

# **THE P-BLOCK ELEMENTS**

#### **p-Block Elements:**

Groups of groups 13 to 18 are known as p-block elements.

**General electronic configuration of p-block objects:** Pblock elements are usually identified by ns2np1-6 valence shell electronic configuration.

**Representative elements:** The elements that are part of the s and p-blocks in the periodic table are called representative elements or group elements.

#### **Inert pair Effect:**

The inert pair theory was proposed by Sidgwick. He along with Powell accounted for the shapes of several molecules and correlated the shapes with some of their physical properties.

The non-participation of the two s electrons in bonding due to the high energy needed for unpairing them.

#### **Example of Inert Pair Effect**

The inert pair effect among group 4 and group 5 elements.  $Sn^{2+}$  and  $Pb^{2+}$  and  $Sb^{3+}$  and  $Bi^{3+}$  which are the lower oxidation states of the elements are formed because of the inert pair effect. When the s electrons remain paired the oxidation state is lower than the characteristic oxidation state of the group.

#### **Group 15 elements:**

Nitrogen (N) Phosphorous(P) Non-metals Arsenic (As) Antimony(Sb)

Metalloids

Bismuth (Bi)

metals

**Nitrogen family:** Nutrients 15 - nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi) are part of the  $ns^2np^3$  configuration.

Extra stable half-filled due to half-filled p-orbitals

#### **Electronic configuration:**

Elements	Electronic configuration $(ns^2 np^3)$
$7^N$	[He]2s <sup>2</sup> 2p <sup>3</sup>
15 <sup>P</sup>	[Ne]3s <sup>2</sup> 3p <sup>3</sup>
33 <sup>As</sup>	$[Ar]_{3d}^{10}_{4s}^{2}_{4p}^{3}_{3d}$
51 <sup>Sb</sup>	$[Kr]_{4d}^{10}_{5s}^{2}_{5p}^{3}_{3p}^{3}$
83 <sup>Bi</sup>	$[Xe]_4 f^{14}_{5d} f^{10}_{6s} f^{2}_{6p}^3$

#### **Atomic and Ionic Radii**

If you see the electronic configuration of elements in the table above, you will notice that with every step you move downwards, new orbitals are added to the atom.

This addition of new orbitals increases both the Atomic and the Ionic radii of group 15 elements.

However, we see that from Arsenic to Bismuth only a small increase in ionic radius is observed.

This is due to the presence of completely filled d and/or f orbitals in heavier members.

#### **Ionization Enthalpy**

Ionization Energy is the amount of energy required to remove an electron from the outermost orbit

This is basically a measure of how hard the nucleus is holding on to the electron.

The closer the electron is to the nucleus the stronger its hold and thus the energy required is more.

As we move down the group, the radius of the atom increases, and therefore the Ionization energy decreases due to the weaker hold of the nucleus.

## Note

because of the extra stable half-filled orbitals, electronic configuration and small size, the first ionisation enthalpy is much greater than that of group 14 elements in the corresponding period.

The order of successive ionisation enthalpy is as follows:

 $\Delta i H_1 < \Delta i H_2 < \Delta i H_3$ 

#### Electronegativity

The electronegativity value decreases down the group with increasing atomic size.

This again is due to the increasing distance between the nucleus and the valence shell as we move down the group.

## Occurrence

**Q**.

Molecular nitrogen comprises about 78% by volume of the Earth's atmosphere, it is not very abundant in the earth's

crust. Since nitrates are very soluble in water so these are not widespread in the earth's crust. The only major nitrate minerals are NaNO $_3$  and KNO $_3$ 

Nitrogen is also an important constituent of proteins, amino acids and nucleic acids in plants and animals. The continuous interchange of nitrogen between the atmosphere and biosphere is called nitrogen cycle.

Phosphorus is the eleventh element in order of abundance in crystal rocks of the earth. All its known minerals are orthophosphates.

#### The common minerals of phosphorus are:

- (i) Phosphorite Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>
- (ii) Fluorapatite Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F or Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>CaF<sub>2</sub>
- (iii) Chlorapatite Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl or 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. CaCl<sub>2</sub>
- (iv) Hydroxyapatite : Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH or 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.Ca(OH)<sub>2</sub>

Phosphorus is essential for life, both as a structural material in animals and plants. It is present in bones as well as in living cells. About 60% bones and teeth are  $Ca_3(PO_4)_2$  or  $[3\{Ca_3(PO_4)_2.CaF_2]$ .

It also occurs in nucleic acids (DNA and RNA) which control the hereditary effects in human beings. Phosphorus is also found in ATP (adenosine triphosphate and ADP (adenosine diphosphate).

The elements arsenic, antimony and bismuth are not very abundant. These are obtained as metallurgical by-products from roasting sulphide ores.

#### Nitrogen exists as diatomic molecule and phosphorus as P<sub>4</sub> why?

**Sol.** Due to its small size and high electronegativity, nitrogen atom forms  $p\pi-p\pi$  multiple bonds with itself (triple bond); so it exists as a discrete diatomic molecule in elemental form. On moving down a group, the tendency to form  $p\pi-p\pi$  bonds decreases (because of the large size of heavier elements). The phosphorus atom has a large size and less electronegativity so it forms single bond instead of  $p\pi-p\pi$  multiple bonds. Therefore, phosphorus (like other heavier metals) exists as P4 molecule in its elemental form.

## **Q.** Dinitrogen is a gas but phosphorus is a solid.

**Sol.** Nitrogen due to small size and high electronegativity forms  $\rho\pi-\rho\pi$  multiple bonds and exists as a diatomic molecule. These molecules are held together by weak Van der Waal forces and hence N<sub>2</sub> exist as a gas at room temperature. In contrast due to larger size and lower electronegativity P does not form  $\rho\pi-\rho\pi$  bond with itself rather it prefer to form single P–P bonds and exist as tetrahedral P<sub>4</sub> molecules. Due to bigger size, the force of attraction holding P<sub>4</sub> molecules are quite strong and cannot broken by the collision of molecules at room temperature and hence solid at room temperature.

#### Allotropy:

Except nitrogen and bismuth, all other elements of this group show allotropy.

Exampl	e
<ul><li>(a) Phosphorus exists as white, black or red phosphorus.</li><li>(c) Antimony exists as yellow or silvery grey allotropic forms.</li></ul>	(b) Arsenic exists as yellow or grey arsenic
<b>Metallic Character</b> Metallic character: The elements of group 15 are less metallic. However, on moving down the group, the metallic character	increases from N to Bi. For example: N and P are non-metallic, As and Sb are partly non-metallic while Bi is a metal.

Due to increased nuclear charge and higher electronegativity, the elements of group 15 are less metallic than the corresponding elements of group 14.

On moving down the group, the atomic size as well as the screening effect of the intervening electrons increases. As a result, the ionization enthalpy decreases and therefore, metallic character increases down the group.

#### Melting point and boiling point

Melting and boiling points: The melting points of group 15 elements first increase from nitrogen to arsenic and then decreases to antimony and bismuth. However, the boiling points increase regularly on going from nitrogen to bismuth.

#### **Explanation**:

The melting points increase down the group due to increase in atomic size However, the unexpected decrease in the melting points of Sb and Bi is because of their tendency to form three covalent bonds instead of five covalent bonds, due to inert pair effect. As a result, the attraction among their atoms is weak and hence their melting points are low. Because of large size of atoms, Bi has still weaker interatomic forces than Sb and therefore, has still lower melting point. The boiling points increase down the group from N to Bi because of increase in their atomic size.

#### **Physical properties:**

All the elements of the group exist in a polyatomic state.

First, Nitrogen is gas, but as you move down, there is a significant increase in the metallic character of the elements.

Nitrogen and Phosphorus are non-metals, Arsenic and Antimony are metalloids and Bismuth is a metal.

These changes can be attributed to the decrease in Ionization enthalpy and increase in atomic size.

Boiling points also, in general, show an increasing trend as you move down.

Except for Nitrogen, all the other elements have allotropes.

#### **Oxidation state:**

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

Group 15 elements usually show -3, +3 and +5 oxidation state. The tendency to show a state of 3 oxidation decreases as we go down the group due to the increase in atomic size and the metal element.

Group 15 elements also show good oxidation conditions of +3 & +5 by forming bonds. Due to the inert pair effects the stability of +5 oxidation state decreases below the group, while that of +3 oxidation state increases. Nitrogen has only s- and p-orbitals, but no d-orbitals in its valance shell. Therefore, nitrogen can show up to 4 covalency. The fourth covalency is obtained by sharing one pair of electrons with another atom or ion.

Phosphorus and other heavier elements can exhibit five coagulation and higher coagulation, also called extensor covalency of the sixth. This may be due to the presence of empty d-orbitals in the valence shell. All fifteen compounds of the group elements, showing an oxidation state +5.

In the case of +3 oxidation, both ionic and covalent compounds are formed.

In a group of fifteen elements, the covalent character decreases from nitrogen to bismuth. Nitrogen, due to its small size, high electro-negativity and strong tendency to form multiple p pi-p pi bonds, exhibits various oxidation conditions from -3 to +5.

Compound	Oxidation State	
NH <sub>3</sub> Ammonia	-3	
N <sub>2</sub> H <sub>4</sub> Hydrazine	-2	
NH <sub>2</sub> OH	1	
Hydroxylamine	-1	
N <sub>2</sub> Dinitrogen	0	
N <sub>2</sub> 0 Nitrous oxide	+1	
NO Nitric oxide	+2	
N <sub>2</sub> O <sub>3</sub> Nitrogen	+3	
trioxide		
N <sub>2</sub> O <sub>4</sub> Nitrogen	+4	
tetroxide		
N <sub>2</sub> O <sub>5</sub> Nitrogen	+5	
pentoxide	+J	

## **Q**. Why +3 oxidation state is stable in heavier elements of Group 15?

**Sol.** As we move down in Group 15, we can see the inert pair effect. This effect impacts the penetration effect of 's orbitals. These orbitals penetrate and come closer to the nucleus and enjoy greater nuclear attraction. Also, these orbitals, then, don't participate in bonding. This is the reason why the stability of +3 oxidation state increases in heavier elements of Group 15 in comparison with +5 oxidation state.

#### Note

in the case of nitrogen, all oxidation state from +1 to +4 tend to disproportionate in acid solution.

Example

Nitrogen is restricted to a maximum covalency of 4 since only four orbitals are available for bonding.

# Q. Give reason for the anomalous behaviour of nitrogen in group 15. Also give the chemical evidence for the same.

**Sol.** Nitrogen being small in size, highly electronegative, has high ionisation energy and non-availability of valence electrons in d orbital oxygen shows anomalous behaviour.

## Reasons for anomalous behaviour of nitrogen

Small size: Due to its small size, it possesses high electronegativity, high ionisation enthalpy and absence of d-orbitals.

Pi bond formation: N<sub>2</sub> has a unique ability to form  $p\pi$ -  $p\pi$  multiple bonds whereas the heavier members belonging to this group (15) do not form  $p\pi$ -  $p\pi$  bond because their atomic orbitals are so large and diffused that they cannot have effective overlapping.

Diatomic molecule: Nitrogen exists as a diatomic molecule with a triple bond between the two atoms whereas other elements form a single bond in the elemental state.

## Q. Why dinitrogen is inert at room temperature?

**Sol.** This is because of high bond dissociation enthalpy of triple bond in nitrogen molecule

#### Note

the single N-N bond is weaker than single P-P bond because of high inter-electronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.

## **Reactivity towards Hydrogen:**

- 15 group elements react with H to form hydrides of type EH<sub>3</sub> where E = N, P, As, Sb or Bi.
- As you move down from NH<sub>3</sub> to BiH<sub>3</sub>, the stability of hydrides decreases.
- For example, the PH<sub>3</sub> bond in PH<sub>3</sub> is slightly stable than the N-H bond in NH<sub>3</sub>.
- The strength of the E-H bond weakens as the size of the central atom increases.
- The stability of the E-H bond (where E is a group of 15 elements) can be represented as
- N-H> P-H> As-H> Sb-H> Bi-H

#### Note

Ammonia is a mild reducing agent and BiH3 is the strongest reducing agent amongst all the hydrides (because down the group, there are weaker bonds, so bond length will increase and reducing character increases)



**Basicity:**  $NH_3$  and other hydrides are basic in nature because of presence of lone pair.

## Basicity decreases down the group



Basic character decreases down the group because of increase in size of the central atom and thus reduction, in its tendency to give lone pair with decrease in electron density.

## Q. PH<sub>3</sub> when passed through water forms bubbles while NH<sub>3</sub> doesn't why?

**Sol.** PH<sub>3</sub> forms bubbles because it is insoluble in water and cannot form hydrogen bonds with water whereas NH<sub>3</sub> dissolves because it is soluble in water and can form hydrogen bonds with water.

#### Bond angle:

## NH<sub>3</sub> (107.8°) > PH<sub>3</sub> (99.5°) > AsH<sub>3</sub> (91.8°) $\approx$ SbH<sub>3</sub> (91.3°) > BiH<sub>3</sub> (90°)

Bond angle decreases  $\rightarrow$  The hydrides of these elements are pyramidal in shape with a lone pair of electrons in one of the orbitals. On moving down the group the bond angles gradually decrease due to a decrease in bond pair-bond pair repulsion.

#### **Reactivity towards Oxygen:**

- Fifteen group elements react with O to form  $E_2O_3$  and  $E_2O_5$  oxides in which E = N, P, As, Sb or Bi.
- Oxide of the element with a high oxidation state is much more acidic than those with low oxidation conditions.
- Under the group, the acidity of the oxide is reduced.

#### **Reactivity towards Halogen:**

• 15 group elements form halides of type EX<sub>3</sub> and EX<sub>5</sub> where E = N, P, As, Sb or Bi.

- However, N does not form pentahalides EX5 as it does not contain d-orbital.
- All 15 group elements form trihalides but N's trihalides are not stable.

## Q. All the bonds in PCl<sub>5</sub> are not equivalent. Why?

**Sol.** PCl<sub>5</sub> has a triagonal bipyramidal structure due to dsp<sup>3</sup> hybridization. Due to this two Cl atoms lie along axial line and other three Cl-atoms lie along the equitorial plane. Hence, the bond lengths are different.



## Q. Pentahalides are more covalent than trihalides. Explain.

**Sol.** The oxidation state of +5 in pentahalides is more as compared to +3 oxidation state in trihalides. Due to the higher positive oxidation state of central atom in pentahalide state, these atoms will have larger polarizing power than the halogen atom attached to them.

But In case of trihalides due to +3 oxidation state the central atom will polarize the halogen atom to a lesser extent as compared to pentahalide state.

Hence due to larger polarization of bond in pentahalide state as compared to trihalide state, the pentahalides are more covalent than trihalides.

## Q. Bromides are more covalent than chlorides. Why?

Sol. Size of bromide > size of chloride It is because larger the size of an anion, more is its polarizibility and hence greater is the covalent character (FAZAN's rule)

## **Q**. **BiF**<sup>3</sup> is predominantly ionic. Why?

**Sol.** Bismuth is a metal and fluorine is a nonmetal. Also, the electronegativity of fluorine is the highest and hence, greater electronegativity difference between them, makes BiF<sub>3</sub> ionic.

## Q. PCl<sub>5</sub> exists while NCl<sub>5</sub> doesn't, why?

**Sol.** PCl<sub>5</sub> forms five bonds by using the dorbitals to "expand the octet" and have more places to put bonding pairs of electrons. NCl<sub>5</sub> does not exist because there are no d-orbitals in the second energy level. Therefore there is no way to arrange five pairs of bonding electrons around a nitrogen atom.

## **Try yourself**

- **Q.** Illustrate with the help of an equation, why +5 oxidation state of Bi is less stable than +3 state?
- **Q.** The H-N-H angle value is higher than H-P-H, H-As-H, H-Sb-H angles. Why?

## **Reactivity towards Metals:**

- 15 group elements react with metals to form compounds of the common formula  $M_3E_2$  where E = N, P, As, Sb or Bi.
- Binary combinations formed by the reaction of 15 group elements with metal show oxidation state -3.

## Dinitrogen:

#### **Preparation:**

NH<sub>4</sub>Cl (aq) + NaNO<sub>2</sub> (aq)  $\rightarrow$  N<sub>2</sub> (g) + 2H<sub>2</sub>O (l) + NaCl (aq) (NH<sub>4</sub>)<sub>2</sub> Cr<sub>2</sub>O<sub>7</sub>  $\rightarrow$  N<sub>2</sub> + 4H<sub>2</sub>O + Cr<sub>2</sub>O<sub>3</sub> Ba(N<sub>3</sub>)<sub>2</sub>  $\rightarrow$  Ba + 3N<sub>2</sub>

#### **Properties:**

Colourless, odourless, tasteless and non-toxic gas

Inert at room temperature

Low solubility in water and low freezing and boiling point

- $6Li + N_2 \xrightarrow{heat} 2Li_3N$  (lithium nitride)
- $N_2$  (g) +  $3H_2$   $\frac{773 \text{ K}}{2NH_3}$  2NH<sub>3</sub>
- $N_2 + O_2 \rightarrow 2NO \rightarrow only$  at high temperature

#### Uses:

In the manufacture of ammonia and other industrial chemicals

Used where inert atmosphere is required

Liquid dinitrogen is used as refrigerant to preserve biological materials and food items.

#### Ammonia:

The ammonia molecule is a triangular pyramid with a nitrogen atom at the top. It has three bond pairs and one pair. N is a sp<sup>3</sup> compound.

## Preparation

 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ 



## **Properties:**

Azane is a gas which is colourless in nature and has a pungent smell.

It boils at 198.4K and 239.7K.

This gas is highly dissolvable in water. The aqueous solution of NH3 is a weak base as OH- ions are formed.

 $NH_3+H_2O \rightarrow NH_4^++OH^-$ 

Ammonium salts are formed when it reacts with an acid.  $ZnSO_4+2NH_4OH(g) \rightarrow Zn(OH)_2+(NH_4)_2SO_4$ 

## Uses:

- Properties of Ammonia in its aqueous state are used as a refrigerant.
- It is used in the manufacturing of urea. Urea is an excellent fertilizer of nitrogen.
- Azane can be used to remove grease due to its cleansing properties.

## Nitric acid:



## **Ostwald process:**

**Step 1:** Catalytic oxidation of ammonia  $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ 

**Step 2:** Oxidation of nitric oxide  $2NO + O_2 \rightarrow 2NO_2$ 

**Step 3:** Reaction with water and oxygen to form nitric acid:  $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$ 

The synthetic NO is then recycled and the aqueous  $HNO_3$  can be concentrated by immersion in up to 68% in quantity. An additional concentration of 98% can be achieved by dehydration with concentrated  $H_2SO_4$ .

Nitric acid is a strong oxidizing agent in the form of concentrates and dilute.

## **Properties:**

It is colourless in nature.

The boiling point of the liquid is 84.1°C and it freezes at -41.55 °C to form a white solid.

It acts as a strong acid which dissociates to form nitrate ions and hydronium.

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

 $HNO_{3}\xspace$  in its concentrated state acts as a strong oxidising state

 $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ Uses:

- The main use of nitric acid is in preparation of fertilizers.
- It is used in manufacturing several types of polymers like polyamides and polyurethane.
- Nitric Acid is also used mostly for the purification of precious metals like platinum, gold, and silver.
- Diluted nitric acid is used in wood works to fabricate maple and pine wood and make them look aged.

## **Phosphorus:**

It shows the area of catenation at a high level due to the stable P-P bond.

It has many allotropes, the most important of which are:

- White phosphorus
- Red phosphorus
- Black phosphorus

## White phosphorus:

- Translucent like white waxy solid
- Poisonous in nature
- Less stable and more reactive
- Does not dissolve in water
- When mixed with carbon disulphide it dissolves
- Glows in the dark(chemiluminescence)
- Further, the white form of it dissolves in NaOH in an inert atmosphere giving PH<sub>3</sub>. The reaction that takes place is as follows:
- $P_4$  + 3NaOH + 3H<sub>2</sub>O  $\rightarrow$  PH<sub>3</sub> + 3NaH<sub>2</sub>PO<sub>2</sub>

(sodium Hypophospite)



- Due to the angular strain in P<sub>4</sub> molecule (wherein the angle is 60°), In the presence of air, it readily catches fire and gives out dense white fumes of P<sub>4</sub>O<sub>10</sub>. The reaction is as follows: P<sub>4</sub>+5O<sub>2</sub>→P<sub>4</sub>O<sub>10</sub>
- The below figure shows that it has a discrete tetrahedral P<sub>4</sub> molecule:
- On heating white P<sub>4</sub> at 573K in an inert atmosphere for several days, red phosphorus is obtained. Further, on heating it under high pressure, a series of phases of black form is formed.

## **Red phosphorus:**

- Has iron grey lustre
- Odourless
- Non-poisonous
- Solubility properties: does not dissolve in water and carbon disulphide
- Does not glow in the dark
- Chemically, white phosphorus is more reactive than red phosphorus
- It is polymeric and consists of chains of P<sub>4</sub> tetrahedral linked together



#### **Black phosphorus:**

 $\alpha$ -black and  $\beta$ -black are two forms of black phosphorus. When red phosphorus is heated in a sealed tube at 803K, an  $\alpha$ -black form is formed. It can be sublimed in the air and has either rhombohedral crystals or opaque monoclinic. It does not oxidize in the air. When white form is heated under high pressure at 473 K  $\beta$ -Black is formed. It does not burn in the air up to 673K.



- 1. Translucent like white waxy solid
- 2. Poisonous in nature
- 3. Less stable and more reactive
- 4. Does not dissolve in water
- 5. When mixed with carbon disulphide it dissolves
- 6. Glows in the dark(chemiluminescence)
- 7. Further, the white form of it dissolves in NaOH in an inert atmosphere giving PH<sub>3</sub>. The reaction that takes place is as follows:

## **Phosphine:**



It is highly toxic, colourless and smells of rotten fish.

## **Preparation:**

 $\begin{array}{l} \text{Ca}_{3}\text{P}_{2} + 6\text{H}_{2}\text{O} \rightarrow 3\text{Ca}(\text{OH})_{2} + 2\text{PH}_{3} \\ \text{Ca}_{3}\text{P}_{2} + 6\text{HCl} \rightarrow 3\text{Ca}\text{Cl}_{2} + 2\text{PH}_{3} \\ \text{P}_{4} + 3\text{Na}\text{OH} + 3\text{H}_{2}\text{O} \rightarrow 3\text{Na}\text{H}_{2}\text{PO}_{2} + \text{PH}_{3} \end{array}$ 

## **Properties**:

- It is a highly poisonous gas.
- PH<sub>3</sub> is sparingly soluble in water and soluble in organic solvents.
- PH<sub>3</sub> acts as a Lewis base by donating its lone pair of electrons when it reacts with hydrogen iodide.
- Under normal conditions, it is a non-combustible gas, but when heated it catches fire which results in the formation of phosphoric acid.
- $PH_3 + 2O_2 \rightarrow H_3PO_4$
- When it comes in contact with oxidising agents it explodes violently.

## **Uses:**

- In semiconductor industries, it is used in small amounts as a dopant.
- PH<sub>3</sub> is used in Holme's signal due to its property of spontaneous combustion.

## **Phosphorus Chloride:**

(1) Phosphorus Trichloride



Phosphorus trichloride is a colourless oily liquid and highly toxic compound. The compound has a triangular pyramidal shape in which phosphorus is sp<sup>3</sup> hybridized.

## Preparation

When dry chlorine is passed over heated white phosphorus, phosphorus trichloride is produced.

 $P_4 \textbf{+} 6Cl_2 \textbf{\rightarrow} 4PCl_3$ 

When thionyl chloride reacts with white phosphorus, phosphorus trichloride is produced.

 $P + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$ 

## **Chemical Properties**

• Phosphorus trichloride hydrolyses in presence of moisture.

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

• It reacts with organic compounds containing -OH group to produce their chloro- derivatives.  $3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$ 

## (2) Phosphorus Pentachloride

Phosphorus pentachloride is a yellowish-white, water sensitive solid. It is soluble in carbon tetrachloride, carbon disulfide, benzene, and diethyl ether. It has a trigonal bipyramidal structure in gaseous and liquid phases. In a 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.



Due to greater repulsion at axial positions in comparison to equatorial positions the two axial bonds are longer than equatorial bonds.

## Properties

When white phosphorus reacts with an excess of dry chlorine, phosphorus pentachloride is produced.  $P_4 + 10Cl_2 \rightarrow 4PCl_5$ 

- It can also be prepared by the reaction of  $\mathsf{SO}_2\mathsf{Cl}_2$  and phosphorus.

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

## **Chemical properties**

- In moist air, phosphorus pentachloride hydrolyses to POCl<sub>3</sub> which finally converts to phosphoric acid. PCl<sub>5</sub> + H<sub>2</sub>O→POCl<sub>3</sub> + 2HCl POCl<sub>3</sub> + 3H<sub>2</sub>O→H<sub>3</sub>PO<sub>4</sub> + 3HCl
- It sublimes on heating and further decomposes to phosphorus trichloride in case of stronger heating. PCl<sub>5</sub>→PCl<sub>3</sub> + Cl<sub>2</sub>
- It reacts with finely divided metals under the influence of heat to produce metal chlorides.  $2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$
- It reacts with organic compounds containing –OH group to produce their chloro- derivatives.  $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

Q.	How does PCl <sub>5</sub> exists in solid state?
Sol.	In the solid state, $PCl_5$ exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which cation is $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ anion is octahedral.

#### Oxo acids of phosphorus

In oxoacids, phosphorus is tertrahedrally surrounded by other atoms. All these acids contain atleast one P = O bond and one P-OH bond.

The oxoacids in which phosphorus has oxidation state less than (+5) contain either P-P bond or P-H bond in addition to P-OH and P = 0 bonds but not both.



## **Q.** Why is H<sub>3</sub>PO<sub>3</sub> Dibasic?

Sol.	The above diagram describes the structure of Oxoacids of Phosphorus, H <sub>3</sub> PO <sub>3</sub> . If we observe the structure, two -OH groups are bonded to the phosphorus atom, and one hydrogen atom is bonded directly to the phosphorus atom. Breaking the O-H bond is easy. Therefore, to make this compound as diprotic, the two -OH groups are responsible. Whereas another hydrogen is directly bonded to the phosphorus atom, it is difficult to break the bond due to its highly stable nature.
0.	Because of this, H <sub>3</sub> PO <sub>3</sub> is a diprotic acid, but not the triprotic. What happens when H <sub>3</sub> PO <sub>3</sub> is heated?
Sol.	Orthophosphorous acid disproportionate to give orthophosphoric acid and phosphine $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

#### **Group 16 Elements:**

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Oxygen	8	[He] 2s <sup>2</sup> 2p <sup>4</sup>	16	2
Sulphur	16	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>	16	3
Selenium	34	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	16	4
Tellurium	52	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	16	5
Polonium	84	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>	16	6

## **Occurrence of Group 16 Elements**

Oxygen is the most abundant element available in nature. It contributes 20.946 percent of the volume of air and 46.6% of the earth's crust by mass as silicates and other compounds such as carbonates, oxides, and sulphates.

Photosynthesis in plants provides the vast majority of the oxygen in the air. It can also be found as ozone.

Sulphur is the sixteenth most abundant element. Ores contain sulphur in their combined state.

Gypsum CaSO<sub>4</sub>.2H<sub>2</sub>O, Epsom salt MgSO<sub>4</sub>.7H<sub>2</sub>O, and barytes BaSO<sub>4</sub> are all examples of sulphate ores.

Galena (PbS), zinc blende (ZnS), and copper pyrites (CuFeS<sub>2</sub>) are examples of sulphide ores.

Sulphur can also be found in a variety of organic substances, including mustard, eggs, seeds, onion, wool, garlic, and hair.

Metal selenides and tellurides of selenium and tellurium are found in sulphide ores.

Polonium is a naturally occurring radioactive element.

#### **Electronic Configuration of Group 16 Elements**

The elements in Group 16 have 6 electrons in their valence shell and have the following general electronic configuration:  $ns^2np^4$ .

#### **Atomic and Ionic Radii of Group 16 Elements**

The atomic and ionic radii of this group's elements are smaller than those of group 15's corresponding elements. As one moves down the group, the atomic and ionic radii of the elements increase.

## **Ionisation Enthalpy**

The ionization enthalpy of this group's elements is smaller than those of group 15's corresponding elements. As one moves down the group, the ionization enthalpies of the elements decrease.

Members of group 16 have higher second ionisation enthalpies than members of group 15. This is due to the fact that after the first electron is removed, the second electron must be removed from a more symmetrical half-filled configuration, which is more stable.

- Q. Elements of group 16 generally show less value of 1<sup>st</sup> ionisation enthalpy compared to the corresponding period of group 15 why?
- **Sol.** Ans. Due to relatively stable half filled porbitals of group -15 elements. Large amount of energy is required to remove the eletrons.

#### **Electron Gain Enthalpy**

The electron gain enthalpy decreases as the atomic size increases down the group. The electron gain enthalpy of oxygen is less negative than that of sulphur. Because of its compact nature, oxygen experiences more repulsion between the electrons already present and the incoming electron. Because of these electron-electron repulsions, the oxygen atom has a lower proclivity to accept the extra electron than the sulphur atom.

#### Electronegativity

The elements of group 16 have higher electronegativity values than the elements of group 15. The second most electronegative element is oxygen, with fluorine being the first. As one moves down the group, the electronegativity decreases. The increase in atomic radii of elements causes a decrease in electronegativity.

#### Note

Next to fluorine, oxygen has the highest electronegativity value amongst the elements.

#### **Metallic Character**

Metallic character increases down the group. The first two elements- oxygen and sulphur are non-metals. Selenium and

tellurium being the metalloid, and polonium can be classified as a metal.

#### Melting point and boiling point:

As the size of an atom rises from oxygen to tellurium, boiling point also increase. The main difference between melting and boiling points of oxygen and sulphur can be explained by the fact that oxygen exists as a diatomic atom whereas sulphur exists as polyatomic particles.

## **Q**. There is a large difference between the melting and boiling point of oxygen and sulphur. Why Explain?

**Sol.** Oxygen exists as diatomic molecule (O<sub>2</sub>) whereas sulphur exists as polyatomic molecule (S<sub>8</sub>). The van der Waals forces of attraction between O2 molecules are relatively weak owing to their much smaller size. The large van der Waals attractive forces in the S8 molecules are due to large molecular size. Therefore oxygen has low m.pt. and b.pt. as compared to sulphur.

#### **Chemical Properties**

#### **Oxidation state:**

The group 16 elements have an outer shell configuration of  $ns^2np^4$ ; they can achieve noble gas configuration by gaining two electrons, forming M<sup>-2</sup> ion, or by sharing two electrons, forming two covalent bonds. As a result, these elements represent both negative and positive oxidation states. The elements in group 16 have regular oxidation states of -2, +2, +4 and +6.

- **O.** SF<sub>6</sub> exists while OF<sub>6</sub> doesn't why?
- **Sol.** SF<sub>6</sub> exists but OF<sub>6</sub> does not because oxygen does not have vacant d-orbitals in the valence shell. Electrons in oxygen cannot be excited to higher levels to six unpaired electrons. In 'S' it is possible to do so as it has vacant d-orbital



#### Anomalous Behaviour of oxygen

- The small size of these atoms
- High electronegativity
- Large charge/radius ratio
- These elements also have only 4 valence orbitals available (2s and 2p) for bonding as compared to the 9 available (3s,

3p, and 3d) to the other members of the respective groups, so their maximum covalency is 4.

#### **Reactivity with Hydrogen:**

When group 16 elements combine with hydrogen they form hydrides with the common formula  $H_2$ 

Hydrides formed are:

H<sub>2</sub>O H<sub>2</sub>S H<sub>2</sub>Se H<sub>2</sub>Te

(Water) (hydrogen sulphide) (hydrogen selenide)( hydrogenteluride)

They all have curved geometry with sp3 hybridization. The geometry shown by them is:

Meltingpoint:Forcovalenthydrides,Melting point $\propto$ Van der waal's force $\propto$ Molecular massThus, melting point order is  $H_2Te > H_2Se > H_2S.$ 

**Boiling point**: The boiling points of the hydrides of group 16 elements is as follows:

 $\begin{array}{l} H_2O \rightarrow 100^{\circ}C \\ H_2S \rightarrow - (60^{\circ}C) \\ H_2Se \rightarrow - (41.25^{\circ}C) \\ H_2Te \rightarrow - (2.2^{\circ}C) \end{array}$ 

Gradual increase in boiling points down the rest of the group happens as the relative molecular mass of the molecules increases.

Also, boiling point of water is anomalously high.

**Thermal stability**: The thermal stability of the hydrides of group 16 elements decreases down the group, i.e.,  $H_2O > H_2S > H_2Se > H_2Te > H_2Po$ . This is because M-H bond dissociation energy decreases down the group with the increase in the size of central atom.

**Reducing character**: All hydrides of group 16 elements, except  $H_2O$ , are reducing agent. The reducing power of these hydrides increase in going from  $H_2S$  to  $H_2Te$ , which may be due to increase in the size of the atom and hence decrease in the M-H bond energy.

#### **Reactivity with Oxygen:**

• All elements of group 16 react with oxygen and form oxides of types EO<sub>2</sub> and EO<sub>3</sub> when E = S, Se, Te or Po.

## Example

## are: SO<sub>2</sub>, SeO<sub>2</sub>, TeO<sub>2</sub>, SO<sub>3</sub>, TeO<sub>3</sub>, etc.

• SO<sub>2</sub> and SeO<sub>2</sub> are naturally acidic and react with water to form acids.

 $SO_2 + H_2O \rightarrow H_2SO_3$ Sulphurous acid  $SeO_2 + H_2O \rightarrow H_2SeO_3$ Selenious acid

• Reducing power decreases from SO<sub>2</sub> to TeO<sub>2</sub>.

#### Note

 $S \ SO_2$  is an oxidising agent, while TeO2 is a reducing agent.

SO<sub>3</sub>, SeO<sub>3</sub> and TeO<sub>3</sub> are also naturally acidic. They react in water to form acids.
 SeO<sub>3</sub> + H<sub>2</sub>O → H<sub>2</sub>SeO<sub>4</sub>

Selenic acid  $TeO_3 + 3H_2O \rightarrow H_6TeO_6$ Telluric acid

## **Reactivity with Halogen:**

They react with halogen to form halides of formulas  $\text{EX}_4$ ,  $\text{EX}_6$  and  $\text{EX}_2$ .

The stable order of the halides are:

F>Cl>Br>I

A group 16 elements react with iodine to form tetra iodides. Oxygen makes only halides  $OF_2$  and  $O_2F$ .

Sulphur forms SCl<sub>2</sub> (sulphur dichloride), SF<sub>6</sub> (sulphur hexafluoride) and SF4 (sulphur tetra fluoride).

Geometry of SF<sub>4</sub> is a tetrahedral with hybridization sp3d and geometry of SF<sub>6</sub> trigonal bipyramidal and hybridization sp $^3d^2$  as shown:

## **Q.** SF<sub>6</sub> exists while SCl6 doesn't why?

**Sol.** Due to small size of fluorine, six F atoms can be accommodated around sulphur whereas chloride ion is comparatively larger in size, therefore, there will be interatomic repulsion

## **Q.** SF6 is inert towards hydrolysis. Explain.

**Sol.** In SF<sub>6</sub>, 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<sub>2</sub>O molecules. Due to these reasons, SF<sub>6</sub> is kinetically an inert substance.

## Q. H<sub>2</sub>S is gas while H<sub>2</sub>O is liquid. Why?

**Sol.** In H<sub>2</sub>O there is hydrogen bonding because oxygen has a high electronegativity.

So, the hydrogen atoms from other molecules of water form a hydrogen bonds with oxygen resulting in intermolecular hydrogen bonding.

Therefore at room temperature,  $H_2O$  is a liquid and  $H_2S$  is a gas.

## Oxygen:

Preparation:  $2KClO_3 \rightarrow 2KCl + 3O_2$   $2H_2O_2 (aq) \rightarrow 2H_2O (l) + O_2 (g)$   $2Ag_2O (s) \rightarrow 4Ag (s) + O_2 (g)$   $2HgO (s) \rightarrow 2Hg (l) + O2 (g)$   $2Pb_3O_4 (s) \rightarrow 6PbO (s) + O_2 (g)$  $2PbO_2 (s) \rightarrow 2PbO (s) + O_2 (g)$ 

Hydrogen peroxide in the presence of finely divided metals and manganese dioxide decomposes to give water and dioxygen.

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

Salts of chlorates, permanganates and nitrates decompose on heating to give  $O_2$ 2KCl $O_3 \rightarrow$  2KCl +  $3O_2$ 

## Industrial preparation of O<sub>2</sub>

 $O_2$  is obtained on a large scale from the air. Carbon dioxide and water are removed from the air, and the remaining gases are eliminated by fractional distillation and liquefaction, which releases dinitrogen and  $O_2$ .

#### **Properties of Dioxygen**

It is a colourless, odourless diatomic gas and paramagnetic in nature.

Oxygen is highly reactive non-metal.

This diatomic gas is a strong oxidizing gas.  $250 \pm 0 = 2250$ 

 $2SO_2 + O_2 \rightarrow 2SO_3$ 

It is the second most electronegative element after fluorine. Dioxygen reacts with metals, and non-metals to give oxides of the respective element.

 $2Ca + O_2 \rightarrow 2CaO$ 

## **Uses of Dioxygen**

Oxygen is used in many applications. Oxygen is used:

- As an oxygen supplement in medicine.
- For respiration purposes.
- In the industries for the smelting of iron ore to form steel.
- In metal cutting and welding.
- As an oxidizer in water treatment and rocket fuel.

## Q. Why is O<sub>2</sub> paramagnetic?

**Sol.** Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. According to molecular orbital Theory (MOT), there is 1 unpaired electron in the  $\pi^2 p_x$  antibonding orbital and another unpaired electron in  $\pi^2 p_y$  antibonding orbital.

As molecules containing unpaired electrons are strongly attracted by magnetic field, hence oxygen has paramagnetic nature.

Unpaired electrons spin in the same direction as each other which increases magnetic field effect.

## **Oxides:**

Oxygen and other nutrients are called oxides.  $SO_2 + H_2O \rightarrow H_2SO_3$  (Sulphurous acid)  $Na_2O + H_2O \rightarrow 2NaOH$   $K_2O + H_2O \rightarrow 2KOH$  $CaO + H_2O \rightarrow Ca(OH)_2$ 

## Types of oxides:

Acidic oxide:

Non-metallic oxides are usually naturally acidic. SO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  H<sub>2</sub>SO<sub>3</sub> (Sulphurous acid)

## **Basic oxide:**

Metallic oxides are very basic in nature. Basic oxides dissolve in water-soluble foundations e.g.  $Na_2O + H_2O \rightarrow 2NaOH$  $K_2O + H_2O \rightarrow 2KOH$  $CaO + H_2O \rightarrow Ca(OH)_2$ 

## Amphoteric oxide:

They show your properties both acidic and basic oxides.  $Al_2O_3 + 6HCl (aq) \rightarrow 2AlCl_3 (aq) + 3H_2O$   $Al_2O_3 + 6NaOH (aq) + 3H_2O (l) \rightarrow 2Na_3[Al(OH)_6] (aq)$ Neutral oxides:

These oxides are acidic and non-essential.

Example

CO, NO, N<sub>2</sub>O

## Q. Why does O<sub>3</sub> act as a powerful oxidizing agent?

**Sol.** Ozone is actually not a very stable compound in normal conditions. It decomposes readily on heating to form a molecule of oxygen along with nascent oxygen. Nascent oxygen is a free radical which is very reactive in nature.

 $0_3 \longrightarrow 0_2 + 0$ 

Ozone on heating, decomposes readily to form oxygen along with nascent oxygen which is very reactive. Hence, it acts as a powerful oxidizing agent.

## **O.** How is O<sub>3</sub> estimated quantitatively?

**Sol.** Quantitatively, ozone can be estimated with the help of potassium iodide. When ozone is made to react with potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated. This liberated iodine can be titrated against a standard solution of sodium thiosulphate using starch as an indicator.

 $\begin{array}{rcl} 2 \ I^- + H_2O + O_3 & \longrightarrow 2 \ OH^- + I_2 + O_2 \\ \mbox{lodide} & Ozone & Iodine \\ I_2 \ + \ 2 \ Na_2S_2O_3 & \longrightarrow & Na_2S_4O_6 \ + \ 2 \ NaI \\ & Sodium & Sodium \\ & thiosulphate & tetrathionate \end{array}$ 

#### Ozone: Preparation:

It is repaired by passing silent electricity through pure and dry oxygen 10-15% oxygen is converted to ozone.  $3O_2$  (g)  $\rightarrow 2O_3$  (g);  $\Delta$ H = +142 kJ/mol

**Ozone structure:** ozone has an angular structure. Both O = O bonds have the same bond length due to sound.

## **Properties of ozone**

• Ozone is a gas with a light blueish colour.

(-)

- It has a fishy smell.
- It condenses at 120°C to give a dull blue fluid. On further cooling, it hardens to give dark violet crystals.
- Thermodynamically, it is very unstable and disintegrates to oxygen. This is an exothermic process and is catalyzed by numerous materials. However, we must know that high concentration of the gas can be very dangerous.

## Uses:

- Ozone used at water treatment plants without filtration systems.
- Ozone may also be formed by commonly used equipment such as photocopiers, laser printers, and other electrical devices.
- In medicine, by limiting the effects of bacteria, viruses, fungi, yeast, and protozoa, ozone therapy is used to disinfect and treat diseases.

## Sulphur: Sulphur exhibits allotropy.

- **1** yellow rhombic
- 2 Monoclinic: Alpha-Sulphur <u>369 K</u> Bita-Sulphur

- **3** At 369 K both forms are stable. It is called the temperature change.
- $\label{eq:states} \textbf{4} \quad \text{Both contain } S_8 \text{ molecules}.$
- **5** The ring is puckered and has the shape of a crown.
- **6** Another allotrope of sulphur the cyclo ring takes the form of a chair.
- **7** S<sub>2</sub> is formed at high temperatures (1000 K).
- 8 Paramagnetic due to 2 uncoated electrons present in antibonding orbitals \* like O<sub>2</sub>.

## **Sulphur Allotropes:**

Rhombic sulphur (α-sulphur)

Rhombic sulphur is crystalline in nature and has an octahedral shape. On heating the solution of roll sulphur in  $CS_2$  we get rhombic sulphur. It is yellow with a melting point of 385.8K and specific gravity of 2.06. Rhombic sulphur cannot be dissolved in water but can be dissolved in benzene, ether, alcohol etc.

## **Monoclinic sulphur (β-sulphur)**

When we take a dish and melt rhombic sulphur in that dish we obtain monoclinic sulphur after cooling it. In this process, we make two holes in the crust and pour out the remaining liquid. After this, we get colourless needle-shaped crystals of  $\beta$ -sulphur when the crust is removed.

## **Q.** Do you know why 369K is called transition temperature?

**Sol.** 369K is called transition temperature because both the allotropes of sulphur are stable at this temperature. In other words, we can conclude that  $\alpha$ -sulphur is stable below 369K and it becomes  $\beta$ -sulphur above that temperature.

Rhombic and monoclinic sulphur, both have  $S_8$  molecules. The alternative packing of  $S_8$  molecules gives different crystal structures.

## **Q**. Which form of sulphur shows paramagnetic behaviour?

**Sol.** Sulphur exists as  $S_8$  molecule at ordinary temperature and pressure but at elevated temperature it gets dissociated and partly exists as  $S_2$  molecule in vapour phase.  $S_2$  molecule has two unpaired electrons in the antibonding  $\pi *$  orbitals like  $O_2$  molecule and hence, exhibits paramagnetism. Hence, sulphur in  $S_2$  form shows paramagnetic behaviour.

#### Sulphuric acid:

**Preparation:** Through the communication process

 $1/8 S8 + 02 \rightarrow S02$ 2S02 (g) + 02 (g) V<sup>205</sup> <sub>2 bar/720 K</sub>

2SO2 (g) + O2 (g)  $\xrightarrow{V2O5_{2 \text{ bar}/720 \text{ K}}}$  2SO3 (g)  $\Delta H^0 = -196.6$  kJ/mol

Exothermic reactions and therefore low temperatures and high pressures are desirable.

 $SO_3(g) + H_2SO_4 \rightarrow H_2S_2O_7$  (Oleum)

 $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4 (96 - 98\%)$ 

Dibasic acid or diprotic acid.

It is a dehydration agent.

It is a moderately strong oxidizing agent.

## **Properties of Sulphur Dioxide**

• It is a colourless gas with a rotten egg odour. It is highly soluble in water.

#### **Oxo-acids of sulphur**

- It liquefies easily.
- $SO_2$  dissolves in water to form sulphurous acid due to which it possesses an acidic character. H<sub>2</sub>O + SO<sub>2</sub>  $\rightarrow$  H<sub>2</sub>SO<sub>3</sub>
- It does not support combustion nor is it combustible.
- $SO_2$  is a strong oxidizing agent.  $2H_2S + SO_2 \rightarrow 3S + 2H_2O$
- It also acts as a reducing agent.  $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$

#### **Uses of Sulphur Dioxide**

- In the food industries, as a food preservative.
- It acts as a bleaching agent to remove the excess chlorine and as a disinfectant.
- In cold storage plant, it acts as a refrigerant.
- It is used as a reagent and a solvent in the laboratory.



## **Group 17 Elements:**

## Occurrence

The halogens are very reactive and therefore, do not occur in the free state. However, all except astatine are abundant in the earth's crust as halide ions, X<sup>-</sup>.

Fluorine and chlorine are fairly abundant while bromine and iodine are comparatively less abundant. Fluorine is the thirteenth element in order of abundance in crystal rocks of the earth. It is present mainly as insoluble fluorides. The three most important minerals are

(i) fluorite : CaF<sub>2</sub>

(ii) cryolite : Na<sub>3</sub>AlF<sub>6</sub> and

(iii) fluoroapatite : 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.CaF<sub>2</sub> or Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F.

#### (1) Electronic Configuration

The elements of this group have seven electrons in the outermost shell and have the general electronic configuration  $ns^2np^5$ .

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Fluorine	9	[He] 2s <sup>2</sup> 2p <sup>5</sup>	17	2
Chlorine	17	[Ne] 3s <sup>2</sup> 3p <sup>5</sup>	17	3
Bromine	35	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	17	4
Iodine	53	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	17	5
Astatine	85	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>	17	6

 Note

 Group 17 elements are collectively known as halogens. [Halo means salt and gens means born]

## (2) Atomic and ionic radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. The atomic and ionic radii increase with increase in atomic number. This is due to increase in the number of electron shells. The radius of the halide ion is always greater than the corresponding halogen atom. This is because the halide ion is formed by the gain of one electron by the atom. As a result, the number of electrons increases while the magnitude of nuclear charge remains the same. Therefore, the same nuclear charge acts on large number of electrons than are present in the neutral atom. Effective nuclear charge per electron is reduced and the electron cloud is held less tightly by the nucleus. This causes increase in size.

#### (3) Ionisation enthalpies

The ionisation enthalpies of halogens are very high. This indicates that they have very little tendency to lose electrons. However, on-going down the group from fluorine to astatine, the ionisation enthalpy decreases. This is due to gradual increase in atomic size which is maximum for iodine.

## (4) Melting and boiling points

The melting and boiling points of halogens increase with increase in atomic number as we go down the group.

## Explanation

The forces existing between these molecules are weak van der Waal's forces which increase down the group.

At room temperature, fluorine and chlorine are gases,

bromine is a liquid while iodine and astatine are

solids.

## (5) Electron Gain Enthalpies

(i) All these have maximum negative electron gain enthalpies in their respective periods. This is due to the fact that the atoms of these elements have only one electron less than the stable noble gas (ns2np6) configurations. Therefore, they have maximum tendency to accept an additional electron.

(ii) Electron gain enthalpy becomes less negative from top to bottom in a group. This is due to the fact that the effect of increase in atomic size is much more than the effect of increase in nuclear charge and thus, the additional electron feels less attraction by the large atom. Consequently, electron gain enthalpy decreases. (iii) Fluorine has less negative electron gain enthalpy than chlorine. Therefore, chlorine has the highest negative electron gain enthalpy in this group. The less negative electron gain enthalpy of fluorine as compared to chlorine is due to very small size of the fluorine atom. As a result, there are strong inter electronic repulsions in the relatively small 2p subshell of fluorine and thus, the incoming electron does not feel much attraction. Therefore, its electron gain affinity is small.

Thus, negative electron gain enthalpy among halogens varies as: F < Cl < Br

(6) Electronegativity

Halogens have large electronegativity values. The values decrease down the group from fluorine to iodine because the atomic size increases and the effective nuclear charge decreases. Fluorine is the most electronegative element in the periodic table.

## (7) Metallic or non-metallic character

Because of very high ionisation energy values, all halogens are non-metallic in character. The nonmetallic character decreases as we go down the group.

## **Colour:**

These elements come in a variety of colours. For example, while Fluorine is pale yellow, iodine is dark violet.

#### **Oxidizing Power:**

All halogens are oxidizing agents. In this list, fluorine is the most oxidizing agent. It is able to oxidise all halide particles in halogen. The oxidizing power decreases as we go down in the group. The halide particles also act as reducing agents. However, their reduction potential also decreases with the group.

#### **Reactivity with H<sub>2</sub>:**

All halogens react with hydrogen and produce acidic hydrogen halide. The acidity of these hydrogen halides decreases from HF to HI. Fluorine reacts violently and chlorine needs sunlight. On the other hand, bromine reacts with heat and iodine requires a catalyst.

#### **Reactivity with metals:**

As halogens are highly active, they react with many metals immediately and form metal halides that result in. For example, sodium mixes with chlorine gas and forms sodium chloride. This process is exothermic and provides a bright yellow light and high thermal energy. 2Na (s) + Cl<sub>2</sub> (g)  $\rightarrow$  2NaCl (s)

Metal halides are naturally ionic. This is due to the high electronegative nature of halogens and the high electropositivity of metals. This ionic component of halides degrades from fluorine to iodine.

#### Halogens oxoacids:

Fluorine produces only one oxoacid HOF (fluoric acid or hypofluorous acid) due to its lack of electronegativity.

#### Acidic Energy:

 $HOCl < HClO_2 < HClO_3 < HClO_4$ 

Reason

 $HClO_4 \rightarrow H^+ + ClO_4^-$ 

Most stable This is because fluorine is very electronegative.

#### Chlorine gas (Cl<sub>2</sub>)

It was discovered by Scheele .The name of chlorine was given by Davy.

Preparation

By heating pyrolusite ore that is  $MnO_2$  with HCl  $MnO_2$  + HCl  $\rightarrow$   $MnCl_2$  +  $Cl_2$  +  $H_2O$ (Manganese (Hydrogen (Manganese Chloride) Dioxide) Chloride)

- (b) By heating potassium permanganate with KCl:  $KMnO_4 + HCl \rightarrow MnCl_2 + KCl + Cl_2 + H_2O$ Potassium Manganese Permanganate Chloride
- It is greenish yellow gas.
- It has strong pungent suffocating odour.
- It is poisonous gas.
- It is soluble in water and the solution so formed is chlorine water.

#### **Uses of chlorine gas**

• It is used for bleaching purpose.

- It is used in extraction of gold and silver.
- It is used in manufacture of dyes etc.

#### Hydrogen chloride

It was discovered by Glauber and the Davy was the one who said that it consist of H and Cl.

Preparation of hydrogen chloride

#### **Preparation:**

It is prepared by reacting sodium chloride with sulphuric acid and the following reaction occurs:

NaCl+H<sub>2</sub>SO<sub>4</sub>→Na<sub>2</sub>SO<sub>4</sub>+HCl

Sodium chloride sodium sulphate

#### hydrogen chloride

# sulphuric acid hydroperties of hydrogen chloride

- It is colorless gas with pungent smell.
- It can be easily liquefied.
- It freezes to white crystalline solid.
- It is highly soluble in water.
- It readily reacts with ammonia forming ammonium chloride:

HCI+NH<sub>3</sub>-->NH<sub>4</sub>CI

hydrogen chloride ammonium chloride

## Uses of hydrogen chloride

- It is used in manufacturing of chlorine gas, ammonium chloride, etc.
- It is used for extracting glue from bones.
- It is used in making medicines.
- It is used in making aqua regia.

#### **Oxy acids of halogens**

The oxy acids of halogens are:

#### Fluorine

HFO(+1) Hypofluorous acid

#### Chlorine

HClO (+1) Hypochlorous acid HClO<sub>2</sub> (+2) Chlorous acid HClO<sub>3</sub>(+3) Chloric acid HClO<sub>4</sub>(+4) Perchloric acid

#### Bromine

HBrO(+1) Hypobromous acid HBrO<sub>3</sub>(+3) Bromic acid HBrO<sub>4</sub>(+4) Perbromic acid

#### Iodine

HIO (+1) Hypoiodous acid HIO<sub>3</sub> (+3) Iodic acid HIO<sub>4</sub>(+4) Periodic acid

## Properties of oxy acids of halogens

## Acidic strength:

The acidic strength of these oxy acids having same oxidation number decreases with increase in size because the electro negativity decreases as we go down the group from chlorine to iodine.

This is the reason that to withdraw electrons from oxygen atom towards itself decreases from chlorine to iodine.

As a result the tendency to pull the electrons from hydrogen decreases and the release of hydrogen ion becomes difficult.

The order of acidic strength is : HClO<HClO<sub>2</sub><HClO<sub>3</sub><HClO<sub>4</sub>

Oxidizing power and thermal stability :

As the oxidation number increase the oxidation power decreases in order:

HClO>HClO<sub>2</sub>>HClO<sub>3</sub>>HClO<sub>4</sub>

This is because the halogen oxygen bond becomes more covalent. As a result the thermal stability increases. Thus the hypohalites are stronger oxidizing agents than perhalates.

With increase in oxidation number of halogen the thermal stability of both the acids and salts increases thus the stability of oxy acids are in order:

HClO<HClO<sub>2</sub><HClO<sub>3</sub><HClO<sub>4</sub>

As the number of oxygen atoms increases in an ion, there is greater dispersal of negative charge therefore, greater is the stability of ion formed.

The acidity of oxo- acids of different halogens which have same oxidation number decreases from chlorine to iodine. This is due to decrease in electro negativity with increase in size.

## **Group 18 elements:**

The group 18 consists of elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). These gases at ordinary temperature do not have chemical reactivity and therefore, these were called inert gases. Because of the low abundance of these gases on earth, they have also been called rare gases.

## **Occurrence of Noble Gases**

Due to the inert nature of noble gases, they always occur in the free state. Except radon, all these gases are present in atmosphere in the atomic state. Their total percentage in dry air is about 1% by volume, of which argon (0.93%) in the major component. It originates in the air mostly from electron capture of potassium.

Helium is also present in natural gas to the extent of 2 to 7%. Helium and sometimes neon are found in small quantities in minerals of radioactive element such as monazite, clevite, pitch blende, etc. Helium, neon and argon are found in the water of certain springs.

Radon is radioactive and does not occur in the free-state because it decays very rapidly.

## **General Characteristics of Group 18 Elements**

## (1) Electronic Configurations

Except helium, the atoms of all noble gases have eight electrons in the valence shell. The general electronic configuration of noble gases (except He) may be expressed as  $ns^2np^6$ . On the other hand, helium has  $1s^2$  electronic configuration.

These configurations being stable, the noble gases neither have any tendency to gain nor lose electrons, and, therefore, they do not enter into chemical combinations. It is, therefore, reasonable to assume that inert nature of the noble gases is due to their stable electronic configurations.

Element	Symbol	Electronic configuration
Helium	2He	1 <i>s</i> <sup>2</sup>
Neon	10Ne	[He] $2s^2 2p^6$
Argon	18Ar	[Ne] 3s <sup>2</sup> 3p <sup>6</sup>
Krypton	36Kr	$[{\rm Ar}]  3d^{10} 4s^2  4p^6$
Xenon	54Xe	[Kr] $4d^{10}5s^25p^6$
Radon	86Rn	[Xe] $4f^{14}5d^{10}6s^26p^6$

## (a) Existence

All the noble gases are monoatomic, colourless and odourless gases. The monoatomic state of these gases is due to stable electronic configuration  $(ns^2np^6)$  of their atoms. As a result, they are not capable of combining even amongst themselves.

## (b) Atomic radii

As we go down the group, the van der Waal's radius increases due to the addition of new electronic shells.

## (c) Ionisation Enthalpies

The ionisation enthalpies of noble gases are very high. This is attributed to the stable completely filled configurations of noble gases. However, the ionisation enthalpies decrease with increase in atomic number from He to Rn due to increasing atomic size.

## (d) Electron Gain Enthalpies

Due to the stable ns<sup>2</sup>np<sup>6</sup> electronic configurations, noble gas atoms have no tendency to accept additional electron. Therefore, their electron gain enthalpies are zero or have large positive values.

## (e) Melting and Boiling Points

The melting and boiling points of noble gases are very low in comparison to those of other substances of comparable atomic and molecular masses. This indicates that only weak van der Waal's forces are present between the atoms of the noble gases in the liquid or the solid state.

These van der Waal's forces increase with the increase in atomic size of the atom, and therefore, the boiling points and melting points increase from He to Rn. Helium has the lowest boiling point (4.2 K) of any known substance.

## (f) Ease of liquefaction

The noble gases are not easily liquefied. This is due to the fact that there are only weak van der Waal's forces which hold atoms together.

Due to increase in atomic size and, therefore, increase in van der Waal forces, the ease of liquefaction increases down the group from He to Rn.

#### (g) Solubility in water

The noble gases are only slightly soluble in water. The solubility, in general, increases from He to Rn.

#### **Chemical properties of group 18**

According to the stable electronic configuration fact they have no compounds but the scientist Neil Bart let found that oxygen and xenon are very much similar.

Like both have almost same masses. Atomic radius of both is same.

So, like oxygen combines with platinum fluoride in the same way xenon also combines:

 $O_2 + PtF_6 \rightarrow^+O_2[PtF_6]$ 

oxygen platinium hexafluoride dioxygenyl hexafluoroplatinate

 $Xe + PtF_6 \rightarrow Xe^{+}[PtF_6]$ 

Xenon hexafluoroplatinate

platinium hexafluoride

## **Compounds of Xenon and fluorine**

Xenon easily combines with fluorine to form xenon fluorides: (a) XeF2

Preparation: Xe + F<sub>2</sub> ---> XeF<sub>2</sub> (Xenon) Fluroide XenonFluoride 2 : 1 (catalyst is nickel, 673k and 1 bar )

#### **Structure:**

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#### **Reaction of it with water:**

 (b) XeF<sub>4</sub> xenon tetrafluoride Xe + 4F<sub>2</sub> → XeF<sub>4</sub>
 1 : 5 (catalyst Ni, temperature 373 K, 6-7 bar)

#### **Preparation:**

The structure of xenon tetrafluoride is:



#### **Reaction with water:**

At normal temperature they are explosive in nature.

 $XeF_4 + H_2O \rightarrow Xe + HF + XeO_3+O_2$ xenon tetrafluoride water xenon hydrogen xenon oxygen gas

temp -80celsius

$$XeF_4 + H_2O \rightarrow HF + XeOF_2$$

xenon tetrafluoride

hydrogen fluoride xenon oxyfluoride

(c) XeF6 xenon hexafluoride Preparation:

> Xe+3F2→XeFs xenon flourine xenon hexafluoride

1: 20(catalyst nickel,temp.573k,60-70 bar)



## **Reaction with water**

(d) XeO<sub>3</sub> xenon trioxide Preparation:

xenon hexafluoride xenon trioxide hydrogen fluoride The hybridization is: sp<sup>3</sup>. The geometry is pyramidal. The structure is:



XeO<sub>3</sub> (e) XeO<sub>4</sub> (xenon tetra oxide) The hybridization is sp<sup>3</sup>. The geometry is tetrahedral. The structure is given below:



 (f) XeOF<sub>2</sub> (xenon oxy fluoride) The hybridization is sp<sup>3</sup>d. The geometry is given below:



(g) XeO<sub>2</sub>F<sub>2</sub>
 The hybridization is sp<sup>3</sup>d<sup>2</sup>.
 The geometry is given below:



## **Compounds Xe and F:**

- $Xe + F_2 \xrightarrow{673k,1bar} XeF_2$
- $Xe + 2F_2 \xrightarrow{873k/7bar} XeF_4$
- $Xe + 3F_2 \xrightarrow{573k/60-70bar} XeF_6$
- $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> are powerful fluorinating agents.

## **Compounds of Xe and O:**

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

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

## **Uses of noble gases**

- Helium is used in weather balloons.
- A mixture of helium and oxygen is used in cylinders by divers etc.
- Liquid helium is used maintain low temperature or we can say it is cryogenic liquid.
- Neon is used in sign board signals.
- Neon is used in filling up sodium vapour lamp.
- Neon is used in protecting electrical instruments like voltmeter.
- Argon is used in filling electric bulbs.
- Argon helps in providing inert atmosphere.
- Krypton is used in flash bulbs of high speed photography.
- Radon is used in treatment of cancer.
- Radon is used to treat metals.

Group 13 to 18 of the periodic table consist of p-block elements with their valence shell electronic configuration ns<sup>2</sup>np<sup>1-6</sup>.

**Group 15** consists of five elements namely N, P, As, Sb and Bi which have general electronic configuration ns2 np3. Nitrogen differs from other elements of this group due to small size, formation of p pi-p pi multiple bonds with itself and with highly electronegative atom like O or C and non-availability of d-orbitals to expand its valence shell. Elements of group 15 show gradation in properties. They react with oxygen, hydrogen, and halogens. They exhibit two important oxidation states, +3 and +5 but +3 oxidation is favoured by heavier elements due to inert pair effect.

Dinitrogen can be prepared in laboratory as well as on industrial scale. It forms oxides in various oxidation states as  $N_2O$ , NO,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$ , and  $N_2O_5$ . These oxides have resonating structure and have multiple bonds. Ammonia can be prepared by Haber's process. HNO<sub>3</sub> is an important industrial chemical. It is strong monobasic acid and is a powerful oxidising agent. Metals and non-metals react with HNO<sub>3</sub> under different condition to give NO or NO<sub>2</sub>.

Phosphorus exists as P4 in elemental form. It exists in several allotropic forms. It forms hydride. PH<sub>3</sub> which is a highly poisonous gas. It forms two types of halides as  $PX_3$  and  $PX_5$ .  $PCl_3$  is prepared by the reaction of white phosphorus with dry chlorine while  $PCl_5$  is prepared by the reaction of phosphorus with  $SO_2Cl_2$ . Phosphorus forms a number of oxoacids. Depending upon the number of P-OH groups. Their basicity varies. The oxoacids which have P-H bonds are good reducing agents.

**Group 16** elements have general electronic configuration ns<sup>2</sup> np<sup>4</sup>. They show maximum oxidation state +6. Gradation in physical and chemical properties is observed in the group 16 elements. In laboratory, dioxygen is prepared by heating KClO<sub>3</sub> in presence of MnO<sub>2</sub>. It forms a number of oxides with metals. Allotropic form of oxygen is O<sub>3</sub> which is a highly oxidising agent. Sulphur forms a number of allotropes. Of these alpha and bita-forms of sulphur are the most important. Sulphur combines with oxygen to give oxides such as SO<sub>2</sub> and SO<sub>3</sub>, SO<sub>2</sub> is used in the manufacture of H<sub>2</sub>SO<sub>4</sub>. It is prepared by contact process. It is a dehydrating and oxidising agent. It is used in the manufacture of several compounds.

**Group 17** of periodic table consists of F, Cl, Br, I and At. These elements are extremely reactive and as such they are found in the combined state only. The common oxidation states of these elements is -1. However, highest oxidation state can be +7. They show regular gradation in physical and chemical properties. They form oxides, hydrogen halides, interhalogen compounds and oxoacids. Chlorine is conveniently obtained by the reaction of HCl with KMnO<sub>4</sub>. HCl is prepared by heating NaCl with concentrated H<sub>2</sub>SO<sub>4</sub>. Halogen combine with one another to form interhalogen compounds of the type XX'n (n – 1,3,5,7) where X' is lighter than X. A number of oxoacids of halogens are known. In the structures of these oxoacids, halogen is the central atom which is bonded in each case with one OH bond as X-OH. In some cases X-0 bonds are also found.

**Group 18** of the periodic table consists of noble gases. They have ns<sup>2</sup> np<sup>6</sup> valence shell electronic configuration except He which has 1s<sup>2</sup>. All the gases except Rn occur in atmosphere. RN is obtained as the decay product of <sup>226</sup>Ra.

Due to complete octet of outermost shell. They have less tendency to form compounds. The best characterised compounds are those of xenon with fluorine and oxygen only under certain conditions. These gases have several uses. Argon is used to provide inert atmosphere, helium is used in filling balloon for meteorological observations, neon is used in discharge tubes and fluorescent bulbs.







## **QUESTIONS FOR PRACTICE**

- **Q1.** The correct option of solubility in water for He, Ne, Ar, Kr. Xe is (a) He > Ne > Ar > Kr > Xe (b) Xe > Kr > Ar > Ne > He(c) Ne > Ar > Kr > He > Xe (d) Ar > Ne > He > Kr > Xe**Q2.** The strongest oxidising agent is (a) F<sub>2</sub> (b)  $Cl_2$ (c) I<sub>2</sub> (d)  $Br_2$ The mixture of concentrated HCl and HNO<sub>3</sub> made in 3:1 03. ratio contains (a)  $ClO_2$ (b) NOCl (c)  $NCl_3$ (d)  $N_2O_4$ **Q4.** For electron affinity of halogens which of the following is correct? (a) Br > F(b) F > Cl(c) Br < Cl(d) F > IThe number of P-O-P bridges in the structure of Q5. phosphorus and phosphorus trioxide are respectively (a) 6, 6 (b) 5,5 (c) 5,6 (d) 6,5 Q6. Tincture of iodine is (a) Aqueous solution of I<sub>2</sub> (b) Solution of I<sub>2</sub> in aqueous KI (c) Alcoholic solution of I<sub>2</sub> (d) Aqueous solution of KI **Q7.** Which of the following statements is not correct for nitrogen? (a) Its electronegativity is very high (b) d-orbitals are available for bonding (c) it is typical non-metal (d) its molecular size is small The statement true for N<sub>3</sub><sup>-</sup> is Q8. (a) It has non-linear structure (b) It is called pseudo halogen (c) The formal oxidation state of nitrogen in this anion is -1
  - (d) It is isoelectronic with NO<sub>2</sub>
- **Q9.** Which of the following group 15 element forms metallic bonds in elemental state?

(a) As	(b) P
(c) Sb	(d) Bi

**Q10.** The three important oxidation states of phosphorus are

(a) -3, +3 and +5	(b) -3, +3 and -5
(c) -3, +3 and +2	(d) -3, +3 and +4

- **Q11.** Nitrogen is relatively inactive element because (a) Its atom has a stable electronic configuration
  - (b) It has low atomic radius
  - (c) Its electronegativity is fairly high
  - (d) Dissociation energy of its molecule is fairly high
- (a) Multiple bond formation in the molecule (b) Absence of bond polarity (c) Short inter-nuclear distance (d) High bond energy **Q13.** Which of the following species has the highest dipole moment?  $(a) NH_3$ (b)  $PH_3$ (c) AsH<sub>3</sub> (d) SbH<sub>3</sub> **Q14.** The correct decreasing order of basic strength is: (a)  $AsH_3 > SbH_3 > PH_3 > NH_3$ (b)  $SbH_3 > AsH_3 > PH_3 > NH_3$ (c)  $NH_3 > PH_3 > AsH_3 > SbH_3$ (d)  $PH_3 > AsH_3 > SbH_3 > NH_3$ **Q15.** Which of the following fluorides does not exist? (a) NF<sub>5</sub> (b)  $PF_5$ (c) AsF<sub>5</sub> (d)  $SbF_5$ **Q16.** PCl<sub>5</sub> is possible but NCl<sub>5</sub> does not exist: (a) In N, no vacant 2d-subshell (b) Ionization energy of N is very high (c) It does not like Cl (d) None of these **Q17.** On heating ammonium dichromate and barium azide separately we get (a) N2 in both cases (b) N2 with ammonium dichromate and NO with barium azide (c) N2O with ammonium dichromate and N2 with barium azide (d) N20 with ammonium dichromate and N20 with barium azide **Q18.** In Haber's process for the manufacture of NH<sub>3</sub>: (a) Finely divided nickel is used as a catalyst (b) Finely divided iron is used as a catalyst (c) Finely divided molybdenum is used as a catalyst (d) No catalyst is necessary **Q19.** Ammonia on reaction with hypochlorite anion can form: (a) NO (b)  $N_2H_4$ (c) NH<sub>4</sub>Cl (d) Both (b) and (c) **Q20.** NH<sub>3</sub> molecule is \_\_\_\_ in shape. (a) Tetrahedral (b) Pyramidal (c) trigonal bipyramidal. (d) Octahedral **Q21.** Fluorine differs from rest of the halogens in some of its properties. This is due to (a) Its smaller size (b) Non availability of d-orbitals.

**Q12.** What causes nitrogen to be chemically inert?

- (c) high electronegativity
- (d) All of these.

- **Q22.** The set with correct order of acidity is (a)  $HCIO < HCIO_2 < HCIO_3 < HCIO_4$ (b)  $HCIO_4 < HCIO_3 < HCIO_2 < HCIO$ (c)  $HCIO < HCIO_4 < HCIO_3 < HCIO_2$ (d)  $HCIO_4 < HCIO_2 < HCIO_3 < HCIO$
- Q23. When chlorine reacts with cold and dilute solution of sodium hydroxide, it forms

  (a) Cl<sup>-</sup> and ClO<sup>-</sup>
  (b) Cl<sup>-</sup> and ClO<sub>2</sub><sup>-</sup>
  (c) Cl<sup>-</sup> and ClO<sub>3</sub><sup>-</sup>
  (d) Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>
- **Q24.** The formation of  $O_{2^+}$  [PtF<sub>6</sub>]<sup>-</sup> is the basis for the formation of first xenon compound. This is because (a) O2 and Xe have different sizes.
  - (b) Both O2 and Xe are gases.
  - (c) 02 and Xe have comparable electro-negativities.
  - (d) O2 and Xe have comparable ionisation enthalpies.
- **Q25.** Partial hydrolysis of XeF<sub>4</sub> gives

(a) XeO <sub>3</sub>	(b) XeOF <sub>2</sub>
(c) XeOF <sub>4</sub>	(d) XeF <sub>2</sub>

- **Q26.** Among the 15th group elements, as we move from nitrogen to bismuth, the pentavalency becomes less pronounced and trivalency becomes more pronounced due to Options
  - (a) Non-metallic character
  - (b) Inert pair effect
  - (c) High electronegativity
  - (d) Large ionization energy
- Q27. Collectively the elements of group 15 are called
  - (a) Pnicogens
  - (b) Pnicopens
  - (c) Nicopen
  - (d) None of these
- **Q28.** Which one of the following elements is most metallic? (a) P
  - (b) As
  - (c) Sb
  - (d) Bi
- **Q29.** Which of the following statement is incorrect for group 15 elements?
  - (a) Order of ionization enthalpies is  $\Delta iH1 < \Delta iH2 < \Delta iH3$
  - (b) The boiling point and melting point increases from top to bottom in the group
  - (c) Dinitrogen is a gas while all others are solids
  - (d) All statements are correct
- **Q30.** Which of the following has the highest  $p\pi p\pi$  bonding tendency?

(a) N	(b) P
(c) As	(d) Sb

- **Q31.** Pick out the wrong statement.
  - (a) Nitrogen has the ability to form  $p\pi$ - $p\pi$  bonds with itself.
  - (b) Bismuth forms metallic bonds in elemental state.
  - (c) Catenation tendency is higher in nitrogen when compared with other elements of the same group.

- (d) Nitrogen has higher first ionisation enthalpy when compared with other elements of the same group.
- $\label{eq:Q32.Nitrogen forms $N_2$, but phosphorus is converted into $P_4$ from $P$, the reason is $$P_4$ for $P_4$ 
  - (a) Triple bond is present between phosphorus atom
  - (b)  $p\pi$   $p\pi$  bonding is strong
  - (c)  $p\pi$   $p\pi$  bonding is weak
  - (d) Multiple bond is formed easily
- **Q33.** Pentavalence in phosphorus is more stable when compared to that of nitrogen even though they belong to same group. This is due to
  - (a) Large size of phosphorus atom
  - (b) Hydrogen and sulphurous acid
  - (c) Reactivity of phosphorus
  - (d) Inert nature of nitrogen
- **Q34.** Among the following, which one is a wrong statement. (a) PH5 and BiCl5 do not exist.
  - (b)  $p\pi$ -d $\pi$  bonds are present in SO<sub>2</sub>
  - (c) SeF<sub>4</sub> and CH<sub>4</sub> have same shape.
  - (d) I<sub>3</sub> has bent geometry.
- **Q35.** Which is strongest acid in the following:
  - (a) HClO<sub>4</sub> (b) H<sub>2</sub>SO<sub>3</sub> (c) H<sub>2</sub>SO<sub>4</sub> (d) HClO<sub>3</sub>
- $\label{eq:Q36.} \begin{array}{l} \mbox{Which one of the following order is correct for the bond} \\ \mbox{dissociation enthalpy of halogen molecule?} \\ \mbox{(a) } Br_2 > I_2 > F_2 > Cl_2 \end{array}$ 
  - (b)  $F_2 > Cl_2 > Br_2 > I_2$
  - (c)  $I_2 > Br_2 > Cl_2 > F_2$ (d)  $Cl_2 > Br_2 > F_2 > I_2$
- Q37. What is the maximum covalency of the nitrogen atom?(a) One(b) Two(c) Three(d) Four
- **Q38.** The correct order of oxidising power is (a)  $HClO_4 > HClO_3 > HClO_2 > HClO$ (b)  $HOCl > HClO_2 > HClO_3 > HClO_4$ (c)  $HClO_3 > HClO_4 > HClO_2 > HClO$ (d)  $HClO_2 > HOCl > HClO_3 > HClO_4$
- Q39. The correct order of bond angles in the following species is
  - (a)  $Cl_2O < ClO_2^- < ClO_2$  (b)  $ClO_2^- < Cl_2O < ClO_2$
  - (c)  $Cl_2O < ClO_2 < ClO$  (d)  $ClO_2 < Cl_2O < ClO_2$
- Q40. When Cl<sub>2</sub> reacts with hot and cone. NaOH, the oxidation number of chlorine changes from
  (a) zero to +1 and zero to +5
  (b) 0 to -1 and 0 to +5
  (c) zero to -1 and zero to +3
  - (d) 0 to + 1 and 0 to 2
  - (d) 0 to +1 and 0 to -3
- **Q41.** Which of the following statement is incorrect?
  - (a) ONF is isoelectronic with  $\rm NO^{-2}$
  - (b)  $OF_2$  is an oxide of fluoride
  - (c)  $Cl_2O_7$  is an anhydride of perchloric acid
  - (d) O<sub>3</sub> molecule is bent

- **Q42.** Chlorine reacts with excess of  $NH_3$  to form
  - (a) NH<sub>4</sub>Cl
  - (b)  $N_2$  + HCl
  - (c)  $N_2 + NH_4Cl$
  - (d)  $NCl_3 + HCl$
- **Q43.** Which of the following reactions is an example of redox reaction?
  - (a)  $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$ (b)  $XeF_2 + PF_5 \rightarrow [XeF] + [PF_6]^-$
  - (c)  $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$
  - (d)  $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 2HF$
- **Q44.** On addition of conc.  $H_2SO_4$  to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet flames come out. This is because
  - (a) H<sub>2</sub>SO<sub>4</sub> reduces HI to I<sub>2</sub>
  - (b) HI is of violet colour
  - (c) HI gets oxidised to I<sub>2</sub>
  - (d) HI changes to HIO<sub>3</sub>
- **Q45.** Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?

(a) HF	(b) HCl
(c) HBr	(d) HI

- - (a) Cu (b) S

(c) C			(d) Zn
	-	-	

- **Q47.**  $H_2S$  is more acidic than  $H_2O$  because
  - (a) Oxygen is more electronegative than sulphur.
  - (b) Atomic number of sulphur is higher than oxygen.
  - (c) H S bond dissociation energy is less as compared to H O bond.
  - (d) H O bond dissociation energy is less also compared to H S bond.
- **Q48.** The boiling points of hydrides of group 16 are in the order
  - (a)  $H_2O > H_2Te > H_2S > H_2Se$
  - (b)  $H_2O > H_2S > H_2Se > H_2Te$
  - (c)  $H_2O > H_2Te > H_2Se > H_2S$
  - (d) None of these
- **Q49.** In the manufacture of sulphuric acid by contact process Tyndall box is used to
  - (a) Convert SO<sub>2</sub> and SO<sub>3</sub>
  - (b) Test the presence of dust particles
  - (c) Filter dust particles
  - (d) Remove impurities
- **Q50.** What catalyst is used for oxidation of ammonia to produce nitric acid?
  - (a) Vanadium (V) oxide
  - (b) Palladium hydride
  - (c) Sodium amalgam
  - (d) Platinum-Rhodium gauze

## ASSERTION AND REASONING

- **Q1. Assertion:** Dinitrogen is inert at room temperature. **Reason:** Dinitrogen directly combines with lithium to form ionic nitrides.
  - (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
  - (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
  - (c) Assertion is correct, reason is incorrect
  - (d) Assertion is incorrect, reason is correct.
- Q2. Assertion: N<sub>2</sub> is less reactive than P<sub>4</sub>.Reason: Nitrogen has more electron gain enthalpy than phosphorus.
  - (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
  - (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
  - (c) Assertion is correct, reason is incorrect
  - (d) Assertion is incorrect, reason is correct.

produces a metal nitrate and nascent hydrogen. The nascent hydrogen then further reduces  $HNO_3 \, to \, NO_2$ 

- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
- (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
- (c) Assertion is correct, reason is incorrect
- (d) Assertion is incorrect, reason is correct.
- **Q4. Assertion:** White phosphorus is more reactive than red phosphorus.

**Reason:** Red phosphorus contains tetrahedral units linked to one another to form linear chains.

White phosphorus is more reactive than red phosphorus.

- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
- (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
- (c) Assertion is correct, reason is incorrect
- (d) Assertion is incorrect, reason is correct.

## **TRUE/FALSE**

- Q1. All p-block elements are metals. (a) True (b) False
- Q2. All metals have 1-3 valence electrons. (a) True (b) False
- Q3. The 6th period is the longest period in the modern periodic table.(a) True(b) False

## **QUESTIONS FOR PRACTICE**

Q1.	The formation of $O_{2^+}$ [P formation of first xenon co (a) O2 and Xe have different	tF <sub>6</sub> ]- is the basis for the mpound. This is because nt sizes.	Q11.	Catenation property is max (a) Phosphorus (c) Sulphur	ximum in (b) Carbon (d) Zinc
	<ul><li>(b) Both O2 and Xe are gas</li><li>(c) O2 and Xe have compa</li><li>(d) O2 and Xe have compa</li></ul>	ses. rable electro-negativities. rable ionisation enthalpies.	Q12.	Element found from sea wa (a) Magnesium (c) Iodine	ater is (b) Sodium (d) None of these
Q2.	Helium is preferred to be hydrogen because it is (a) Incombustible (b) Lighter than hydrogen	used in balloons instead of	Q13.	Which one of the following (a) BF <sub>3</sub> (c) BBr <sub>3</sub>	g is the strongest lewis acid? (b) BCl <sub>3</sub> (d) Bl <sub>3</sub>
	(c) More abundant than hy (d) Non polarizable	drogen	Q14.	Which one of the followin bonding? (a) NH <sub>3</sub>	ng does not form hydrogen (b) H <sub>2</sub> O
Q3.	Which of the following op with the property mention	tions are not in accordance		(c) HCl	(d) HF
	<ul> <li>(a) F2 &gt; Cl2 &gt; Br2 &gt; I2 Oxid</li> <li>(b) MI &gt; MBr &gt; MCI &gt; M halide.</li> </ul>	lising power. F Ionic character of metal	Q15.	Main source of helium is (a) Air (c) Monazite	(b) Radium (d) Water
	<ul> <li>(c) F2 &gt; Cl2 &gt;Br2 &gt; I2 Bond</li> <li>(d) HI &lt; HBr &lt; HCl &lt; H strength.</li> </ul>	l dissociation enthalpy. IF Hydrogen-halogen bond	Q16.	Which one of the following temperature? (a) Zinc	g element is liquid at normal (b) Mercury
Q4.	Which of the following stat	ements are correct?		(c) calcium	(d) sodium
	<ul><li>(i) Among halogens, radiu fluorine is maximum.</li><li>(ii) Leaving F—F bond, all</li></ul>	us ratio between iodine and halogens have weaker X—X	Q17.	Which one of the following (a) NCl <sub>3</sub> (c) NI <sub>3</sub>	g is least basic? (b) NBr <sub>3</sub> (d) NF <sub>3</sub>
	bond than X—X' bond (iii) Among interhaloger number of atoms are p	in interhalogens. compounds maximum present in iodine fluoride.	Q18.	H₂SO₄ is a/an (a) Acid (c) Alkali	(b) Base (d) Salt
	(iv) Interhalogen compounds.	nds are more reactive than	Q19.	Modern periodic table is gi (a) Debonair	iven by (b) Mendeleef
	(a) 1, 11, 111 (c) Ii, iii, iv	(b) I, III, IV (d) I and iv	020	(c) Mendel	(d) None of these
Q5.	Find the amphoteric oxide		Q20.	potential?	nas maximum ionisation
	(a) CaO <sub>2</sub> (c) SnO <sub>2</sub>	(b) CO <sub>2</sub> (d) SiO <sub>2</sub>		(a) Al (c) Si	(b) P (d) Mg
Q6.	Graphite has a structural s	imilarity with	Q21.	The number of P-O-P bond	ds in cyclic metaphosphoric
	(a) $B_2H_6$	(b) B <sub>4</sub> C (d) BN		acid is	(h) ()
07	Ovugen is not released	on heating which of the		(c) 3	(d) 4
Q7.	compounds? (a) (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	(b) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Q22.	Which of the following oxi acid?	des is an hydride of nitrous
	(c) $Zn(ClO_3)_2$	(d) KClO₃		(a) N <sub>2</sub> O <sub>3</sub> (c) NO	(b) $NO_2$ (d) $N_2O_4$
Q8.	$P_4O_{10}$ has bridging $O$	atoms (b) 5	Q23.	Which oxide of nitrogen	n is obtained on heating
	(c) 6	(d) 2		ammonium nitrate at 250° (a) Nitric oxide	C ?
Q9.	Which of the species has a	permanent dipole moment?		(b) Nitrous oxide	
	(a) SF4 (c) BF3	(D) SIF4 (d) XeF4		(c) Nitrogen dioxide (d) Dinitrogen tetraoxide	
Q10.	Boron shows diagonal rela	tion with	Q24.	Atomicity of phosphorus is	5
	(a) Al (c) Si	(b) C (d) Sn		(a) 1 (c) 3	(b) 2 (d) 4

- **Q25.** The structure of white phosphorus is
  - (a) Square-planar
  - (b) Pyramidal
  - (c) Tetrahedral
  - (d) Trigonal planar
- **Q26.** PCl<sub>3</sub> on hydrolysis gives

	5	2	0	
(a) H <sub>3</sub> P	03			(b) HPO3
(c) H <sub>3</sub> P	04			(d) POCl <sub>3</sub>

- Q27. Arrange the following in decreasing Lewis acid strength -PF3, PCI3, PBr3, Pl3 (a)  $Pl_3 > PBr_3 > PCl_3 > PF_3$ (b)  $PF_3 > PCl_3 > PBr_3 > Pl_3$ (c)  $PCl_3 > PBr_3 > Pl_3 > PF_3$ (d)  $PBr_3 > Pl_3 > PF_3 > PCl_3$
- **Q28.** Which of the following is a tetrabasic acid?
  - (a) Hypophosphorus acid
  - (b) Metaphosphoric acid
  - (c) Pyrophosphoric acid
  - (d) Orthophosphoric acid
- **Q29.** The halogen which reacts very slowly with halogen is (a) Fluorine (b) Chlorine (c) Bromine (d) Iodine
- Q30. The halogen which reacts spontaneously with gold (Au) to form Au+3 is

(a) F <sub>2</sub>	(b) Cl <sub>2</sub>
(c) Br <sub>2</sub>	(d) I <sub>2</sub>

## **ASSERTION AND REASONING**

- Assertion: Red phosphorus is used in match industry. Q1. **Reason:** Red phosphorus shows phosphorescence. Red phosphorus is used in match industry.
  - (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
  - (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
  - (c) Assertion is correct, reason is incorrect
  - (d) Assertion is incorrect, reason is correct.
- **Q2.** Assertion: Bond angle of H2S is smaller than H2O. Reason: Electronegativity of the central atom increases, bond angle decreases.
  - (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
  - (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion

- (c) Assertion is correct, reason is incorrect
- (d) Assertion is incorrect, reason is correct.
- Q3. Assertion: Both rhombic and monoclinic sulphur exist as  $S_8$  but oxygen exists as  $O_2$ . **Reason:** 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. (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
  - (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
  - (c) Assertion is correct, reason is incorrect
  - (d) Assertion is incorrect, reason is correct.
- **Q4.** Assertion: Ozone is thermodynamically stable with respect to oxygen.

Reason: Decomposition of ozone into oxygen results in the liberation of heat

- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
- (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
- (c) Assertion is correct, reason is incorrect
- (d) Assertion is incorrect, reason is correct.
- Q5. Assertion: Inert gases are monoatomic,
  - **Reason:** Inert gases have stable configuration.
  - (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
  - (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
  - (c) Assertion is correct, reason is incorrect
  - (d) Assertion is incorrect, reason is correct.

## **TRUE/FALSE**

- Q1. Red phosphorous is less volatile than white phosphorous because the former has tetrahedral structure. (a) True
  - (b) False
- Q2. When PbO<sub>2</sub> reacts with a dilute acid, it gives hydrogen peroxide. (a) True

(b) False

Carbon tetrachloride burns in air when lighted to give Q3. phosgene. (a) True (b) False

## SOLUTIONS

- S1. (b) As the molecular weight of noble gas atoms increases down the group its polarity increases due to which van-der-waal's force between them increases. Due to increased polarity of heavier inert gas, its solubility in water also increases. So, most soluble gas will be Xe and least soluble will be He. So correct order is Xe>Kr>Ar>NeHe.
- S2. (a) Fluorine has although low electron affinity than Chlorine but low dissociation energy and have high hydration energy of its ion, therefore Fluorine is the strongest oxidizing agent.
- S3. (b)  $3HCl + HNO_3 \rightarrow NOCl + Cl_2 + H_2O$
- **S4.** (c) As the atomic size increases down the group, electron affinity generally decreases as the effective nuclear charge decreases. But in group 17 the order of electron affinity is: At<I<Br<F<Cl.

Here, fluorine has a lower electron affinity than chlorine this is due to the small size of fluorine, the electron repulsion will be high between the valence electron and the incoming electron as compared to that in chlorine. Thus, Br<Cl is correct.

**S5.** (a) Looking at the figure we get that in the structure of phosphorus pentaoxide and phosphorus trioxide there are 6P–O–P bridges.



- **S6.** (b) Tincture of iodine is an aqueous solution of I<sub>2</sub> in KI and French iodine is a solution in alcohol.
- s7. (b)  $N_7 \rightarrow 1s^2, 2s^2, 2p^3$

d- orbitals are absent in nitrogen.

- **S9.** (d) Down the group metallic properties increases Bi is the metallic element in group-15
- S10. (a) The most important oxidation numbers for phosphorus are -3, +3, and +5 (see table below). Because it is more electronegative than most metals, phosphorus reacts with metals at

elevated temperatures to form phosphides, in which it has an oxidation number of -3.

- S11. (d) Nitrogen is an inactive element as it has a high bond dissociation energy due to the presence of triple bond N≡N. Hence, viewed as a non-reactive element.
- **S12.** (d) Due to high bond energy of N=N molecule, N<sub>2</sub> is chemically inert.
- S13. (a) As we from top to bottom in a group the dipole moment of hydrides of the elements of that particular group decreases dye to increase in the size of the element
   So the order of dipole moment of the given hydrides
   NH<sub>3</sub>>PH<sub>3</sub>>AsH<sub>3</sub>>SbH<sub>3</sub>
- **S14. (b)** The hydrides of nitrogen family contain one lone pair on the central atom. As we move down the group the size of the central atom increases thereby their orbital become more diffused, hence the nucleophilicity of the lone pair is less dense over the bigger atoms thereby decreasing the basicity. So, the increasing order of their basic character is,

BiH<sub>3</sub><SbH<sub>3</sub><AsH<sub>3</sub><PH<sub>3</sub><NH<sub>3</sub>

- S15. (a) NF<sub>5</sub> does not exist because N does not form pentahalides due to the absence of d-orbital in its valence shell. While P As and Sb form pentahalides of the general formula MX5 where M = P As and Sb due to the presence of vacant d-orbitals in their respective valence shell.
- S16. (a) PCl<sub>5</sub> forms five bonds by using the d-orbitals to "expand the octet" and have more places to put bonding pairs of electrons.NCl<sub>5</sub> does not exist because there are no d-orbitals in the second energy level. Therefore there is no way to arrange five pairs of bonding electrons around a nitrogen atom.

$$\begin{split} (\mathrm{NH}_4)_2\mathrm{Cr}_2\mathrm{O}_7 &\to \mathrm{Cr}_2\mathrm{O}_3 + 4\mathrm{H}_2\mathrm{O} + \mathrm{N}_2.\\ \mathrm{Ba}(\mathrm{N}_3)_2 &\longrightarrow \mathrm{Ba} + 3\mathrm{N}_2. \end{split}$$

- **S18. (b)** Finely divided iron is used as catalyst in the manufacture of ammonia by Haber's process
- **S19.** (b)  $2NH_3 + COl \rightarrow H_2N NH_2 + H_2O + Cl^3$
- **S20.** (c) In NH<sub>3</sub>, N is sp<sup>3</sup> hybridised. N of NH<sub>3</sub> has a lone pair of electrons. The lone pair distorts the normal tetrahedral geometry due to lp–bp interaction to trigonal bipyramidal.

- **S21. (d)** Fluorine differs from other halogens in many respects.
  - **1.** Smallest size of (F) atom
  - **2.** Highest ionization energy and electronegativity of fluorine than other halogens.
  - **3.** Fluorine cannot expand their octet beyond 8 because of lack of d-orbital, but other halogens can expand their octet.
- S22. (b) Oxygen is more electronegative than chlorine. With an increase in the number of O atoms attached to Cl, more electrons are pulled away from O-H bond and more weaker becomes the O-H bond. This increases the acid strength. The decreasing order of acidic strength is HClO<sub>4</sub>>HClO<sub>3</sub>>HClO<sub>2</sub>>HClO.
- S23. (a) When chlorine reacts with cold and dilute sodium hydroxide, the following reaction takes place: 2NaOH+Cl<sub>2</sub>→NaCl+NaClO+H<sub>2</sub>O. Hence the products are Cl<sup>-</sup>and ClO<sup>-</sup> When chlorine reacts with hot and concentrated sodium hydoxide, the following reaction takes place: NaOH+Cl<sub>2</sub>→5NaCl+NaClO<sub>3</sub>+3H<sub>2</sub>O Hence the products are Cl<sup>-</sup>and ClO<sub>3</sub><sup>-</sup>
- S24. (d) The first ionisation energy of xenon is quite close to that of oxygen and the molecular diameter of xenon and oxygen are almost identical. Based on the above facts it is suggested that since oxygen combines with PtF<sub>6</sub>, so xenon should also form similar compound with PtF<sub>6</sub>
- **S25.** (b) On parrial hydrolysis of XeF<sub>4</sub> XeOF<sub>2</sub> is formed.  $XeF_4 + H_2O \rightarrow XeOF_2 + 2HF$
- S26. (b)
- **S27. (a)** Collectively these elements are called pnicogens and their compound pniconides.
- **S28.** (d) Metallic character increases down the group and Bi is the lowest element of group 15 so it is most metallic. It has lowest ionization energy, electronegativity.
- **S29. (b)** The melting point in group 15 increases upto arsenic and then decreases upto bismuth.
- **S30.** (a) Nitrogen due to small size is able to show  $p\pi-p\pi$  lateral overlap forming  $N\equiv N$ , rest elements due to bigger size are not able to show  $p\pi-p\pi$  lateral overlap.
- **S31. (c)** Catenation tendency is higher in phosphorus when compared with other elements of same group.
- **S32.** (a)  $p\pi p\pi$  bonding in nitrogen is strong hence it can form triple bond with another N. Single N–N bond

is weaker than P-P bond due to high interionic repulsion of non-bonding electrons. Hence, N=N is stable and  $P_2$  is not.

- **S33. (a)** Pentavalence in phosphorus is more stable when compared to that of nitrogen even though they belong to same group is due to large size of phosphorus atom and greater ability to accommodate electrons.
- **S34.** (c) PH<sub>5</sub> does not exist due to very less electronegativity difference between P and H. Hydrogen is slightly more electronegative than phosphorus, thus could not hold significantly the sharing electrons. On the other hand, BiCl<sub>5</sub> does not exist due to inert pair effect. This is because on moving down the group, +5 oxidation state becomes less stable while +3 oxidation state become more stable due to inert pair effect. In SO<sub>2</sub>,  $p\pi$ -d $\pi$  and  $p\pi$ - $p\pi$  both types of bonds are present. SeF<sub>4</sub> has sp<sup>3</sup> d-hybridisation whereas CH<sub>4</sub> has sp<sup>3</sup> -hybridisation. Thus, they both have different geometry. I<sub>3</sub><sup>+</sup> has a bent shape due to the presence of 2 lone pairs on central I atom.
- S35. (a) HClO<sub>4</sub> is strong because it has greater no oxygen atom. More the oxygen atom more electron will be pulled away from o-h bond and the more this bond will be weakened. Between H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>3</sub> similar reason. Now between H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>, HClO<sub>4</sub> is strong because the perchlorate ion form by the removal of hydrogen atom is more stabilised than sulphate ion or in other words the negative charge in perchlorate ion.
- S37. (d) Nitrogen has two 2s and three 2p valence electrons. By sharing the three 2p electrons, nitrogen can form three covalent bonds. For example, NH<sub>3</sub>. But still the nitrogen atom has a lone pair of electrons from 2s orbital. By donating these two electrons from lone pair, it can form one bond. For example, NH<sub>4</sub><sup>+</sup>. Thus, nitrogen can form four bonds
- S38. (b) The oxiding power of HClO<sub>4</sub>, HClO<sub>3</sub>, HCLO<sub>2</sub>, HClO are in the following order: HClO > HCLO<sub>2</sub> > HClO<sub>3</sub>> HClO<sub>4</sub> because the oxidizing power of oxyacids of chlorine is inversely related to the thermal stability of these acids i.e. higher the thermal stability, lower will be oxidizing power of the oxyacid and vice versa.

- **S39. (a)** The correct order of increasing bond angles in the following species is  $Cl_2O < ClO_2^- < ClO_2$  This is because, In  $ClO_2^-$  there are two lone pairs of electrons which repel each other due to which two oxygen atom come closer leading to decrease in bond angle. Therefore the bond angle in  $ClO_2^-$  is less than 118° which is bond angle in  $ClO_2$  which has less number of electrons on chlorine.
- S40. (b) The reaction of chlorine gas with hot and concentrated sodium hydroxide solution is 3Cl<sub>2</sub>+6NaOH→NaClO<sub>3</sub>+5NaCl+3H<sub>2</sub>O
  Oxidation number of Cl is 0 in Cl<sub>2</sub>, -1 in NaCl and +5 in NaClO<sub>3</sub>
  So the oxidation number of chlorine changes from Zero to -1 and Zero to +5.
- S41. (b) Option B. Is incorrect because OF<sub>2</sub> is a fluoride of oxygen because electronegativity of fluorine is more than that of oxygen. No. Of electrons in ONF=24 No. of electrons in O<sub>2</sub>N-=24 The structure of O3 is bent due to lone pair. 2HClO<sub>4</sub>+heat→Cl<sub>2</sub>O<sub>7</sub> i.e Cl<sub>2</sub>O<sub>7</sub> is anhydride of perchloric acid.
- S42. (c) Chlorine reacts with excess of ammonia to form ammonium chloride and nitrogen.
   8NH<sub>3</sub>+3Cl<sub>2</sub>→6NH<sub>4</sub>Cl+N<sub>2</sub>
- **S43.** (a)  $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

Where Xenon (Xe) is oxidized and Oxygen  $(O_2)$  is reduced. In the above-given chemical equation, the oxidation number of Xe increases from +4 to +4 and the oxidation number of oxygen decreases from +1 to 0. Therefore, it is an example of a redox reaction.

- **S44.** (c) Because hydrogen iodide is a more powerful reducing agent than sulphuric acid, it converts  $H_2SO_4$  to SO and HI to I<sub>2</sub>. When chloride salts are treated with sulfuric acid, HCl gas is formed, which produces a colourless gas. NaCl +  $H_2SO_4 \rightarrow Na_2SO_4 + HCl$ Violet fumes are produced during the reaction as a result of the formation of iodine gas.
- S45. (a) Fluorine is the most reactive element and reacts with hydrogen gas to hydrogen fluoride. A high amount of energy is required to break the bond between hydrogen and fluorine due to less bond length between the two atoms. Therefore, the bond dissociation energy decreases as we go down the group.

**S46.** (c) 
$$C + 2H_2SO_4(conc \cdot) \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O$$

- S47. (b)
- **S48.** (c) Higher BP's mean higher forces (because more thermal energy needed to separate the molecules

in liquid state) Even though Sulfur is more electronegative than Se or Te (so you would expect a higher dipole moment and so higher attractive forces between molecules) the size of the molecules is a bigger factor in their interactions. More energy is needed simply because the molecules of the hydrides get bigger as you go down the Group.

Oxygen is so much more electronegative that the molecules have H-bonding in water. This give rise to almost a different (and higher) order of intermolecular force, which gives rise to such a high BP in water.

S49. (b) The manufacture of sulphuric acid by contact process, Tyndall box is used to test the presence of dust particles.The Tyndall effect is useful to detect the presence of colloidal particles.

A beam of light is passed through a colloidal solution and observed.

S50. (d) Sol. Ammonia is oxidized to nitrogen (II) oxide in the presence of Pt/Rh gauze catalyst at a temperature of 500 K and a pressure of 9 bars. The nitrous oxide is then converted to nitrogen dioxide which is further reacted with water to produce nitric acid. The NO formed is recycled.

## ASSERTION AND REASONING

- **S1.** (c) At higher temperatures, dinitrogen combines with metals to form ionic nitrides.
- S2. (c) Nitrogen gas has complete octet for both the atoms and it is unreactive due to the presence of strong triple bond. On the other hand phosphorous has bonds with unstable angle strains compared to that of nitrogen due to which it burns quickly, hence easily reacts. Nitrogen has lower electron gain enthalpy than phosphorous.

S3. (a) When a metal is treated with conc. HNO<sub>3</sub> it generally yields a nitrate, NO<sub>2</sub> and H<sub>2</sub>O. Conc. HNO<sub>3</sub> reacts with metal and first produces a metal nitrate and nascent hydrogen. The nascent hydrogen then further reduces HNO<sub>3</sub> to NO<sub>2</sub>.

$$\begin{split} &\underset{\text{metal}}{\text{M}} + \underset{\text{conc.}}{\text{HNO}_3} \rightarrow \underset{(\text{metal nitrate})}{\text{MNO}_3} + \underset{(\text{nascent hydrogen})}{\text{H}} \\ & 2\text{HNO}_3 + \underset{(\text{nascent hydrogen})}{\text{2H}} \rightarrow 2\text{NO}_2 + 2\text{H}_2\text{O} \end{split}$$

S4. (a) White phosphorous is more reactive than red phosphorous because red phosphorous has more stability due to its structure.Red phosphorus atoms form a network of more number of atoms and are less reactive and not

much flammable. White phosphorous  $(P_4)$  has a tetrahedral structure that is thermodynamically unstable so that it combusts in air.

Thus, the reason is the correct explanation for the assertion.



Structure of white phosphorus



- S1. (b) As we move from left to right across the periodic table; non-metallic character increases. Since p block elements are present on the extreme right of the periodic table, it consists of metals, non-metals and metalloids.
- S2. (a) All the metals have 1-3 electrons in their valence shell and they lose their valence electrons to form positive ions. However, other properties like hardness, high melting and boiling points, malleability and ductility are not shown by all metals. Even though sodium and potassium are solids, they are soft, non-malleable and non-ductile metals. Further, they have low melting and boiling points. Similarly, mercury is found in liquid state at room temperature.
- S3. (a) [HINT]: When the last s-orbital in the electronic configuration of an element is ns, then the element belongs to the nth period. Which means the electrons of the element occupies the nth s-orbital, nth p-orbital, (n-1)th d-orbital and (n-2)th f-orbital. S-orbital can accommodate at most 2 electrons, p-orbital can accommodate at most 6 electrons, d-orbital can accommodate at most 10 electrons and f-orbital can accommodate at most 14 electrons.

## **QUESTIONS FOR PRACTICE**

S1. (d) The first ionisation energy of Xenon (1170 KJ/mol) is quite close to that of dioxygen (1180 KJ/mol). The molecular diameters of xenon and dioxygen are almost identical. Based on the above similarities Barlett (who prepared O<sub>2</sub>\*[PtF<sub>6</sub>]-compound)suggested that since oxygen combines

with  $PtF_6$ , so xenon sould also form similar compound with  $PtF_6$ .

- S2. (a) Helium is used in balloons in place of hydrogen because it is incombustible. It do not catch fire like hydrogen. He is a inert element.
- (b), (c) (a) Halogen readily accepts electrons, so they have strong oxidising power. F2 is the strongest oxidising halogen and this oxidising power decreases down the group.
  - $F_2 > Cl_2 > Br_2 > I_2$

**(b)** Halogens react with metals to form metal halides. The ionic character of the halides decreases in the order of

MF > MCl > MBr > MI

(c) Bond dissociation enthalpy of Halogens decreases in the order of  $Cl_2 > F_2 > Br_2 > I_2$ . Bond dissociation enthalpy of  $Cl_2$  is greater than  $F_2$  because of  $F_2$  molecule.

(d) Hydrogen-halogen bond strength decreases down the group due to decrease in bond dissociation enthalpy. HF > HCl > HBr > HI

S4. (b) Among halogens, radius ratio between iodine and fluorine is maximum . Among interhalogen compounds, maximum number of atoms are present in iodine fluoride. Interhalogen

compounds are more reactive than halogen compounds.

- SnO2 reacts with acid as well as the base. So SnO2 is an amphoteric oxide. CaO is basic in nature, while SiO2 and CO2 are acidic in nature.
- S6. (d) The structure of boron nitride BN is similar to the structure of graphite. It consists of flat planes of hexagons. Each hexagon having alternate B and N atoms. In graphite, each corner of the hexagon has C atom.

A)  $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$ 

S7. (a) B)  $Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2 + 3O_2$ 

**C)** 
$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

**D)** (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 
$$\xrightarrow{\Delta}$$
 N<sub>2</sub> + Cr<sub>2</sub>O<sub>3</sub> + 4H<sub>2</sub>O

S8. (c) In P<sub>4</sub>O<sub>10</sub> the number of oxygen atoms attached to each phosphorus atom is 4. 6 bridging oxygen atoms are present in P<sub>4</sub>O<sub>10</sub>. In this P<sub>4</sub>O<sub>10</sub>, there are 4 phosphorus atoms and 10 oxygen atom. There are 6 P-O-P bond present and each are sp<sup>3</sup> hybridized. These six oxygen combine to form tetrahedron.

S9. (a)

- **S10.** (c) Boron and silicon are both semiconductors, form halides that are hydrolysed in water and form acidic oxides. Boron and silicon have diagonal relationship.
- **S11. (b)** Catenation property is maximum in carbon because high C–C bond energy, tetra valency, etc.

S12. (b)

 S13. (c) Order of back bonding BF<sub>3</sub>>BCl<sub>3</sub>>BBr<sub>3</sub> Back bonding 2p-2p, 2p-3p, 2p-4p Stronger is the back bonding weaker the tendency to act as a lewis acid BF<sub>3</sub>< BCl<sub>3</sub>< BBr<sub>3</sub>

S14. (c)

- S15. (c)
- S16. (b) Mercury exists in liquid state at room temperature. Bromine(Br) also exists as liquid at room temperature however it is a non-metal. Some other metals like caesium, gallium and rubidium exists as liquid slightly above room temperature.
- S17. (c)
- S18. (a)
- S19. (d)
- **S20. (d)** Maximum ionisation potential energy is of Mg i.e. (Magnesium) because the ionisation energy increase from right to left in a group
- **S21. (c)** The number of P-O-P bond in cyclic metaphosphoric acid is three.



- **S22.** (a) Two oxides of nitrogen are acid anhydrides; that is, they react with water to form nitrogen-containing oxyacids. Dinitrogen trioxide(N<sub>2</sub>O<sub>3</sub>) is the anhydride of nitrous acid, HNO<sub>2</sub>, and dinitrogen pentoxide(N<sub>2</sub>O<sub>5</sub>) is the anhydride of nitric acid, HNO<sub>3</sub>.
- S23. (b) The oxide of nitrogen is obtained on heating ammonium nitrate at 250°C is nitrous oxide(N2O) NH<sub>4</sub>NO<sub>3</sub>→N<sub>2</sub>O+2H<sub>2</sub>O
- **S24.** (d) The formula of Phosphorus is P<sub>4</sub>. So the atomicity of phosphorus is 4.
- **S25. (c)** White phosphorus (P<sub>4</sub>) has a tetrahedral structure.
- **S26. (a)** The product is phosphorus acid. Hence, one molecule of phosphorus trichloride reacts with three molecules of water to form three molecules of hydrogen chloride and one molecule of phosphorous acid.
- **S27.** (b) The sequence for the Lewis acid strength for:  $PF_3 > PCl_3 > PBr_3 > PI_3$ Because: Lewis acids have a tendency to accept electrons. As mentioned above, phosphorous has empty d orbital in its valence shell to accept electrons. Also, the electronegativity of the halides decreases as F> Cl>Br>I. So, fluorine has

stronger affinity towards electrons making  $PF_3$  stronger lewis acid while making PI3 weakest lewis acid.

- **S28.** (c) Acids having 4 replaceable hydrogen atoms is known as tetrabasic acids Pyrophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) contains four replaceable H-atoms. Hence, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is a tetrabasic acid.
- S29. (d)
- S30. (b)

## ASSERTION AND REASONING

- **S1. (c)** Red phosphorus is largely used in the match industry. It is preferred to yellow phosphorus because it is non-poisonous in nature. It is dark red in colour and is used to make the tip of the match. It is white phosphorus that shows phosphorescence and not the red phosphorus.
- S2. (c) Bond angle of H<sub>2</sub>S(92<sup>0</sup>) < H<sub>2</sub>O(104<sup>0</sup>31). As the electronegativity of the central atom decreases, bond angle decreases. In the present case, S is less electronegative than oxygen. Thus bond pairs in H<sub>2</sub>S are more away from the central atom than in H<sub>2</sub>O and thus repulsive forces between bond pairs are smaller producing smaller bond angle.

Hence, assertion is correct but reason is incorrect.

S3. (a) Both rhombic and monoclinic sulphur exist as S<sub>8</sub> but oxygen exists as O<sub>2</sub>. Oxygen form pπ-pπ multiple bond due to small size and small bond length but pπ-pπ bonding is not possible in sulphur due to its larger atomic size than oxygen.

## S4. (d)

**S5.** (a) Yes, both the assertion and reason are correct. Inert gases such as helium, neon, argon, krypton, xenon and radon have stable electronic configuration.

their octet is completely filled except helium, it has its duplet complete.

They are happy by themselves and hence they are monoatomic in nature.

## **TRUE/FALSE**

- S1. (b) Red phosphorous is polymeric substance. It exists as the chains of P4 tetrahedral linked together. Therefore, it is less volatile.
- **S2.** (b) PbO<sub>2</sub> is a dioxide and it does not give hydrogen peroxide when it reacts with a dilute oxide. PbO<sub>2</sub> + 4HCl  $\rightarrow$  PbCl<sub>2</sub> + Cl<sub>2</sub> + 2H<sub>2</sub>O
- **S3.** (b) CCl4 gives phosgene with superheated steam. CCl<sub>4</sub> + H<sub>2</sub>O  $\rightarrow$  COCl<sub>2</sub> + 2HCl.