linear (*c*) square planar (*d*) tetrahedral

21. In which of the following pairs, the two species are isostructural?

(*a*) SF_4 and XeF_4 (*b*) BF_3 and NF_3 (*c*) BrO_3^- and XeO_3 (*d*) SO_3^{2-} and NO_3^-

22. Which of the following statement is not true for helium?

(*a*) He is used in gas-cooked nuclear reactors.

(*b*) He is used as cryogenic agent for carrying out experiments at low temperature.

(*c*) He is used to fill gas balloons instead of hydrogen because it is lighter than hydrogen and non-inflammable.

(*d*) He is used as a diluent for oxygen in modern diving apparatus.

Answers

1. (*d*) **2.** (*d*) **3.** (*d*) **4.** (*c*) **5.** (*a*) **6.** (*c*) **7.** (*b*) **8.** (*b, c*) **9.** (*d*) **10.** (*a, c*)
11. (*c*) **12.** (*c*) **13.** (*b*) **14.** (*b*) **15.** (*a*) **16.** (*d*) **17.** (*c*) **18.** (*c*) **19** (*d*) **20.** (*a*)
21. (*c*) **22.** (*c*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***

(*b*) ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***

(*c*) ***Assertion (A) is correct, but Reason (R) is incorrect statement.***

(*d*) ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. Assertion (*A*) : Nitrogen does not form compounds in +5 oxidation state with halogens.
Reason (*R*) : All oxidation states of nitrogen from +1 to +4 tend to disproportionate in acid solution.

2. **Assertion (*A*) :** The O—O bond length in ozone is identical with that in molecular oxygen.
Reason (*R*) : The ozone molecule is a resonance hybrid of two canonical structures.

3. **Assertion (*A*) :** Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2.
Reason (*R*) : Oxygen forms $p\pi - p\pi$ multiple bond due to small size and small bond length but $p\pi - p\pi$ bonding is not possible in sulphur.

4. **Assertion (*A*) :** The transition temperature of sulphur is 369 K.
Reason (*R*) : At 369 K, both α-sulphur and β-sulphur are stable. Below 369 K, only α-sulphur is stable whereas above 369 K, only β-sulphur is stable.

5. **Assertion (*A*) :** SO_3 has a planar structure.
Reason (*R*) : S atom in SO_3 is sp^2-hybridized and O–S–O bond angle is 120º.

6. **Assertion (*A*) :** SF_6 cannot be hydrolysed but SF_4 can be.
Reason (*R*) : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

7. **Assertion (*A*) :** NaCl reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. But on adding MnO_2 the fumes become greenish yellow.
Reason (*R*) : MnO_2 oxidises HCl to chlorine gas which is greenish yellow.

8. **Assertion (*A*) :** Salts of ClO_3^- and ClO_4^- are well known but those of FO_3^- and FO_4^- are non-existent.
Reason (*R*) : F is more electronegative than O while Cl is less electronegative than O.

9. **Assertion (*A*) :** HClO is stronger acid than HBrO.
Reason (*R*) : Greater is the electronegativity of the halogen, greater will be attraction of electron pair towards it and hence more easily the H^+ ion will be released.

10. **Assertion (*A*) :** HI cannot be prepared by the action of conc. H_2SO_4 on KI.
Reason (*R*) : HI is more volatile than H_2SO_4.

11. **Assertion (*A*) :** Hydrolysis of XeF_6 is an example of a redox reaction.
Reason (*R*) : XeF_6 when hydrolysed yields $XeOF_4$ and XeO_2F_2.

Answers

1. (*b*) **2.** (*d*) **3.** (*a*) **4.** (*a*) **5.** (*a*) **6.** (*a*) **7.** (*a*) **8.** (*a*) **9.** (*a*) **10.** (*b*)
11. (*d*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The noble gases have closed shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The chemical reactivity of noble gases involves the loss of electrons and hence it can form compounds with highly electronegative elements like F and O. Although Xe forms several fluorides, xenon tetrafluoride is the most important among fluorides. The various compounds of xenon involve xenon in first, second and third excited states. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6.

1. Noble gases are least reactive elements. Give reason.

Ans. Noble gases have fully filled outermost shells,high ionization enthalpy and positive electron gain enthalpy and therefore they are least reactive elements.

2. The majority of noble gas compounds are those of xenon only. Why?

Ans. Xe has the lowest ionisation energy among noble gases and hence can be easily oxidised by strong oxidising agent like O_2 and F_2. That is why the majority of noble gas compounds are those of xenon.

3. Noble gases have large positive values of electron gain enthalpy. Give reason.

Ans. Since noble gases have stable electronic configurations, they have no tendency to accept electrons and thus have large positive values of electron gain enthalpy.

4. What is the type of hybridisation and shape of XeF_2?

Ans. sp^3d and linear.

5. Xenon does not form fluorides such as XeF_3 and XeF_5. Give reason.

Ans. All the filled orbitals of Xe have paired electrons. The promotion of one,two or three electrons from the 5*p* filled orbital to the 5*d* vacant orbitals will give rise to two, four and six half filled orbitals respectively. So, Xe can combine with even but not odd number of F-atoms. Hence, it cannot form XeF_3 and XeF_5.

PASSAGE–2

Each halogen can combine with other halogens to form several compounds amongst themselves. These are known as interhalogens or interhalogen compounds. The main reason for the formation of these compounds is the large electronegativity and size differences among the halogens. Thus fluorine, the most electronegative element and the smallest halogen, forms the maximum number of interhalogens. Interhalogen compound having maximum number of halogen atoms is IF_7. In interhalogens, the less electronegative halogen always written first.

1. Can FCl_3 exist? Comment.

Ans. No, because F atom has no *d*-orbital and therefore it cannot expand its valence shell. Further, three big sized Cl atoms cannot be accommodated around a small F atom.

2. In interhalogen compounds of the type AB_5 and AB_7, B is invariably fluorine. Why?

Ans. Fluorine being the strongest oxidising agent, can form interhalogen compounds in +5 and +7 oxidation state.

3. Why are interhalogens are more reactive than halogens?

Ans. This is because the bond in the interhalogen (X—X′) is weaker than X—X and X′—X′ bond in halogens.

4. What is the structure of IF_7?

Ans. Pentagonal bipyramidal.

5. Give one use of interhalogen compounds.

Ans. These compounds are used as non-aqueous solvents. They are very useful fluorinating agents.

Very Short Answer Questions [1 mark]

Q. 1. On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved which forms a blue coloured complex with Cu^{2+} ion. Identify the gas. *[CBSE Delhi 2016]* *[HOTS]*

Ans. Ammonia, NH_3.

Q. 2. On heating Cu turnings with conc. HNO_3, a brown coloured gas is evolved which on cooling dimerises. Identify the gas. *[CBSE (F) 2016]* *[HOTS]*

Ans. Nitrogen dioxide (NO_2)

Q. 3. Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic? *[NCERT Exemplar]*

Ans. In gaseous state NO_2 exists as monomer which has one unpaired electron but in solid state it dimerises to N_2O_4 so no unpaired electron is left hence solid form is diamagnetic.

Q. 4. BH_4^- and NH_4^+ are isolobal. Explain.

Ans. Both BH_4^- and NH_4^+ have tetrahedral shapes, *i.e.*, four lobes of sp^3-hybridised orbitals. Hence, they are isolobal.

Q. 5. In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $N(SiH_3)_3$, it has a planar geometry. Why?

Ans. $(CH_3)_3N$ is pyramidal due to sp^3 hybridisation and has a lone pair of electrons. $(SiH_3)_3N$ has sp^2 hybridisation because lone pair of nitrogen is donated to vacant *d*-orbital of Si.

Q. 6. PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why. *[NCERT Exemplar]*

Ans. NH_3 forms hydrogen bonds with water therefore it is soluble in it but PH_3 cannot form hydrogen bond with water so it escapes as gas.

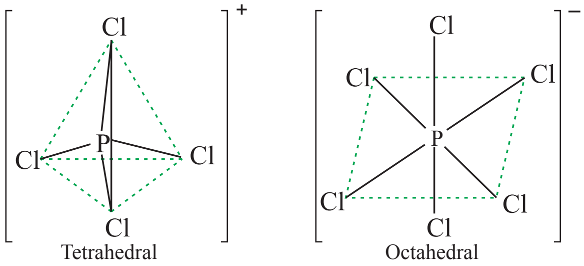
Q. 7. Write the formula of the compound of phosphorous which is obtained when conc. HNO_3 oxidises P_4. *[CBSE (AI) 2017]*

Ans. H_3PO_4

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Q. 8. Draw the structure of solid PCl_5. *[CBSE (F) 2013]*

Ans.



Q. 9. Out of H_2O and H_2S, which one has higher bond angle and why? *[NCERT Exemplar]*

Ans. Bond angle of H_2O is larger, because oxygen is more electronegative than sulphur. Therefore, bond pair electron of O—H bond will be closer to oxygen and there will be more bond pair–bond pair repulsion between bond pairs of two O—H bonds.

Q. 10. Arrange the following hydrides of Group-16 elements in the decreasing order of their reducing character:

H_2O, H_2S, H_2Se, H_2Te *[CBSE (F) 2017]*

Ans. $H_2Te > H_2Se > H_2S > H_2O$

Q. 11. Explain why ozone is thermodynamically less stable than oxygen. *[NCERT Exemplar]*

Ans. Ozone is thermodynamically unstable with respect to oxygen as its decomposition into oxygen results in the liberation of heat (ΔH is –ve) and an increase in entropy (ΔS is +ve). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

Q. 12. On heating copper turnings with conc. H_2SO_4, a colourless gas with pungent smell is evolved which decolourises acidified $KMnO_4$ solution. Identify the gas. *[CBSE East 2016]* *[HOTS]*

Ans. Sulphur dioxide (SO_2)

Q. 13. Write the formula of the compound of sulphur which is obtained when conc. HNO_3 oxidises S_8. *[CBSE (AI) 2017]*

Ans. H_2SO_4

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

Q. 14. Why sulphurous acid acts as a reducing agent?

Ans. Due to the presence of a lone pair of electrons on the sulphur atom, sulphurous acid can be easily oxidised to sulphuric acid. Therefore, it acts as a reducing agent.

$$H_2O + Br_2 + H_2SO_3 \longrightarrow 2HBr + H_2SO_4$$

Q. 15. Concentrated H_2SO_4 is used as a dehydrating agent. Explain.

Ans. Sulphuric acid has a strong affinity for water. It, therefore, removes water not only from materials which contain it but frequently removes oxygen and hydrogen from other compounds in the proportion required to form water (H_2O).

Q. 16. Sulphur disappears when boiled with sodium sulphite. Why?

Ans. When sodium sulphite is heated with sulphur, we get sodium thiosulphate which is soluble in water that is why sulphur disappears.

$$Na_2SO_3 + S \xrightarrow{\text{heat}} Na_2S_2O_3$$

Q. 17. 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, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

Q. 18. Why is F_2O referred to as a fluoride but Cl_2O is an oxide?

Ans. F_2O is called oxygen fluoride because fluorine is more electronegative than oxygen whereas Cl_2O is called chlorine oxide because oxygen is more electronegative than chlorine.

Q. 19. Iodine forms I_3^- but F_2 does not form F_3^- ions. Why?

Ans. I_2, because of the presence of vacant *d*-orbitals, accepts electrons from I^- ions to form I_3^- ions but F_2 because of the absence of *d*-orbitals does not accept electrons from F^- ions to form F_3^- ions.

Q. 20. Why is I_2 more soluble in KI than in water?

Ans. It is due to formation of soluble complex KI_3.

$$I_2 + KI \longrightarrow KI_3$$

Q. 21. How does xenon atom form compounds with fluorine even though the xenon atom has a closed shell configuration?

Ans. This is because 1, 2 or 3 electrons from the 5*p*-orbitals can be excited to empty 5*d*-orbitals and thus making 2, 4 or 6 half-filled orbitals available for bond formation.

Q. 22. Complete the following reaction:

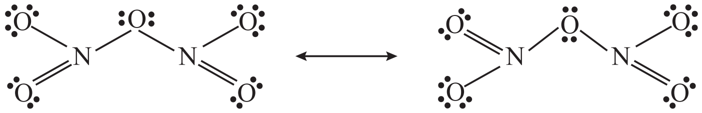
$XeF_6 + 2H_2O \longrightarrow$ **[*CBSE Delhi 2017; 2020 (56/3/2)*]**

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

Short Answer Questions–I [2 marks]

Q. 1. Nitric acid forms an oxide of nitrogen on reaction with P_4O_{10}. Write the reaction involved. Also write the resonating structures of the oxide of nitrogen formed. **[*NCERT Exemplar*]**

Ans. $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$



Q. 2. When dilute ferrous sulphate solution is added to an aqueous solution containing nitrate ion followed by careful addition of concentrated sulphuric acid along the sides of test tube, a brown ring is formed at the interface between the solution and sulphuric acid layers. Which anion is confirmed by the appearance of brown ring? What is the composition of the brown ring? **[*CBSE 2019 (56/4/1)*]**

Ans. Nitrate ion—NO_3^-

$[Fe(H_2O)_5(NO)]^{2+}$

Q. 3. Name the two most important allotropes of sulphur. Which one of the two is stable at room temperature? What happens when the stable form is heated above 370 K? **[*CBSE (F) 2014*]**

Ans. Two most important allotropes of sulphur are rhombic sulphur and monoclinic sulphur. The stable form at room temperature is rhombic sulphur. When rhombic sulphur is heated above 370 K, it gets converted into monoclinic sulphur.

Q. 4. Complete the following equations:

(*i*) $P_4 + H_2O \longrightarrow$ **(*ii*) $XeF_4 + O_2F_2 \longrightarrow$** **[*CBSE (AI) 2014*]**

Ans. (*i*) $P_4 + H_2O \longrightarrow$ No reaction

(*ii*) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

Q. 5. Complete the following chemical equations:

(*i*) $Ca_3P_2 + H_2O \longrightarrow$ **(*ii*) $Cu + H_2SO_4(\text{conc.}) \longrightarrow$** **[*CBSE Delhi 2014*]**

Ans. (*i*) $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$

(*ii*) $Cu + 2H_2SO_4(\text{conc.}) \longrightarrow CuSO_4 + SO_2 + 2H_2O$

Q. 6. Complete the following equations:

(*i*) $2Ag + PCl_5 \longrightarrow$

(*ii*) $CaF_2 + H_2SO_4 \longrightarrow$ **[*CBSE (AI) 2014*]**

Ans. (*i*) $2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$

(*ii*) $CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4$

Q. 7. What happens when

(*i*) $(NH_4)_2Cr_2O_7$ is heated **(*ii*) H_3PO_3 is heated?**

Write the equations. *[CBSE Delhi 2017]*

Ans. (*i*) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

(*ii*) $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$

Q. 8. What happens when

(*i*) Conc. H_2SO_4 is added to Cu?

(*ii*) SO_3 is passed through water?

Write the equations. *[CBSE Delhi 2017]*

Ans. (*i*) $Cu + 2H_2SO_4\,(conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(*ii*) $SO_3 + H_2O \longrightarrow H_2SO_4$

Q. 9. What happens when

(*i*) HCl is added to MnO_2?

(*ii*) PtF_6 and xenon are mixed together? *[CBSE Delhi 2017]*

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

(*ii*) $PtF_6 + Xe \longrightarrow Xe^+[PtF_6]^-$

Q. 10. Complete the following equations:

(*i*) $C + conc.\ H_2SO_4 \longrightarrow$ **(*ii*) $XeF_2 + H_2O \longrightarrow$** *[CBSE (AI) 2014]*

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

(*ii*) $2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

Q. 11. Complete the following reactions:

(*i*) $Cl_2 + H_2O \longrightarrow$ **(*ii*) $XeF_6 + 3H_2O \longrightarrow$** *[CBSE Delhi 2017]*

Ans. (*i*) $Cl_2 + H_2O \longrightarrow HCl + HOCl$

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

Q. 12. Complete the following chemical equations:

(*i*) $F_2 + 2Cl^- \longrightarrow$ **(*ii*) $2XeF_2 + 2H_2O \longrightarrow$** *[CBSE Delhi 2017]*

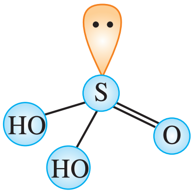
Ans. (*i*) $F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$

(*ii*) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

Q. 13. Draw the structures of the following: *[CBSE (AI) 2017]*

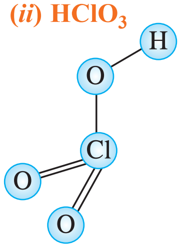
(*i*) H_2SO_3 **(*ii*) $HClO_3$**

Ans. (*i*)



Sulphurous acid
(H_2SO_3)

(*ii*)

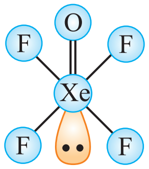


Chloric acid
($HClO_3$)

Q. 14. Draw the structures of the following:

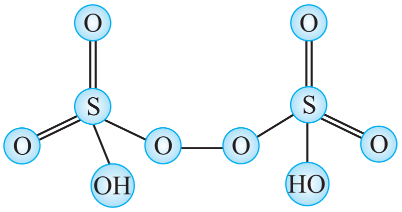
(*i*) $XeOF_4$ **(*ii*) $H_2S_2O_8$** *[CBSE Ajmer 2015; 2020 (56/5/1)]*

Ans. (*i*)



$XeOF_4(sp^3d^2)$
Square pyramidal

(*ii*)

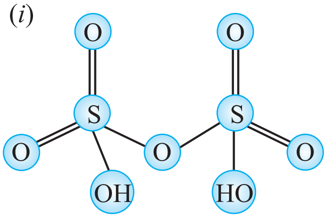


Peroxodisulphuric acid
($H_2S_2O_8$)

Q. 15. Draw the structures of the following:

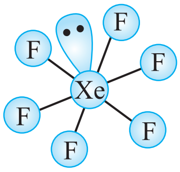
(*i*) $H_2S_2O_7$ **(*ii*) XeF_6** **[*CBSE Delhi 2017, 2020 (56/3/2)*]**

Ans. (*i*)



$H_2S_2O_7$

(*ii*)

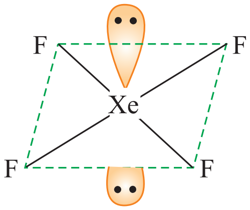


XeF_6
Distorted octahedral

Q. 16. Draw the structures of the following: **[*CBSE (AI) 2017*]**

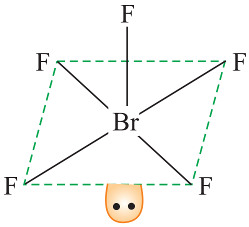
(*i*) XeF_4 **(*ii*) BrF_5**

Ans. (*i*)



XeF_4: Square planar

(*ii*)

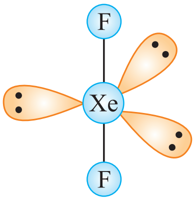


BrF_5: Square pyramidal

Q. 17. Draw the structures of the following:

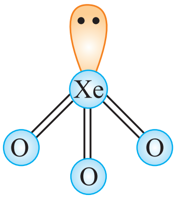
(*i*) XeF_2 **(*ii*) XeO_3** **[*CBSE (AI) 2014*]**

Ans. (*i*) There are two bond pairs and three lone pairs of electrons around central Xe atom in XeF_2. Therefore, according to VSEPR theory, XeF_2 should be linear.



XeF_2

(*ii*) There are three bond pairs and one lone pair of electrons around Xe atom in XeO_3. Therefore, according to VSEPR theory, XeO_3 should be pyramidal.



XeO_3, Pyramidal

Q. 18. Give reasons for the following:

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

(*ii*) NO_2 dimerises to form N_2O_4.

Ans. (*i*) Nitrogen being smaller in size forms ρπ-ρπ multiple bonding with carbon, so CN^- ion is known, but phosphorus does not form ρπ-ρπ bond as it is larger in size.

(*ii*) This is because NO_2 is an odd electron molecule and therefore gets dimerised to stable N_2O_4.

Q. 19. Give reasons:

(*i*) NH_3 has a higher proton affinity than PH_3.

(*ii*) NO (Nitric oxide) is paramagnetic in the gaseous state but diamagnetic in the liquid and solid states.

Ans. (*i*) 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 the bigger size of P than N, P—H bond thus formed is much weaker than the N—H bond. Thus, NH_3 has higher proton affinity than PH_3.

(*ii*) NO has an odd number of electrons (11 valence electrons) and hence is paramagnetic in the gaseous state. But in liquid and solid states, it exists as a symmetrical or asymmetrical dimer and hence is diamagnetic in these states.

Q. 20. Assign a reason for each of the following:

(*i*) SCl_6 is not known but SF_6 is known.

(*ii*) Sulphur hexafluoride is used as a gaseous electrical insulator. [*NCERT Exemplar*]

Ans. (*i*) Due to small size of fluorine, six F^- ions can be accommodated around sulphur whereas chloride ion is comparatively larger in size, therefore, there will be interionic repulsion.

(*ii*) SF_6 is a colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. Because of its inertness and high tendency to suppress internal discharges, it is used as a gaseous electrical insulator in high voltage generators and switch gears.

Q. 21. How would you account for the following:

(*i*) H_2S is more acidic than H_2O.

(*ii*) Both O_2 and F_2 stabilise higher oxidation states but the ability of oxygen to stabilise the higher oxidation state exceeds that of fluorine. [*CBSE (AI) 2011*]

Ans. (*i*) This is because bond dissociation enthalpy of H—S bond is lower than that of H—O bond.

(*ii*) This is due to tendency of oxygen to form multiple bonds with metal atom.

Q. 22. Account for the following:

(*i*) Bleaching of flowers by chlorine is permanent while that by sulphur dioxide is temporary.

(*ii*) Sulphur exhibits greater tendency for catenation than selenium.

Ans. (*i*) Cl_2 bleaches coloured material by oxidation.

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

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

Hence, bleaching is permanent.

In contrast, SO_2 bleaches coloured material by reduction and hence bleaching is temporary since when the bleached colourless material is exposed to air, it gets oxidised and the colour is restored.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

$$\text{Coloured material} + H \longrightarrow \text{Colourless material} \xrightarrow[\text{oxidation}]{\text{aerial}} \text{Coloured material}$$

(*ii*) As we move from S to Se, the atomic size increases and hence the strength of E—E bond decreases. Thus, S—S bond is much stronger than Se—Se bond. Consequently, S shows greater tendency for catenation than selenium.

Q. 23. Account for the following:

(*i*) Iron on reaction with HCl forms $FeCl_2$ and not $FeCl_3$.

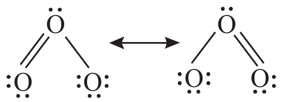
(*ii*) The two O—O bond lengths in the ozone molecule are equal. [*CBSE (AI) 2014*]

Ans. (*i*) Iron reacts with HCl to form $FeCl_2$ and H_2.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

H_2 thus produced prevents the oxidation of $FeCl_2$ to $FeCl_3$.

(*ii*) Ozone is a resonance hybrid of the following two main structures:



As a result of resonance, the two O—O bond lengths in O_3 are equal.

Q. 24. Account for the following observations:

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

(*ii*) Acidity of oxo-acids of chlorine is $HOCl < HOClO < HOClO_2 < HOClO_3$.

Ans. (*i*) This is due to the

(*a*) low enthalpy of dissociation of F—F bond.

(*b*) high hydration enthalpy of F^-.

(*ii*) Oxygen is more electronegative than chlorine, therefore, dispersal of negative charge present on chlorine increases from ClO^- to ClO_4^- ion because number of oxygen atoms attached to chlorine is increasing. Therefore, stability of ions will increase in the order given below:

$ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$

This is due to increase in stability of conjugate base, acidic strength of corresponding acid increases in the following order:

$HClO < HClO_2 < HClO_3 < HClO_4$

Q. 25. (*i*) Why is HF acid stored in wax coated glass bottles?

(*ii*) ClF_3 exists but FCl_3 does not. Explain.

Ans. (*i*) HF does not attack wax but reacts with glass. It dissolves SiO_2 present in glass forming hydrofluorosilicic acid.

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

(*ii*) (*a*) Cl has vacant *d*-orbitals and hence can show an oxidation state of +3 but F has no *d*-orbitals, so, it cannot show positive oxidation states. Since F can show only –1 oxidation state, FCl_3 does not exist.

(*b*) Because of bigger size, Cl can accommodate three small F atoms around it while F being smaller cannot accommodate three large sized Cl atoms around it.

Q. 26. (*i*) Boiling points of interhalogens are little higher as compared to pure halogens. Why?

(*ii*) Out of He and Xe, which one can easily form compound and why? **[*CBSE South 2016*]**

Ans. (*i*) This is due to some amount of polarity associated with X—X′ bond in interhalogens whereas pure halogens are non-polar.

(*ii*) Xe, due to much lower ionisation enthalpy of Xe (1170 kJ mol^{-1}) than He (2372 kJ mol^{-1}).

Short Answer Questions–II [3 marks]

Q. 1. Complete the following equations:

(*i*) $PCl_3 + H_2O \longrightarrow$ **(*ii*) $XeF_2 + PF_5 \longrightarrow$**

(*iii*) $NaN_3 \xrightarrow{\text{Heat}}$ **[*CBSE (F) 2013*]**

Ans. (*i*) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

(*ii*) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

(*iii*) $2NaN_3 \xrightarrow{\text{Heat}} 2Na + 3N_2$

Q. 2. Illustrate how copper and zinc give different products on reaction with HNO_3. **[*HOTS*]**

Ans. With conc. HNO_3:

$$\begin{array}{l}
2HNO_3 \longrightarrow H_2O + 2NO_2 + O \\
Cu + O \longrightarrow CuO \\
CuO + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O \\
\hline
Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2 \\
\hline
\end{array}$$

$$\begin{array}{l}
\mathrm{Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H} \\
\mathrm{HNO_3 + H \longrightarrow H_2O + NO_2] \times 2} \\
\hline
\mathrm{Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2} \\
\hline
\end{array}$$

With dil HNO_3:

$$\begin{array}{l}
\mathrm{2HNO_3 \longrightarrow H_2O + 2NO + 3O} \\
\mathrm{Cu + O \longrightarrow CuO] \times 3} \\
\mathrm{CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O] \times 3} \\
\hline
\mathrm{3Cu + 8HNO_3 \longrightarrow 3Cu\,(NO_3)_2 + 4H_2O + 2NO} \\
\hline
\mathrm{Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4} \\
\mathrm{HNO_3 + 8H \longrightarrow 3H_2O + NH_3} \\
\mathrm{NH_3 + HNO_3 \longrightarrow NH_4\,NO_3} \\
\mathrm{NH_4\,NO_3 \longrightarrow N_2O + 2H_2O} \\
\hline
\mathrm{4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O} \\
\hline
\end{array}$$

Q. 3. (*i*) Complete the following chemical equations.

(*a*) $NH_4Cl\,(aq) + NaNO_2\,(aq) \longrightarrow$

(*b*) $P_4 + 3NaOH + 3H_2O \longrightarrow$

(*ii*) Why does orthophosphoric acid acid exist as a syrupy liquid?

Ans. (*i*) (*a*) $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$

(*b*) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$

(*ii*) Orthophosphoric acid contains three -OH groups and hence undergoes extensive hydrogen bonding.

Q. 4. Give reasons for the following:

(*i*) N_2O_5 is more acidic than N_2O_3. ***[CBSE (AI) 2017]***

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

(*iii*) Both NO and ClO_2 are odd electron species but NO dimerises while ClO_2 does not.

Ans. (*i*) In N_2O_5, N is in +5 oxidation state whereas in N_2O_3 it is in +3 oxidation state. Higher the +ve oxidation state of the atom, more will be its acidic character.

(*ii*) Both H_3PO_2 and H_3PO_3 have P—H bonds, so they act as reducing agents. H_3PO_4, has no P—H bond but has O—H bonds, so it cannot act as a reducing agent.

(*iii*) In NO, the odd electron on N is attracted by only one O-atom but in ClO_2, the odd electron on Cl is attracted by two O-atoms. Thus, the odd electron on N in NO is localised while the odd electron on Cl in ClO_2 is delocalised. Consequently, NO has a tendency to dimerise but ClO_2 does not.

Q. 5. Account for the following:

(*i*) NH_3 has a higher boiling point than PH_3. ***[CBSE Guwahati 2015]***

(*ii*) Bond angle in NH_4^+ is higher than NH_3. ***[CBSE (F) 2015]***

(*iii*) The molecules NH_3 and NF_3 have dipole moments which are of opposite directions. ***[CBSE (F) 2014]***

Ans. (*i*) Due to small size and high electronegativity of N, NH_3 undergoes extensive intermolecular H-bonding and hence exist as an associated molecule. In contrast due to low electronegativity of P, PH_3 does not undergo H-bonding and thus exist as a discrete molecule. That is why, boiling point of NH_3 is higher than PH_3.

(*ii*) N atom both in NH_3 and NH_4^+ is sp^3 hybridised. In NH_4^+ all the four orbitals are bonded whereas in NH_3 there is a lone pair on N , which is responsible for lone pair-bond pair repulsion in NH_3 reducing the bond angle from 109°28′ to 107°.

(*iii*) This is because in NH_3 nitrogen is more electronegative than hydrogen while in NF_3, nitrogen is less electronegative than fluorine.

Q. 6. Complete the following chemical equations:

(*i*) $Fe^{3+} + SO_2 + H_2O \longrightarrow$ **(*ii*) $P_4 + 10SOCl_2 \longrightarrow$**

(*iii*) $\underset{\text{(excess)}}{XeF_6 + H_2O} \longrightarrow$ [*CBSE (F) 2011*]

Ans. (*i*) $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4H^+ + SO_4^{2-}$

(*ii*) $P_4 + 10SOCl_2 \longrightarrow 4PCl_5 + 10SO_2$

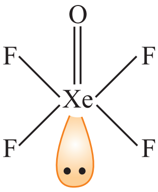
(*iii*) $XeF_6 + \underset{\text{(excess)}}{3H_2O} \longrightarrow XeO_3 + 6HF$

Q. 7. (*i*) Draw the structures of the following molecules:

(*a*) $XeOF_4$ **(*b*) H_2SO_4**

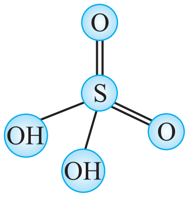
(*ii*) Write the structural difference between white phosphorus and red phosphorus. [*CBSE Delhi 2014*]

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



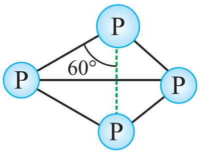
$XeOF_4$

(*b*)

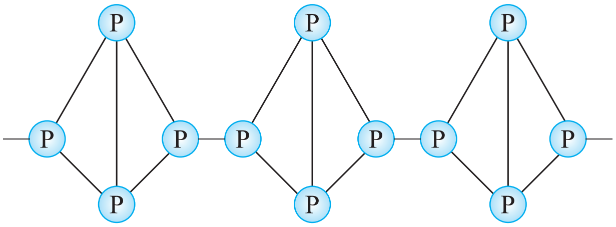


H_2SO_4

(*ii*) White phosphorus consists of discrete tetrahedral P_4 molecule with six P—P covalent bonds.



Red phosphorus has polymeric structure in which P_4 tetrahedra are linked together through P—P covalent bond to form chain.



Q. 8. Give reasons for the following:

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

(*ii*) Solid phosphorus pentachloride exhibits some ionic character.

(*iii*) Ammonia acts as a ligand.

Ans. (*i*) Nitric oxide readily combines with O_2 of air to form nitrogen dioxide which is brown in colour.

$$\underset{\substack{\text{Nitric oxide}\\\text{(Colourless)}}}{2NO} + O_2 \longrightarrow \underset{\substack{\text{Nitrogen dioxide}\\\text{(Brown)}}}{2NO_2}$$

(*ii*) Solid PCl_5 exists as $[PCl_4]^+ [PCl_6]^-$ and hence exhibits some ionic character.

(*iii*) Due to the presence of lone pair of electrons on N, NH_3 acts as a ligand.

$$\underset{\text{Silver chloride}}{AgCl} + 2NH_3 \longrightarrow \underset{\text{Diamminesilver (I) chloride}}{[Ag(NH_3)_2]Cl}$$

Q. 9. Give reasons for the following:

(*i*) Reducing character decreases from SO_2 to TeO_2. [*CBSE (F) 2015*]

(*ii*) Bond angle decreases from H_2O to H_2Te.

(*iii*) Halogens have the maximum negative electron gain enthalpy. [*CBSE Chennai 2015*]

Ans. (*i*) Because the stability of + 4 oxidation state increases from S to Te on moving down the group in group 16 due to inert pair effect.

(*ii*) As we move down the group from O to Te, the size of central atom goes on increasing and its electronegativity goes on decreasing. Consequently, the bond pairs of electrons tend to lie away from the central atom as we move from H_2O to H_2Te. As a result of this the force of repulsion between the bond pairs decreases as we move from O to Te and hence the bond angle decreases in the same order.

(*iii*) Halogens have one electron less than the nearest noble gas configuration. Therefore, they have a strong tendency to accept an additional electron to acquire nearest noble gas configuration and hence they have maximum negative electron gain enthalpy.

Q. 10. How would you account for the following:

(*i*) The electron gain enthalpy with negative sign is less for oxygen than that for sulphur.

(*ii*) Fluorine never acts as the central atom in polyatomic interhalogen compounds. **[*CBSE (AI) 2010*]**

(*iii*) H_2S has lower boiling point than H_2O. **[*CBSE (F) 2015*]**

Ans. (*i*) This is due to smaller size of oxygen the electron cloud is distributed over a small region of space, making electron density high which repels the incoming electrons.

(*ii*) Fluorine never acts as the central atom in polyatomic interhalogen compounds since it is the most electronegative element of the group.

(*iii*) Due to high electronegativity and small size of oxygen, H_2O undergoes extensive intermolecular H-bonding and exists as an associated molecule. On the other hand, due to low electronegativity of S, H_2S is unable to form effective H-bonds and exists as a discrete molecule which are held by weak van der Waal forces. To overcome these forces only small amount of energy is required. Therefore, H_2S has lower boiling point than H_2O.

Q. 11. Assign appropriate reasons for each of the following statements:

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

(*ii*) Addition of Cl_2 to KI solution gives it a brown colour but excess of Cl_2 turns it colourless.

(*iii*) Perchloric acid is a stronger acid than sulphuric acid.

Ans. (*i*) According to Fajan's rule, a bigger anion is more easily polarised than a smaller anion. As a result, same metal cation can polarise a bigger Cl^- ion more easily than the smaller F^- ion. In other words, for the same metal, the metal fluoride is more ionic than metal chloride. So, in general, we can easily say that metal fluorides are more ionic than metal chlorides.

(*ii*) Cl_2 being a stronger oxidising agent than I_2 first oxidises KI to give I_2 which imparts brown colour to the solution.

$$2KI(aq) + Cl_2(g) \longrightarrow 2KCl(aq) + \underset{\text{Brown}}{I_2(s)}$$

If Cl_2 is passed in excess, the I_2 thus formed gets further oxidised to iodic acid (HIO_3) which is colourless.

$$5Cl_2 + I_2 + 6H_2O \longrightarrow 10HCl + \underset{\text{(Colourless)}}{2HIO_3}$$

(*iii*) The oxidation state of Cl in perchloric acid is +7 while that of S in sulphuric acid is +6. Greater the oxidation state of central atom, more readily the O–H bond breaks and hence stronger is the acid.

Q. 12. Explain the following observations:

(*i*) H_2S is more acidic than H_2O.

(*ii*) Fluorine does not exhibit any positive oxidation state.

(*iii*) Helium forms no real chemical compound. **[*CBSE (AI) 2012*]**

Ans. (*i*) Due to smaller size of O as compared to S, the bond dissociation enthalpy of O–H bond is higher than that of S–H bond. As a result, in aqueous solution, S–H bond can break more easily to form H^+ ion than O–H bond. Hence, H_2S is more acidic than H_2O.

(*ii*) This is because fluorine is the most electronegative element and it does not have *d* orbitals.

(*iii*) This is because the valence shell orbital of helium is completely filled ($1s^2$) and it has high ionisation enthalpy and more positive electron gain enthalpy.

Q. 13. A colourless inorganic salt A decomposes at about 250°C to give only two products B and C leaving no residue. The oxide C is a liquid at room temperature and is neutral to litmus paper while B is neutral oxide. White phosphorus burns in excess of B to produce strong dehydrating agent. Give balanced equations for above processes. [*HOTS*]

Ans. A = NH_4NO_3 (Ammonium nitrate), B = N_2O (Nitrous oxide), C = H_2O

Reactions involved:

$$\underset{\substack{\text{Ammonium nitrate}\\ \text{(A)}}}{NH_4NO_3} \xrightarrow{250°C} \underset{\substack{\text{Nitrous oxide}\\ \text{(B)}}}{N_2O} + \underset{\text{(C)}}{2H_2O}$$

$$\underset{\text{(B)}}{10N_2O} + P_4 \longrightarrow 10N_2 + \underset{\substack{\text{Phosphorus pentoxide}\\ \text{(dehydrating agent)}}}{P_4O_{10}}$$

Q. 14. On reaction with Cl_2, phosphorus forms two types of halides 'A' and 'B'. Halide A is yellowish-white powder but halide 'B' is colourless oily liquid. Identify A and B and write the formulas of their hydrolysis products. [*NCERT Exemplar*]

Ans. A = PCl_5 (Yellowish white powder)

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

B = PCl_3 (Colourless oily liquid)

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Hydrolysis products are formed as follows:

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

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Long Answer Questions [5 marks]

Q. 1. (*i*) Although nitrogen and chlorine have nearly same electronegativity yet nitrogen forms hydrogen bonding while chlorine does not. Why? [*CBSE (F) 2017*]

(*ii*) What happens when F_2 reacts with water?

(*iii*) Write the name of the gas evolved when Ca_3P_2 is dissolved in water.

(*iv*) Write the formula of a noble gas species which is isostructural with IBr_2^-.

(*v*) Complete the equation:

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow$$

Ans. (*i*) Atomic size of nitrogen is smaller than chlorine. Due to this, electron density per unit volume on nitrogen atom is higher than that of chlorine atom. Therefore, nitrogen form hydrogen bonds while chlorine does not although nitrogen and chlorine have nearly same electronegativity.

(*ii*) It oxidises H_2O to O_2.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

(*iii*) Phosphine (PH_3).

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(*iv*) XeF_2.

IBr_2^- has 2 bond pairs and 3 lone pairs of electrons, therefore, it should be linear. Like IBr_2^-, XeF_2 has 2 bond pairs and 3 lone pairs of electrons, therefore, it is also linear.

(*v*) $$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

Q. 2. (*i*) Draw the structures of ClF_3.

(*ii*) Explain the following observations:

(*a*) Oxygen is a gas but sulphur is a solid.

(*b*) Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water.

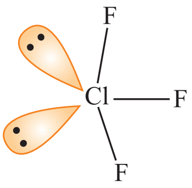
(*c*) The halogens are coloured. [*CBSE (AI) 2012*]

Ans. (*i*) No. of electron pairs around central atom Cl = 5

No. of bond pairs = 3

No of lone pairs = 2

The shape would be slightly bent "T".



ClF_3

(*ii*) (*a*) Because of its small size, oxygen is capable of forming ρπ–ρπ bond and exists as diatomic O_2 molecule. The intermolecular forces in oxygen are weak van der Waals force, due to which it is a gas at room temperature. On the other hand, sulphur, due to its larger size prefers to form S–S single bond and exist as octaatomic S_8 molecule having puckered ring structure. Because of larger size the force of attraction holding the S_8 molecules together are much stronger. Hence sulphur is a solid at room temperature.

(*b*) This is because in H_2O hydrogen bond formed is three dimensional whereas in H–F it is linear.

(*c*) All halogens are coloured. This is due to absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level while the remaining light is transmitted. The colour of the halogen is the colour of transmitted light.

Q. 3. (*i*) When conc. H_2SO_4 was added into an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified 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 the equations for the reactions involved.

(*ii*) Arrange the following in order of property indicated for each set:

(*a*) F_2, Cl_2, Br_2, I_2 —increasing bond dissociation enthalpy.

(*b*) HF, HCl, HBr, HI—increasing acidic strength.

Ans. (*i*) A = $NO_2(g)$, B = $N_2O_4(g)$

$$MNO_3 + H_2SO_4 \xrightarrow{\text{Heat}} MHSO_4 + HNO_3$$

$$4HNO_3 \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitrogen dioxide}\\ \text{(Brown gas)}}}{4NO_2} + 2H_2O + O_2$$

$$\underset{\text{Copper turnings}}{Cu} + 4HNO_3 \xrightarrow{\text{Heat}} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$\underset{\text{(Brown gas)}}{2NO_2} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{\text{(Colourless)}}{N_2O_4}$$

(*ii*) Refer to Ans. 36 of NCERT Textbook Exercises.

Q. 4. (*i*) Arrange the following in the order of property indicated against each set:

(*a*) HF, HCl, HBr, HI — increasing bond dissociation enthalpy

(*b*) H_2O, H_2S, H_2Se, H_2Te — increasing acidic character

(*ii*) X_2 is a greenish yellow gas with pungent smell and used in purification of water. On dissolving water it gives a solution which turns blue litmus red. When it is passed through NaBr solution Br_2 is obtained.

(*a*) Identify the gas.

(*b*) What are products obtained when X_2 reacts with ammonia? Give chemical equations.

(*c*) What happens when X_2 reacts with cold and dilute NaOH solution? Write chemical equation and give the name of reaction.

Ans. (*i*) (*a*) Shorter the bond length, higher is the bond dissociation enthalpy of hydrogen halide. As the atomic size increases down the group the E–H (E = F, Cl, Br, I) bond length increases and hence the bond dissociation enthalpy increases in the reverse order *i.e.*,

$$HI < HBr < HCl < HF$$

(*b*) $H_2O < H_2S < H_2Se < H_2Te$

The increase in acidic character from H_2O to H_2Te is due to decrease in bond enthalpy for dissociation of H—E (E = O, S, Se, Te) bond down the group.

(*ii*) (*a*) $X_2 = Cl_2$

(*b*) $\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow \underset{\text{(oxidation)}}{NCl_3} + 3HCl$

(*c*) $\underset{\text{(cold and dil.)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$, Disproportionation reaction

Q. 5. (*i*) Give reasons for the following:

(*a*) Bond enthalpy of F_2 is lower than that of Cl_2.

(*b*) PH_3 has lower boiling point than NH_3.

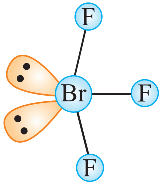
(*ii*) Draw the structures of the following molecules:

(*a*) BrF_3 (*b*) $(HPO_3)_3$ (*c*) XeF_4 **[*CBSE Delhi 2013*]**

Ans. (*i*) (*a*) Bond dissociation enthalpy decreases as the bond distance increases from F_2 to I_2 because of the corresponding increase in the size of the atom as we move from F to I. The F—F bond dissociation enthalpy is, however, smaller than that of Cl—Cl and even smaller than that of Br—Br. This is because F atom is very small and hence the three lone pairs of electrons on each F atom repel the bond pair holding the F-atoms in molecule resulting lower bond enthalpy than Cl_2.

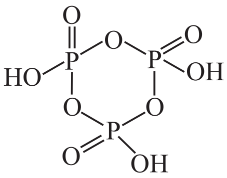
(*b*) Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

(*ii*) (*a*) BrF_3

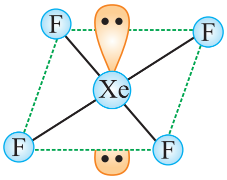


Slightly bent 'T'

(*b*) $(HPO_3)_3$



(*c*) XeF_4



Square planar

Q. 6. (*i*) Which allotrope of phosphorus is more reactive and why?

(*ii*) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers?

(*iii*) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(*iv*) Which noble gas is used in filling balloons for meteorological observations?

(*v*) Complete the equation: $XeF_2 + PF_5 \longrightarrow$ **[*CBSE Delhi 2015*]**

Ans. (*i*) White or yellow phosphorus is more reactive than the other allotropes because it is less stable due to angular strain in the P_4 molecule of white phosphorus where the angles are only 60°.

(*ii*) Nitrogen oxides (particularly nitric oxide) emitted from the exhaust system of supersonic jet aeroplanes are responsible for depletion of ozone layer.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

(*iii*) Bond dissociation enthalpy of F_2 is lower than Cl_2 due to small size of fluorine and relatively larger electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

(*iv*) Helium, as it is non-inflammable and light gas.

(*v*) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

Q. 7. (*i*) Account for the following: **[*CBSE 2019 (56/2/1)*]**

(*a*) Acidic character increases from H_2O to H_2Te.

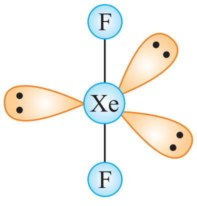
(*b*) F_2 is more reactive than CIF_3, whereas CIF_3 is more reactive than Cl_2.

(*ii*) Draw the structure of (*a*) XeF_2, (*b*) $H_4P_2O_7$.

Ans. (*i*) (*a*) The increase in acidic character from H_2O to H_2Te is due to decrease in bond enthalpy for the dissociation of H—E bond down the group.

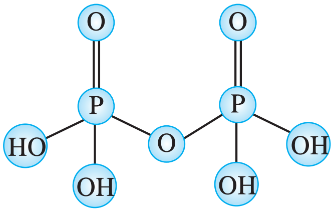
(*b*) F_2 is more reactive than ClF_3 because F–F bond in F_2 is weaker than Cl–F bond in ClF_3. In contrast Cl—F bond in ClF_3 is weaker that Cl—Cl in Cl_2, therefore, ClF_3 is more reactive than Cl_2.

(*ii*) (*a*) There are two bond pairs and three lone pairs of electrons around central Xe atom in XeF_2. Therefore, according to VSEPR theory XeF_2 should be linear.



XeF_2

(*b*)



Pyrophosphoric acid
($H_4P_2O_7$)

Q. 8. (*i*) Give one example to show the anomalous reaction of fluorine. [*CBSE 2019 (56/2/1)*]

(*ii*) What happens when XeF_6 reacts with NaF?

(*iii*) Why is H_2S a better reducing agent than H_2O?

(*iv*) Arrange the following acids in the increasing order of their acidic character:

HF, HCl, HBr and HI

Ans. (*i*) (*a*) Fluorine is the strongest oxidising agent among halogens. It oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic acid and hypohalic acid.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq) \qquad \text{(where X = Cl or Br)}$$

(*b*) As fluorine usually does not show positive oxidation states, therefore, F_2 does not undergo disproportionation reaction in alkaline medium while other halogens do.

$$X_2 + 2NaOH \xrightarrow{\text{Cold}} NaX + NaOX + H_2O \qquad \text{(where X = Cl, Br, I)}$$

(*c*) Due to small size and high electronegativity:

- Fluorine forms only one oxo acid, HOF, the other halogen form several oxo acids.
- Fluorine in HF forms intermolecular H-bonds which results in association of HF molecules. Therefore HF is a liquid (b.p. 293 K) while other hydrogen halides are gases.

(*ii*) $XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$

(*iii*) Lesser the bond dissociation enthalpy lesser is the stability of the hydride and hence stronger is the reducing agent. Since bond dissociation enthalpy of S—H bond is lesser than O—H therefore, H_2S is a stronger reducing agent than H_2O.

(*iv*) $HF < HCl < HBr < HI$

Q. 9. (*i*) What happens when

(*a*) chlorine gas is passed through a hot concentrated solution of NaOH?

(*b*) sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt?

[*CBSE 2019 (56/2/1)*]

(*ii*) Answer the following:

(*a*) Why does fluorine not play the role of a central atom in interhalogen compounds?

(*b*) Why do noble gases have very low boiling points? [*CBSE (AI) 2011*]

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

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

(*ii*) (*a*) This is due to smaller size and absence of *d* orbitals in the valence shell of fluorine.

(*b*) Noble gases being monoatomic gases have no interatomic forces except weak dispersion forces, therefore they have low boiling points.

Q. 10. **(*i*) Draw structure and name the shape of the following:** ***[CBSE 2019 (56/5/2)]***

(*a*) SF_4 **(*b*) ICl_3**

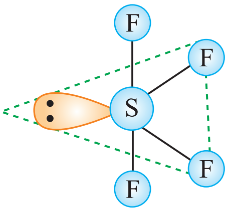
(*ii*) What happens when (Support your answer with equation)

(*a*) Chlorine gas is passed through hot and concentrated sodium hydroxide solution?

(*b*) Xenon hexafluoride is subjected to complete hydrolysis?

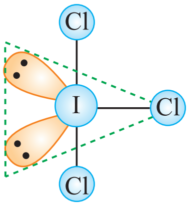
(*c*) Concentrated sulphuric acid is poured over cane sugar?

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



SF_4
See-saw

(*b*)



ICl_3
T-shaped

(*ii*) (*a*) It forms sodium chlorate and sodium chloride.

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

(*b*) Xenon hexafluoride on complete hydrolysis gives XeO_3.

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

(*c*) Charring of cane sugar takes place.

$$C_{12}H_{22}O_{11} + \text{conc.}\, H_2SO_4 \longrightarrow 12C + 11H_2O$$

Q. 11. **Explain the following:**

(*i*) Hydrogen fluoride is a weaker acid than hydrogen chloride in aqueous solution.

(*ii*) SF_6 is inert towards hydrolysis.

(*iii*) H_3PO_3 is diprotic.

(*iv*) Out of noble gases only xenon is known to form established chemical compounds.

[CBSE Sample Paper 2016]

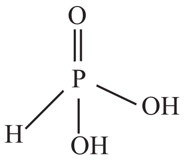
Ans. (*i*) It is due to

(*a*) Higher H—F bond dissociation energy than H—Cl.

(*b*) Stronger H-bonding of F^- ion with H_3O^+ than Cl^-,

(*ii*) In SF_6, S atom is sterically protected by six F atoms and does not allow water molecules to attack the S atom. Further, F does not have *d*-orbitals to accept the electrons donated by H_2O molecules. Due to these reasons, SF_6 is kinetically an inert substance.

(*iii*)



Since it contains only two ionisable H-atoms which are present as OH-groups, it is diprotic.

(*iv*) Except radon which is radioactive, xenon has least ionization enthalpy among noble gases hence it forms compounds particularly with O_2 and F_2.

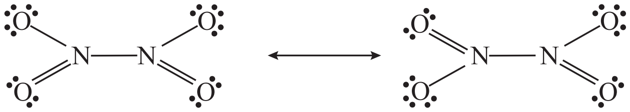
Q. 12. **On heating, lead (II) nitrate gives a brown gas "A". The gas "A" on cooling changes to colourless solid "B". Solid "B" on heating with NO changes to a blue solid 'C'. Identify 'A', 'B', 'C' and also write reactions involved and draw the structures of 'B' and 'C'.** ***[NCERT Exemplar]*** ***[HOTS]***

Ans. $$2Pb(NO_3)_2 \xrightarrow[673\text{ K}]{\Delta} 2PbO + \underset{\substack{\text{(A)}\\\text{(Brown colour)}}}{4NO_2} + O_2$$

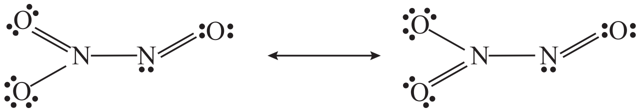
$$2NO_2 \underset{\text{On heating}}{\overset{\text{On cooling}}{\rightleftharpoons}} \underset{\substack{\text{(B)}\\ \text{(Colourless solid)}}}{N_2O_4}$$

$$2NO + N_2O_4 \xrightarrow[250\text{ K}]{\Delta} \underset{\substack{\text{(C)}\\ \text{(Blue solid)}}}{2N_2O_3}$$

Structure of N_2O_4



Structure of N_2O_3



Q. 13. **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).** **[*HOTS*]**

Ans. A = White phosphorus B = Red phosphorus

C = Phosphine (PH_3) D = Phosphorus pentachloride (PCl_5)

E = Phosphoric acid (H_3PO_4)

Reactions are:

$$\underset{\substack{\text{White phosphorus}\\ \text{(A)}}}{P_4(s)} \xrightarrow[\text{Inert gas}]{\Delta} \underset{\substack{\text{Red phosphorus}\\ \text{(B)}}}{P_4(s)}$$

$$\underset{\substack{\text{White phosphorus}\\ \text{(A)}}}{P_4(g)} + 3KOH(aq) + 3H_2O \xrightarrow{\Delta} \underset{\substack{\text{Potassium}\\ \text{hypophosphite}}}{3KH_2PO_2(aq)} + \underset{\substack{\text{Phosphine}\\ \text{(C)}}}{PH_3(g)}$$

$$\underset{\substack{\text{Phosphine}\\ \text{(C)}}}{PH_3(g)} + 4Cl_2(g) \longrightarrow \underset{\substack{\text{Phosphorus}\\ \text{pentachloride}\\ \text{(D)}}}{PCl_5(g)} + 3HCl(g)$$

$$\underset{\substack{\text{Phosphorus pentachloride}\\ \text{(D)}}}{PCl_5(g)} + 4H_2O(l) \longrightarrow \underset{\substack{\text{Phosphoric acid}\\ \text{(E)}}}{H_3PO_4(aq)} + 5HCl(aq)$$

Q. 14. **(*i*) When concentrated sulphuric acid was added to an unknown salt present in a test tube a brown gas (*A*) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, the gas (*A*) changed into a colourless solid (*B*).**

(*a*) Identify (*A*) and (*B*).

(*b*) Write the structures of (*A*) and (*B*).

(*c*) Why does gas (*A*) change to solid on cooling?

(*ii*) Arrange the following in the decreasing order of their reducing character:

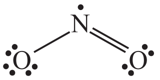
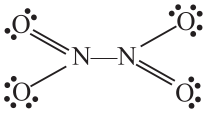
HF, HCl, HBr, HI

(*iii*) Complete the following reaction:

$$XeF_4 + SbF_5 \longrightarrow$$ **[*CBSE 2018*]**

Ans. (*i*) (*a*) *A* = $NO_2(g)$, Nitrogen dioxide

B = $N_2O_4(s)$, Dinitrogen tetroxide

(*b*)  ; 

(A) (B)

(*c*) $NO_2(A)$ contains odd number of valence electrons. On cooling it undergoes dimerisation, and converted to stable $N_2O_4(B)$ molecule with even number of electrons.

(*ii*) $HI > HBr > HCl > HF$

(*iii*) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

Q. 15. (*i*) Complete the following reactions:

(*a*) $PbS(s) + O_3 \longrightarrow$

(*b*) $XeF_6 + NaF \longrightarrow$

(*ii*) Arrange the following in increasing order of property indicated, giving reason:

(*a*) Hydrides of group 15 — boiling points

(*b*) Hydrides of group 17 — acidic strength

(*c*) Hydrides of group 16 — reducing character **[*CBSE 2019 (56/4/3)*]**

Ans. (*i*) (*a*) $PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$

(*b*) $XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$

(*ii*) (*a*) $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

(*b*) $HF < HCl < HBr < HI$

(*c*) $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. The most powerful oxidising agent is:

(*a*) fluorine (*b*) chlorine

(*c*) bromine (*d*) iodine

2. Geometry of $XeOF_4$ molecule is:

(*a*) square planar (*b*) square pyramidal

(*c*) triangular pyramidal (*d*) octahedral

3. The hybridisation state of XeF_6 is

(*a*) sp^3d (*b*) sp^3d^2

(*c*) d^2sp^3 (*d*) sp^3d^3

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. (3 × 1 = 3)

4. **Assertion (*A*) :** Higher noble gases are soluble in water.
Reason (*R*) : Noble gases are monoatomic in nature.

5. **Assertion (*A*) :** SO_2 acts as a Lewis base.
Reason (*R*) : S atom in SO_2 contains one lone pair of electrons.

6. **Assertion (*A*) :** HI cannot be prepared by the reaction of KI with concentrated H_2SO_4.
Reason (*R*) : HI has lowest H–X bond strength among halogen acids.

Answer the following questions:

7. Complete the equation: **(1)**

$$XeF_4 + O_2F_2 \longrightarrow$$

[*CBSE Delhi 2014; (AI) 2014*]

8. Why does PCl_3 fumes in moisture? **(1)**

9. Complete the following equations:

(*i*) $\underset{\text{excess}}{Br_2} + F_2 \longrightarrow$

(*ii*) $PH_3 + HgCl_2 \longrightarrow$ **[*CBSE (F) 2011*] (2)**

10. Give reasons for the least reactivity of nitrogen molecule. **(2)**

11. Give reasons for the following:

(*i*) Noble gases are mostly inert.

(*ii*) Noble gases form compounds with fluorine and oxygen only. **(2)**

12. Give reasons for the following:

(*i*) Solid phosphorus pentachloride behave as an ionic compounds.

(*ii*) Sulphur in vapour state exhibits paramagnetism. **(2)**

13. Explain the following:

(*i*) The N—O bond in NO_2^- is shorter than the N—O bond in NO_3^-. **[*CBSE Delhi 2011*]**

(*ii*) H_3PO_2 is stronger reducing agent than H_3PO_3. **[*CBSE (F) 2014*]**

(*iii*) White phosphorus is more reactive than red phosphorus. **[*CBSE (F) 2013*] (3)**

14. Explain why:

(*i*) NH_3 is a good complexing agent.

(*ii*) iron dissolves in HCl to form $FeCl_2$ and not $FeCl_3$.

(*iii*) group 16 elements are called Chalcogens. **(3)**

15. Predict the shape and the asked angle (90° or more or less) in each of the following cases:

(*i*) SO_3^{2-} and the angle O—S—O

(*ii*) ClF_3 and the angle F—Cl—F

(*iii*) XeF_2 and the angle F—Xe—F **[*CBSE Delhi 2012*] (3)**

16. On heating compound (*A*) gives a gas (*B*) which is a constituent of air. This gas when treated with 3 mol of hydrogen (H_2) in the presence of a catalyst gives another gas (*C*) which is basic in nature. Gas *C* on further oxidation in moist condition gives a compound (*D*) which is a part of acid rain. Identify compounds (*A*) to (*D*) and also give necessary equations of all the steps involved. **(5)**

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*b*)