

# 16. p - BLOCK ELEMENTS

## 1. GROUP 13 ELEMENTS (BORON FAMILY)

### 1.1 Introduction

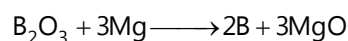
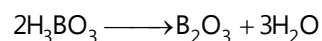
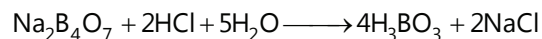
Elements of group 13 belong to p-block elements, since the last electron in them is present in the p-orbital. All these elements have three electrons in the outer most orbit: two in the s-orbital and one in the p-orbital. Thus, the electronic configuration of the outermost energy levels of these elements maybe represented as  $ns^2np^1$ .

**Table 16.1:** Electronic configuration for Group 13

Element with At. No.	Configuration with inert gas core
B 5	[He] $2s^2 2p^1$
Al 13	[Ne] $3s^2 3p^1$
Ga 31	[Ar] $3d^{10} 4s^2 4p^1$
In 49	[Kr] $4d^{10} 5s^2 5p^1$
Tl 81	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$

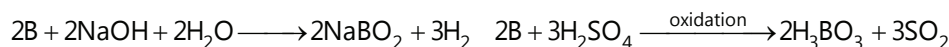
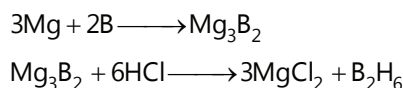
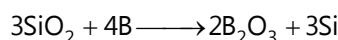
### 1.2 Boron

#### Preparation:

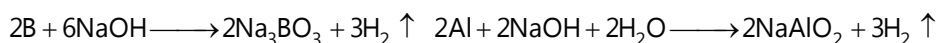


**Physical Properties:** Low electronegativity, hard, absorbs neutrons, steel grey in color. Some dissimilarities of boron with other elements of this group are:

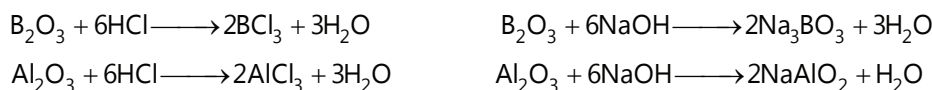
- Boron does not form positive ions in aqueous solution and has low oxidation potential.
- Boron always forms covalent compounds
- Boron is non-metallic

**Chemical Properties****(a)** Reaction with O<sub>2</sub> and N<sub>2</sub>**(b)** Reaction with alkalis and acids**(c)** Boron reacts with Mg, which on hydrolysis give diborane.**(d)** Reaction with silica**PLANCESS CONCEPTS**

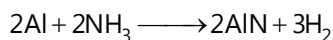
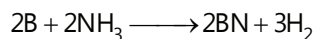
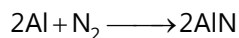
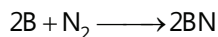
- Boron has high m.p. and b.p.  
Boron has a very high m. p. and b.p. because it exists as a giant covalent, polymeric structure both in solid as well as in liquid state.
- B(OH)<sub>3</sub> is an acid, Al(OH)<sub>3</sub> is amphoteric and Tl(OH)<sub>3</sub> is basic.  
The electropositive or metallic character of gp. 13 elements increases from B to Tl. B being a non-metal and thus forms an acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic from basic hydroxides.

**Nitin Chandrol (JEE 2012, AIR 134)****1.2.1 Comparison between Boron and Aluminium****(a) Action of conc. H<sub>2</sub>SO<sub>4</sub>:** Both react with conc. H<sub>2</sub>SO<sub>4</sub> to liberate SO<sub>2</sub>.**(b) Action of alkalis:** Both liberate H<sub>2</sub>.**(c) Formation of oxides:** Both form oxides when heated with oxygen at high temperature.

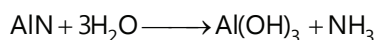
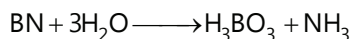
These oxides are amphoteric and dissolve in acids as well as in alkalis to form salts.



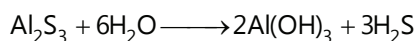
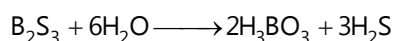
(d) **Formation of nitrides:** Both, when heated with nitrogen or ammonia, form nitrides.



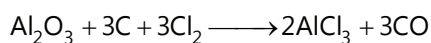
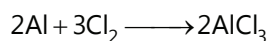
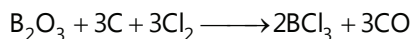
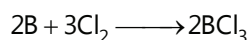
These nitrides are decomposed by steam to form ammonia.



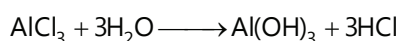
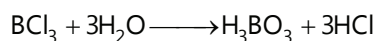
(e) **Formation of sulphides:** Both form sulphides on heating with sulphur at high temperatures. These are hydrolysed by water.



(f) **Formation of chlorides:** They form trichlorides by direct combination with  $Cl_2$  or by passing  $Cl_2$  over a heated mixture of their oxides and charcoal.



These trichlorides are covalent and are hydrolysed by water.



### PLANCESS CONCEPTS

- The  $p\pi - p\pi$  back bonding occurs in the halides of boron but not in the halides of aluminium.

The tendency to show  $p\pi - p\pi$  back bonding is maximum in boron halides and decreases very rapidly with the increase in the size of the central atom and halogen atom. "Since Al is larger in size than B, it does not show back-bonding".

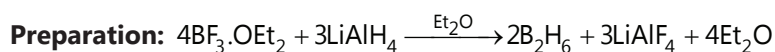
- From boron to thallium, +1 oxidation state becomes more stable.

Reason: inert pair effect.

**GV Abhinav (JEE 2012, AIR 329)**

## 1.2.2 Compounds of Boron

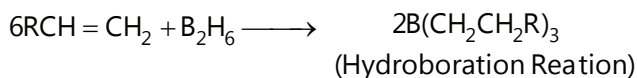
(a) Diborane ( $B_2H_6$ )



**Physical Properties:**

(i) Diborane is a colourless gas (b. p. 183K). It is rapidly decomposed by water with the formation of  $\text{H}_3\text{BO}_3$  and  $\text{H}_2$ :  $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$

(ii) Diborane undergoes a facile addition reaction with alkenes and alkynes in ether solvents at room temperature to form organoboranes:

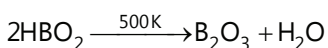
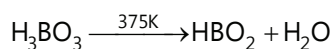


(b) **Boric Acid:** Orthoboric acid,  $\text{H}_3\text{BO}_3$  (commonly known as boric acid) and metaboric acid  $\text{HBO}_2$ , are two well-known, important oxoacids of boron.

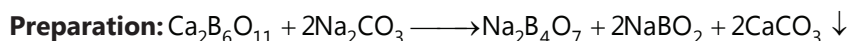
**Properties:**

(i) It is moderately soluble in water.

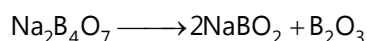
(ii) On heating boric acid at 375K, metaboric acid,  $\text{HBO}_2$  is formed. On further heating above 500K,  $\text{B}_2\text{O}_3$  is formed.



In solution, metaboric acid changes to orthoboric acid.

**(c) Borax (Sodium tetraborate decahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )****Properties:**

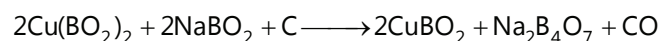
(i) On heating alone, it decomposes to form  $\text{NaBO}_2$  and  $\text{B}_2\text{O}_3$



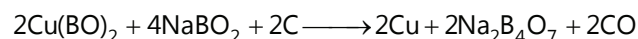
(ii) Borax bead Test: The formation of coloured metaborates by transition metal salts is used in the borax bead test as a qualitative analysis. The distinct colour of the bead depends on the oxidizing or reducing flame of the bunsen burner.

A cupric salt forms blue cupric metaborate in the oxidizing flame:  $\text{Na}_2\text{B}_4\text{O}_7 + \text{CuO} \longrightarrow \text{Cu}(\text{BO}_2)_2 + 2\text{NaBO}_2$

In the reducing flame (ie. In presence of carbon), the coloured salt is reduced to colourless cuprous metaborate:



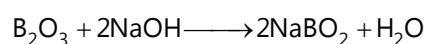
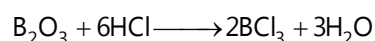
and to metallic copper and hence the bead becomes dull red and opaque.



**Illustration 1:** Show that  $\text{B}_2\text{O}_3$  is amphoteric oxide.

**(JEE MAIN)**

**Sol:** Amphoteric oxide is an oxide that can behave as an acid or a base. Thus, following reactions can be written as-



**Illustration 2:** Boron is trivalent in nature. Explain.

**(JEE MAIN)**

**Sol:** Trivalency is having a valence of three or showing the presence of three valence electrons. Due to  $ns^2np^1$  configuration it can share three electrons with other atoms.

**Illustration 3:**  $B(OH)_3$  is an acid,  $Al(OH)_3$  is amphoteric and  $Tl(OH)_3$  is basic. Explain.

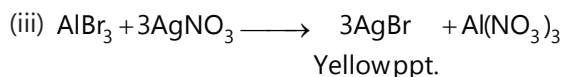
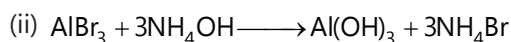
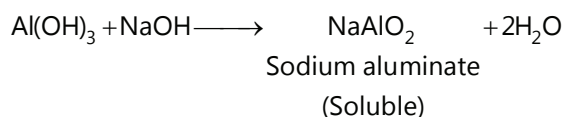
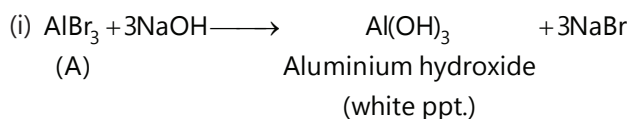
**(JEE MAIN)**

**Sol:** The electropositive or metallic character of gp. 13 elements increases from B to Tl. B being a non-metal and thus forms an acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic form basic hydroxides.

**Illustration 4:** An inorganic compound (A) in its aqueous solution produced a white ppt. with NaOH, which dissolves in excess of NaOH. The aqueous solution of (A) also produced a white ppt. with  $NH_4OH$  which does not dissolve in excess of  $NH_4OH$ . Also, its aqueous solution produced a light yellow ppt. with  $AgNO_3$  solution, soluble in dil.  $HNO_3$ . Identify (A)

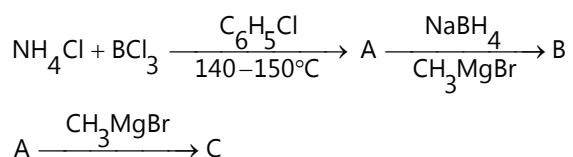
**(JEE ADVANCED)**

**Sol:** The given reactions are:

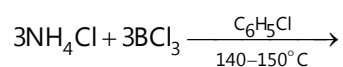
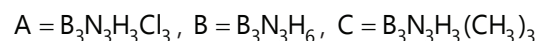


**Illustration 5:** Identify A, B and C in the given reaction sequence:

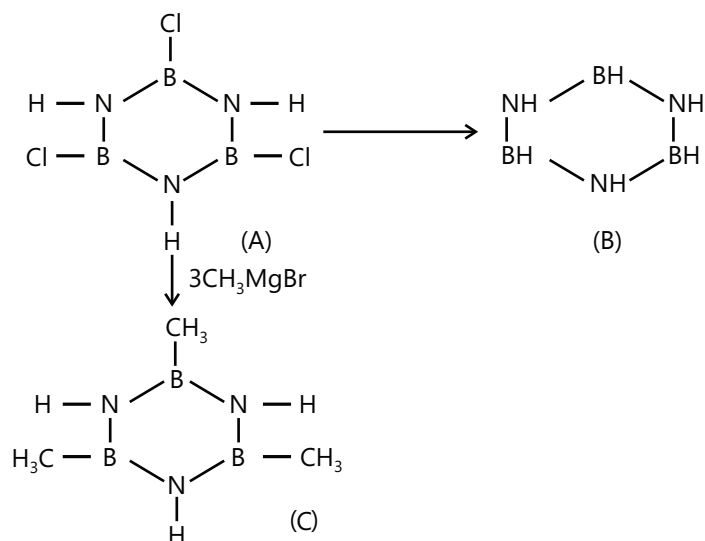
**(JEE ADVANCED)**



**Sol:** The product is Borazine, an inorganic compound formed here, which is isoelectronic and isostructural with benzene.

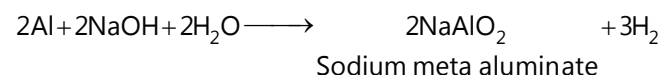


Reactions are:



**Illustration 6:** Aluminium vessels should not be cleaned with a cleansing agent containing washing soda. Why? **(JEE ADVANCED)**

**Sol:** Washing soda (Na<sub>2</sub>CO<sub>3</sub>) reacts with water to form NaOH and Al gets dissolved in caustic soda.



**Illustration 7:** The  $p\pi - p\pi$  back bonding occurs in the halides of boron but not in the halides of aluminium. Explain. **(JEE ADVANCED)**

**Sol:** The tendency to show  $p\pi - p\pi$  back bonding is maximum in boron halides and decrease very rapidly with the increase in the size of central atom and halogen atom. Since, Al is larger in size than B and thus, does not show back bonding.

**Illustration 8:** Borazole or borazine is more reactive than benzene. Explain. **(JEE ADVANCED)**

**Sol:** In Borazine, B=N bonds are polar and therefore, reactivity of borazole is more than benzene which possesses non-polar C=C and C-C bonds. The more negative group attacks boron atom.

**Illustration 9:** From boron to thallium, +1 oxidation state becomes more stable. Explain. **(JEE ADVANCED)**

**Sol:** Inert pair effect is the tendency shown by the outermost s-electrons of the post transition elements to remain unionized or unshared. [Due to inert pair effect.]

## 2. GROUP 14 ELEMENTS (CARBON FAMILY)

### 2.1 Introduction

Carbon, silicon, germanium, tin and lead constitute the group 14 of the periodic table.

The electronic configuration of these elements are as given below.

**Table 16.2:** Electronic Configuration of Group 14 Elements:

Element	At. No	Electronic Configuration
C	6	$1s^2, 2s^2 2p^2$ or $[\text{He}] 2s^2 2p^2$
Si	14	$1s^2, 2s^2 2p^6, 3s^2 3p^2$ or $[\text{Ne}] 3s^2 3p^2$
Ge	32	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^2 4p^2$ or $[\text{Ar}] 3d^{10} 4s^2 4p^2$
Sn	50	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^2 4p^6, 4d^{10}, 5s^2 5p^2$ or $[\text{Kr}] 4d^{10} 5s^2 5p^2$
Pb	82	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^2 4p^6, 4d^{10} 4f^{14}, 5s^2 5p^2 5d^{10}, 6s^2 6p^2$ or $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$

## 2.2 Carbon

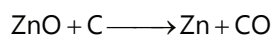
### 2.2.1 Allotropes of Carbon

- (a) Crystalline form: Diamond and graphite are the two crystalline forms of carbon.
- (b) Amorphous form: Coal, Coke, Charcoal (or wood charcoal), animal charcoal (or bone black), Lamp black, Carbon black, Gas carbon and Petroleum coke are the amorphous forms of carbon.

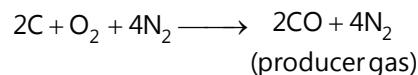
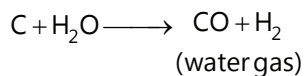
### 2.2.2 Important Compounds of Carbon

#### (a) Carbon Monoxide (CO)

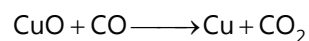
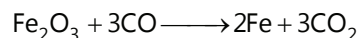
**Preparation:** (i) By heating oxides of heavy metals e. g. iron, zinc etc with carbon.



Two important industrial fuels-water gas and producer gas, contains carbon along with hydrogen and nitrogen, Water gas is obtained by passing steam over hot coke



**Properties:** (i) It is a powerful reducing agent and reduces many metal oxides to the corresponding metal .For e. g.



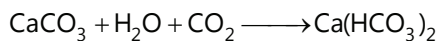
**Tests:** (a) Burns with a blue flame

(b) A filter paper soaked in platinum or palladium chloride turns pink, green or black due to reduction of the chloride by carbon monoxide.

#### (b) Carbon dioxide (CO<sub>2</sub>):

**Preparation:**  $\text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$

**Properties:** (i) It turns lime water milky and the milkiness disappears when  $\text{CO}_2$  is passed in excess.



(ii) Solid carbon dioxide or dry ice is obtained by cooling  $\text{CO}_2$  under pressure. It passes to the solid state straight from gaseous state without liquefying (hence called dry ice).

**3. Carbides:** Carbon reacts with more electropositive elements to form carbides at high temperature. Types of Carbides:

- (a) **Salt-like Carbides:** These are the ionic salts containing either  $\text{C}_2^{2-}$  (acetylide ion) or  $\text{C}^{4-}$  (methanide ion) e. g.  $\text{CaC}_2, \text{Al}_4\text{C}_3, \text{Be}_2\text{C}$ .
- (b) **Covalent Carbides:** These are the carbides of non-metals such as silicon and boron. In Such carbides, the atoms of two elements are bonded to each other through covalent bonds.  $\text{SiC}$  is also known as Carborundum.
- (c) **Interstitial Carbides:** They are formed by transition elements and consist of metallic lattices with carbon atoms in the interstices. e. g. tungsten carbide  $\text{WC}$ , vanadium carbide  $\text{VC}$ .

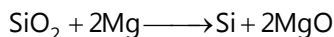
## 2.3 Silicon

**Extraction:** Commercial form of silicon is obtained by the reduction of  $\text{SiO}_2$  with  $\text{C}$  or  $\text{CaC}_2$  in an electric furnace. High purity silicon is obtained either from  $\text{SiCl}_4$  or from  $\text{SiHCl}_3$ .

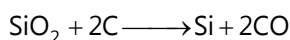
**Properties:** Silicon is obtained by the reduction of silica. It exists in two allotropic forms:

- (a) amorphous      (b) crystalline

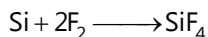
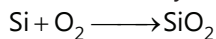
The amorphous variety is obtained by heating dry powdered silica with magnesium.



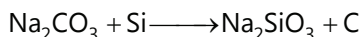
The crystalline variety is obtained by heating a finely powdered sand or quartz with carbon in an electric furnace where, a small amount of iron is added to prevent the formation of carborundum ( $\text{SiC}$ )



Amorphous silicon is chemically more reactive than crystalline silicon. Amorphous silicon is a brownish powder. It burns brilliantly in oxygen and ignites spontaneously in fluorine.



When amorphous silicon is strongly heated, it fuses and on cooling solidifies to the crystalline form. It forms a very hard crystalline silicon, which does not burn in oxygen but readily combines with fluorine. It dissolves in a mixture of  $\text{HNO}_3$  and  $\text{HF}$ . When fused with alkali, it gives a silicate.



### 2.3.1 Silicates

A large number of silicate minerals exist in nature. Some of the important minerals are: feldspars, e.g. Albite

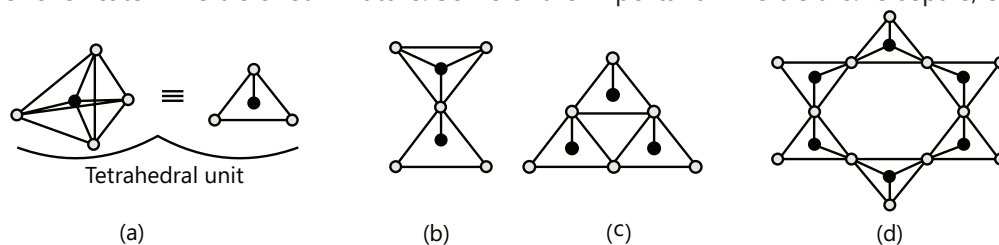
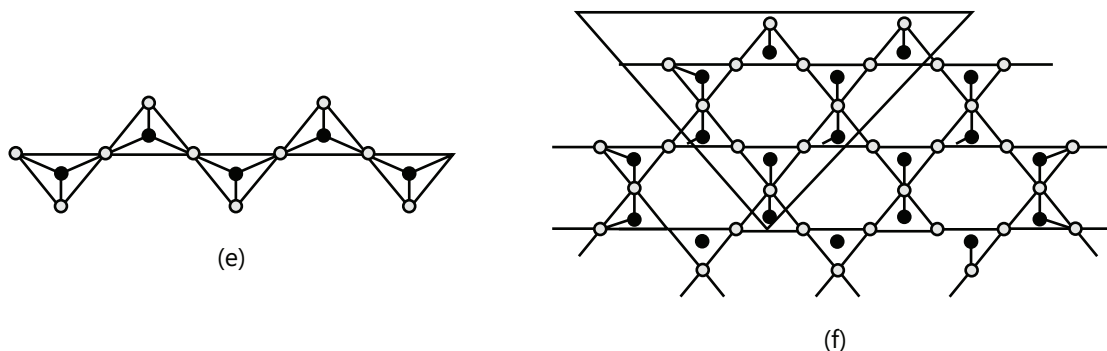


Figure 16.1: Differently bonded silicates



$\text{NaAlSi}_3\text{O}_8$ , zeolites, e.g., chabazite  $\text{Ca}_2[(\text{AlO}_2)_4(\text{SiO}_2)_{28}]\text{H}_2\text{O}$ , micas (muscovite)  $[\text{KAl}_2(\text{Si}_3\text{AlO}_{10})(\text{OH})_2]$  and asbestos  $[\text{Mg}(\text{Si}_2\text{O}_5)(\text{OH})_4]$ . The basic structural unit in silicates is the  $\text{SiO}_4$  tetrahedron. The  $\text{SiO}_4$  tetrahedral can be linked in several different ways. Depending on the number of corners (0, 1, 2, 3 or 4) of the  $\text{SiO}_4$  tetrahedral shared, various kinds of silicates, single or double chains, rings, sheet or three-dimensional networks are formed.

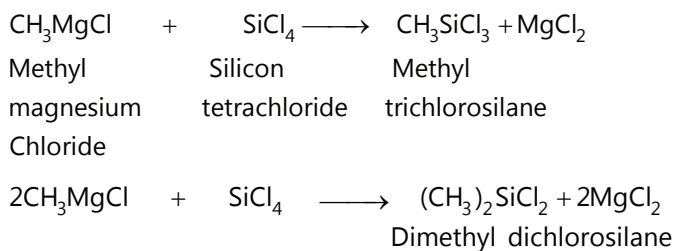


**Figure 16.2:** Normal orthosilicates

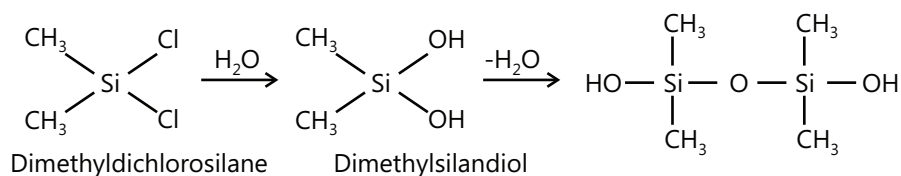
Normal orthosilicates (e.g.  $\text{Mg}_2\text{SiO}_4$ ) contain discrete  $\text{SiO}_4$  units. When two  $\text{SiO}_4$  tetrahedra share a corner (common oxygen atom), we get the  $(\text{Si}_2\text{O}_7)^{6-}$  unit and the silicates are called pyrosilicates. When  $\text{SiO}_4$  units share two oxygen atoms with each other, cyclic or linear single chain silicates are formed with empirical formula  $[(\text{SiO}_3)^2]_n$  as present in beryl (a mineral)  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ . A linear silicate chain is present in pyroxenes (e.g.  $\text{MgCaSi}_2\text{O}_6$ ). If two chains are cross-linked, the resulting double stranded silicates have the composition  $[(\text{Si}_4\text{O}_{11})^{6-}]_n$  and are called amphiboles. Asbestos belongs to this class. Two dimensional sheet structures are formed, three corners of each  $\text{SiO}_4$  tetrahedron are shared as found in clays which contains  $(\text{Si}_2\text{O}_5)^{2-}$  units. When all the four corners of the  $\text{SiO}_4$  tetrahedron are shared, 3D networks are formed, leading to different forms of silica. If in this, three-dimensional network, part of the silicon is replaced by aluminum ( $\text{Al}^{3+}$ ). This will require the incorporation of other cations ( $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$ ) for maintaining the charge balance. The resultant 3D networks give aluminosilicates which include feldspars and zeolites. Two important man-made silicates from a practical point of view are glass and cement.

### 2.3.2 Silicones

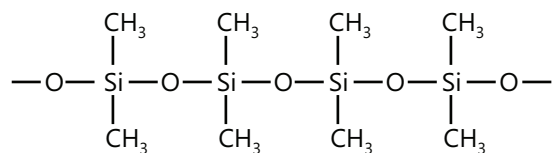
These are organosilicon polymers containing  $\text{Si}-\text{O}-\text{Si}$  linkages. They may be linear, cyclic or cross-linked polymers. These are prepared from alkyl- or aryl-chlorosilanes which in turn are obtained from Grignard reagent and silicon tetrachloride.



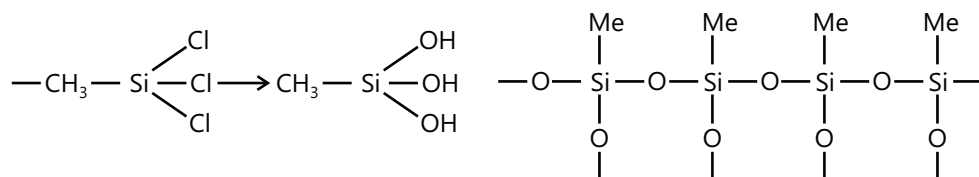
**Preparation:** Hydrolysis of the chlorides yields the corresponding silanols which polymerize by condensation by elimination of one water molecule from 2 molecules of alkyl silanols.



Now, since an active OH group is left at each end of the chain, polymerization continues at both the ends and thus the chain increases in length and ultimately forms a linear thermoplastic polymer.



Hydrolysis of alkyl trichlorosilane  $\text{CH}_3\text{SiCl}_3$  gives the monomethylsilanetriol which then undergoes polymerization to a very complex cross-linked polymer.



### 2.3.3 Glass

Glass is a transparent or translucent amorphous supercooled solid solution of silicates and borates. The most common silicates present are those of potassium, calcium and lead. Its composition is variable as it is not a true compound. An approximate formula for ordinary glass may be given as,  $\text{R}_2\text{O} \cdot \text{MO} \cdot 6\text{Si}_2\text{O}$ , where  $\text{R} = \text{Na}$  or  $\text{K}$  and  $\text{M} = \text{Ca}$ ,  $\text{Ba}$ ,  $\text{Zn}$  or  $\text{Pb}$ .

$\text{SiO}_2$  may be replaced by  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ . When glass is heated, it does not melt at a fixed temperature. However, it gradually softens and can be moulded into any desired shape. It is this property of glass which makes it a useful material for making articles of different shapes. Glass melts into liquid at a very high temperature.

**Acidic oxides:** A number of acidic oxides are useful. The choice depends upon the quality of glass to be manufactured.

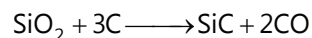
- Silica:** Sand of uniform size is used, i.e., neither too fine nor too coarse. Finer variety makes the reaction violent while coarse variety slows down the reaction. It should be free from iron oxide and organic matter.
- Boron Trioxide,  $\text{B}_2\text{O}_3$ :** This is introduced in the form of boric acid or borax. It is used when a glass of low coefficient of expansion is required.
- Phosphorus pentoxide,  $\text{P}_2\text{O}_5$ :** It is introduced in the form of calcium phosphate. It is used when opalescent glass is required.

**Basic oxides:** One or more of the following basic oxides are used:

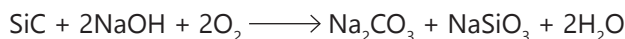
Lithium, sodium, potassium, calcium, barium, magnesium, lead and zinc oxides. Sodium is introduced in the form of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and carbon mixture. Potassium is added as potassium carbonate ( $\text{K}_2\text{CO}_3$ ) or potassium nitrate ( $\text{KNO}_3$ ). Calcium is added as  $\text{CaCO}_3$  or  $\text{CaO}$ . Barium is put in as  $\text{BaCO}_3$ . Magnesium is added as  $\text{MgCO}_3$ . Lead oxide are put in such. Zinc oxide is used when heat resistance glass is to be obtained.

### 2.3.4 Silicon Carbide (Carborundum)

**Preparation:**  $\text{SiC}$  is made commercially by reducing silicon with carbon in an electric resistance furnace.



**Properties:** It is extremely hard and fuses with much difficulty (does not decompose below  $2200^\circ\text{C}$ ) It resists most chemical reagents but is oxidized by a fused  $\text{NaOH}$  in contact with air.



In  $\text{SiC}$ , carbon and silicon atoms are alternate and are each surrounded tetrahedrally. It is widely used as an abrasive for grinding, cutting and polishing.

## PLANCESS CONCEPTS

- Diamond is covalent yet its m.p. is very high. Diamond has a three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence, diamond possesses high m.p. inspite of covalent nature.
- $\text{SiF}_6^{2-}$  is known but  $\text{SiCl}_6^{2-}$  is not,
  - (i) Smaller size of F gives rise to less steric repulsion in  $\text{SiF}_6^{2-}$ .
  - (ii) Interaction of a lone pair of F with Si is stronger than that of a chlorine lone pair.
- The hydrolysis of  $\text{CCl}_4$  is not possible but  $\text{SiCl}_4$  is easily hydrolysed. Silicon can accomodate  $\text{OH}^-$  ion due to the presence of 3d-subshell. whereas C-atom does not possess d-orbitals in its 2<sup>nd</sup> shell

Anand K ((JEE 2011, AIR 47))

**Illustration 10:** Carbon and silicon are always tetravalent but germanium and lead show divalency. Explain. **(JEE MAIN)**

**Sol:** Inert pair effect is more pronounced in Ge and Pb, as it increases down the group. This results in the divalent ionic nature of Ge and Pb.

**Illustration 11:** Producer gas is a less efficient fuel than water gas, why? **(JEE MAIN)**

**Sol:** In water gas ( $\text{CO} + \text{H}_2$ ), both components burn and evolve heat while in producer gas ( $\text{CO} + \text{N}_2$ ), only CO burns, i.e., why the former has a higher calorific value and is good fuel.

**Illustration 12:** Diamond is the hardest substance but graphite is soft in nature. Explain. **(JEE MAIN)**

**Sol:** Diamond possesses a very big three dimensional polymeric structure involving each carbon of  $\text{sp}^3$ -hybridized nature linked to four other neighbouring carbon atoms which makes it hardest. On the other hand, graphite has layer structure involving each carbon of  $\text{sp}^2$ -hybridized nature having a wide separation and weak interlayer bonds and thus two adjacent layers can easily slide over the other to produce its soft nature.

**Illustration 13:** What happens when: **(JEE MAIN)**

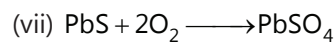
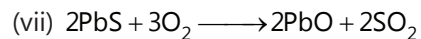
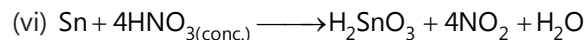
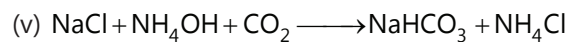
- (i) Dilute nitric acid slowly reacts with tin.
- (ii) Carbon and steam are heated.
- (iii) Red lead is treated with nitric acid.
- (iv) Iodine is added to stannous chloride.
- (v) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia.
- (vi) Tin is treated with concentrated nitric acid.
- (vii) Lead is obtained from galena by air reduction.

**Sol:** (i)  $4\text{Sn} + 10\text{HNO}_3(\text{dil}) \longrightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3$

(ii)  $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$   
(Water gas)

(iii)  $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \longrightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$

(iv)  $2\text{SnCl}_2 + 2\text{I}_2 \longrightarrow \text{SnCl}_4 + \text{SnI}_4$

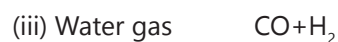


**Illustration 14:** Indicate the principal ingredients of the following:

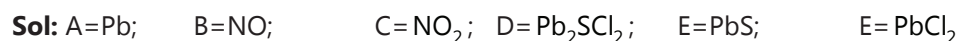
- (i) Coal gas            (ii) Producer gas            (iii) Water gas.

**(JEE MAIN)**

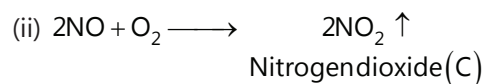
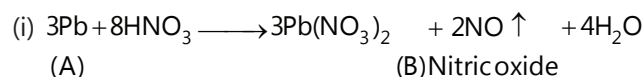
**Sol:**



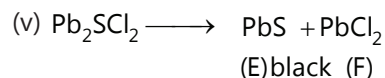
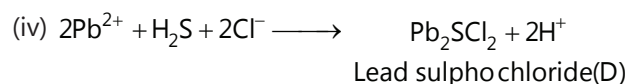
**Illustration 15:** A bluish metal (A) has a high density and readily dissolves in medium concentrated  $\text{HNO}_3$  and liberates a gas (B) which on mixing with air turns into red coloured gas (C). Metal is little affected by dil HCl or  $\text{H}_2\text{SO}_4$ . The solution containing bivalent ions of (A) gives red precipitate (D) when  $\text{H}_2\text{S}$  is passed in presence of saturated solution of KCl. 'D' on dilution turns black forming E and F. Identify A to F. **(JEE ADVANCED)**



Reactions are:



(iii) Metal is a little affected by dilute HCl or  $\text{H}_2\text{SO}_4$  due to the formation of insoluble  $\text{PbCl}_2$  or  $\text{PbSO}_4$  on the surface.



**Illustration 16:** Diamond is covalent yet its m.pt. is very high. Explain.

**(JEE ADVANCED)**

**Sol:** Diamond has a three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence diamond possesses high m. pt. inspite of its covalent nature.

**Illustration 17:**  $\text{SiF}_6^{2-}$  is known but  $\text{SiCl}_6^{2-}$  is not, why?

**(JEE ADVANCED)**

**Sol:** (i) Smaller size of F give rise to less steric repulsion in  $\text{SiF}_6^{2-}$

(ii) Interaction of lone pair of F with Si is stronger than that of the chlorine lone pair.

**Illustration 18:** The hydrolysis of  $\text{CCl}_4$  is not possible but  $\text{SiCl}_4$  is easily hydrolysed. Explain.

**(JEE ADVANCED)**

**Sol:** Silicon can accommodate  $\text{OH}^-$  ion in 3d-subshell whereas C-atom does not possess d-orbitals in its 2<sup>nd</sup> shell.

### 3. GROUP 15 ELEMENTS (NITROGEN FAMILY)

#### 3.1 Introduction

N	} 33 $ns^2np^3$	7
P		15
As		51
Sb		83
Bi		

(a) **Electronic Configuration:**  $ns^2np^3$ .

(i) Atomic and Ionic Radii Covalent and ionic (in a particular state) radii increase in size, down the group.

(b) **Ionisation Enthalpy:** Ionisation enthalpy decreases down the group due to the gradual increase in atomic size. This is due to the extra stability of half-filled p-orbitals leading to a smaller size. The order of successive ionization enthalpies, as expected is  $\Delta_1H_1 < \Delta_1H_2 < \Delta_1H_3$

(c) **Electronegativity:** Decreases down the group with increasing atomic size.

(d) **Physical Properties:** All the elements of this group are polyatomic. Dinitrogen is a diatomic gas. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal. This is due to the decrease in ionization enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases up to arsenic and then decreases up to bismuth. Except nitrogen, all the elements show allotropy.

(e) **Chemical Properties:**

(i) **Oxidation State:** The common oxidation states of these elements are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character. The stability of +5 oxidation state decreases down the group. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.

(ii) **Reactivity towards hydrogen:** All the elements of Group 15 form hydrides of the type  $EH_3$  where E=N, P, As, Sb or Bi. Basicity also decreases in the order  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(iii) **Reactivity towards oxygen:** All these elements form two types of oxides: and  $E_2O_5$ . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group.

(iv) **Reactivity towards halogens:** These elements react to form two series of halides:  $EX_3$  and  $EX_5$

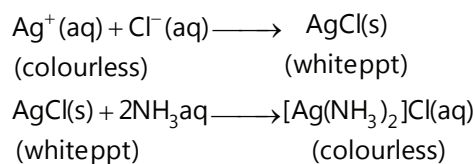
(v) **Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting -3 oxidation state.

Exp.  $Ca_3N_2$  (calcium nitride)  $Ca_3P_2$  (calcium phosphide),  $Na_3As_2$  (sodium arsenide),  $Zn_3Sb_2$  (zinc antimonide) and  $Mg_3Bi_2$  (magnesium bismuthide).

#### 3.1.1 Anomalous Behaviour of Nitrogen

Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionization enthalpy and non-availability of d orbitals. Nitrogen has the unique ability to form  $p\pi - p\pi$  multiple bonds with itself and with other elements having a small size and high electronegativity (e.g., C, O). Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form  $d\pi - p\pi$  bond as the heavier elements can, for e.g.,  $R_3P = O$  or  $R_3P = CH_2$  (R=alkyl group). Phosphorus and arsenic can form  $d\pi - d\pi$  bond also with transition metals, when their compounds like  $P(C_2H_5)_3$  and  $As(C_6H_5)_3$  act as ligands.





**Uses:** Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

### 3.2.3 Oxides of Nitrogen

**Table 16.3:** Oxides of nitrogen

Name	Formula	Oxidation state of nitrogen	Common preparation methods	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	$\text{N}_2\text{O}$	+1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	$\text{NO}$	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	$\text{N}_2\text{O}_3$	+3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$	Blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	$\text{NO}_2$	+4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	$\text{N}_2\text{O}_4$	+4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{cool}} \text{N}_2\text{O}_4$	Colourless solid/liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	$\text{N}_2\text{O}_5$	+5	$2\text{HNO}_3 + \text{P}_4\text{O}_{10} \xrightleftharpoons[\text{Heat}]{\text{cool}} 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	Colourless solid, acidic

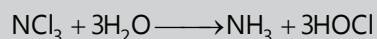
**Table 16.4:** Resonance structure and bond parameters of some oxides

Formula	Resonance Structures	Bond Parameters
$\text{N}_2\text{O}$	$:\text{N}=\text{N}=\ddot{\text{O}}: \leftrightarrow :\text{N}\equiv\text{N}-\ddot{\text{O}}:$	$\text{N} - \text{N} - \text{O}$ 113pm    119pm Linear
$\text{NO}$	$:\text{N} = \ddot{\text{O}}: \leftrightarrow :\ddot{\text{N}} = \ddot{\text{O}}:$	$\text{N} - \text{O}$ 115pm
$\text{N}_2\text{O}_3$		

NO <sub>2</sub>		
N <sub>2</sub> O <sub>4</sub>		
N <sub>2</sub> O <sub>5</sub>		

### PLANCESS CONCEPTS

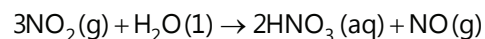
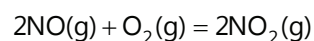
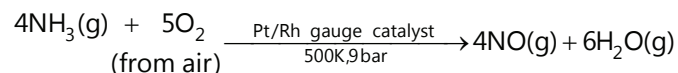
- NO is paramagnetic in its gaseous state but diamagnetic in its liquid or solid state, The NO molecule has eleven valence electrons and is thus paramagnetic in nature due to unpaired electron. In solution or solid state, it forms a loose dimer in such a way that magnetic field of unpaired electrons of two molecules cancel out it behaves as diamagnetic in nature
- NF<sub>3</sub> is stable but NCl<sub>3</sub> and NI<sub>3</sub> are readily hydrolysed and are explosives NF<sub>3</sub> is not hydrolysed because neither N nor F can expand their octet by using d-orbitals. On the other hand NCl<sub>3</sub> and NI<sub>3</sub> hydrolyse violently because Cl and I can expand their octet by using d-orbitals.



Vaibhav Gupta (JEE 2009, AIR 54)

### 3.2.4 Nitric Acid

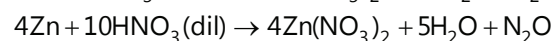
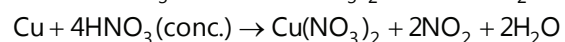
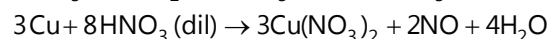
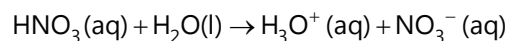
**Preparation:** By Ostwald's process:



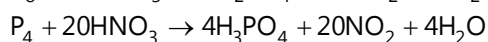
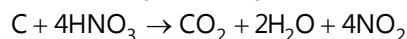
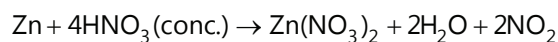
NO thus formed is recycled and the aqueous HNO<sub>3</sub> can be concentrated by distillation upto ~68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H<sub>2</sub>SO<sub>4</sub>

**Properties:** It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~68% of the HNO<sub>3</sub> by mass and has a specific gravity of 1.504.

**Chemical reaction of HNO<sub>3</sub> with metal and non-metals:**







**Brown Ring Test:** The familiar brown ring test for nitrates depends on the ability of  $\text{Fe}^{2+}$  to reduce nitrates to nitric oxide, which reacts with  $\text{Fe}^{2+}$  to form a brown coloured complex. The test is usually carried out by adding a dilute ferrous sulphate solution to an aqueous solution containing nitrate iron, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.

### 3.3 Phosphorus

#### 3.3.1 Types of Phosphorous

(a) Yellow or white phosphorous      (b) Red Phosphorous      (c) Black Phosphorous

**White P:** (a) White P exists as discrete  $\text{P}_4$  molecules. It has tetrahedral geometry. Bond angle is  $60^\circ$  instead of  $109^\circ$ . With this bond angle, white P is associated with the strain accounting for its less stability and greater reactivity.

(b) Ignition temp of white P is  $30^\circ\text{C}$  i.e. it is highly reactive and when it undergoes ignition, it releases a large amount of energy which is emitted in the form of light, termed as Fluorescence.

**Red P:** (a) Formed from white P by breakage of one P – P bond and so chain of  $\text{P}_4$  molecules is formed.

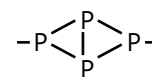


Figure 16.3: a Red

(b) Long Chain of  $\text{P}_4$  molecules are formed and when compared with white P, red P has more density, less reactivity with breakage of P – P bond, strain of  $\text{P}_4$  decreases

(c) Ignition temp of red P is above  $230^\circ\text{C}$

**Black P:** (a) Exists in a hexagonal form like graphite.

(b) It is least reactive and has maximum density.

(c) Black P exists as a solid of high density.

(d) It is a good conductor of electricity.

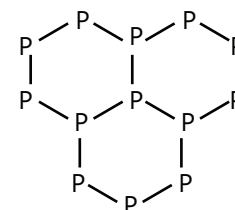


Figure 16.4: b Black

**Uses:**

(a) Phosphorous is largely used in the matches industry.

(b) White phosphorous is used as a rat poison.

#### 3.3.2 Some Important Compounds of Phosphorous

(a) **Phosphorus Trichloride:**  $\text{P}_4 + 8\text{SOCl}_2 \rightarrow 4\text{PCl}_3 + 4\text{SO}_4 + 2\text{S}_2\text{Cl}_2$

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

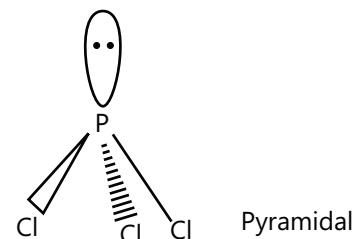
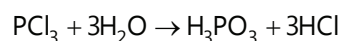
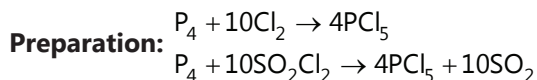
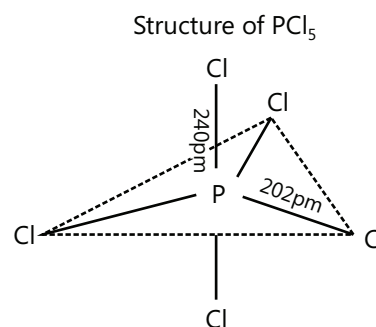
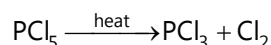
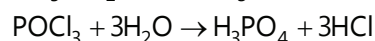
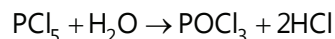


Figure 16.5: Structure of  $\text{PCl}_3$

**(b) Phosphorus Pentachloride**

**Note:** In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P-Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

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



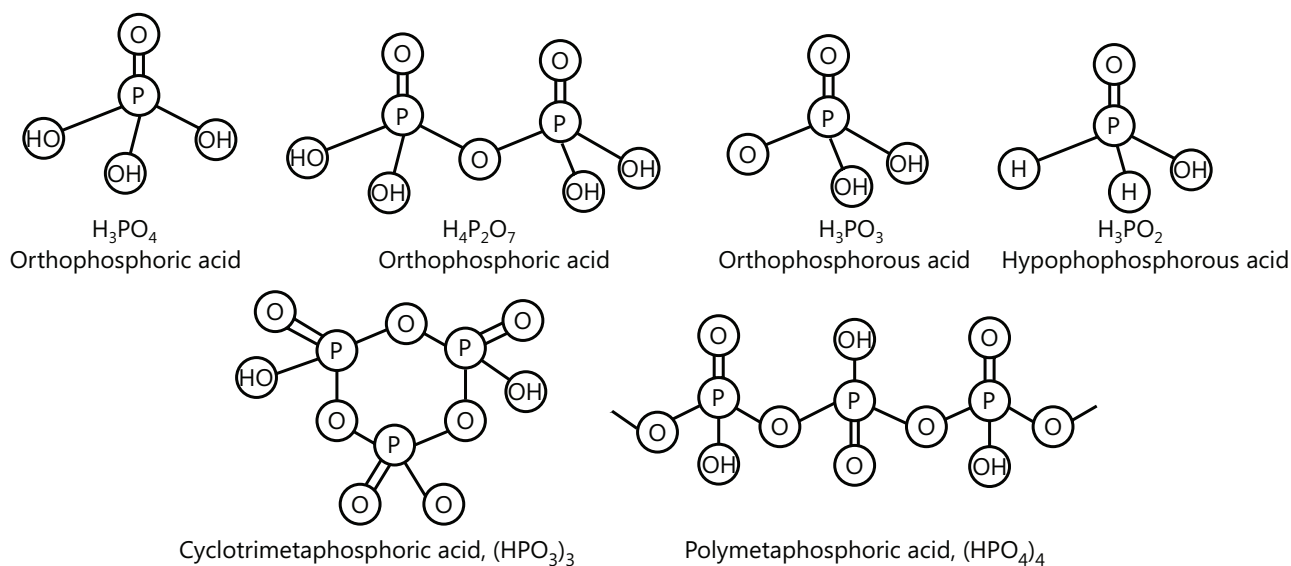
**Figure 16.6:** Structure of  $PCl_5$

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

**3.3.3 Oxoacids of Phosphorus**

**Table 16.5:** Oxoacids of Phosphorus

Name	Formula	Oxidation state of Phosphorous	Characteristic bonds and their number	Preparation
Hypophosphorous (phosphinic)	$H_3PO_2$	+1	One P-OH Two P-H One P=O	white $P_4$ + alkali
Orthophosphorous (Phosphonic)	$H_3PO_3$	+3	Two P-OH One P-H P-O-P One P=O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P-OH Two P-H Two P=O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P-OH Two P=O One P-P	red $P_4$ + alkali
Orthophosphoric	$H_3PO_4$	+5	Three P-OH One P=O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P-OH Two P=O One P-O-P	heat phosphoric acid
Metaphosphoric	$(HPO_3)_n$	+5	Three P-OH Three P=O Three P-O-P	Phosphorus acid + $Br_2$ , heat in a sealed tube

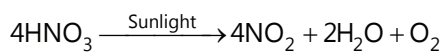


**Figure 16.7:** Halogen acids of Phosphorous

**Illustration 19:** Concentrated  $\text{HNO}_3$  turns yellow in sun light. Explain.

**(JEE MAIN)**

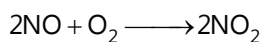
**Sol:**  $\text{HNO}_3$  is partially decomposed in sun light to produce  $\text{NO}_2$ . The  $\text{NO}_2$  formed dissolves in  $\text{HNO}_3$  to produce yellow colour.



**Illustration 20:** Nitric oxide becomes brown when released into air. Explain.

**(JEE MAIN)**

**Sol:** Nitric oxide reacts with air to get oxidized to  $\text{NO}_2$  which has brown yellow vapours.



**Illustration 21:** Aluminium containers can be used for storing conc.  $\text{HNO}_3$ . Why?

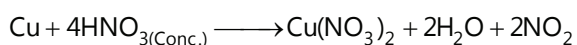
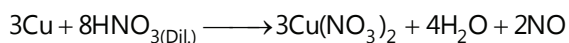
**(JEE MAIN)**

**Sol:** Al becomes passive when in contact with  $\text{HNO}_3$  due to a fine coating of its oxide on its surface and thus, Al containers can be used to store conc.  $\text{HNO}_3$ .

**Illustration 22:** Copper dissolves in  $\text{HNO}_3$ , but not in  $\text{HCl}$ . Why?

**(JEE MAIN)**

**Sol:** Copper is placed below H in electrochemical series and does not liberate  $\text{H}_2$  from acid. However,  $\text{HNO}_3$  oxidises Cu due to its strong oxidant nature.



**Illustration 23:** NO is paramagnetic in gaseous state but diamagnetic in liquid or solid state, why? **(JEE MAIN)**

**Sol:** The NO molecule has eleven valence electrons and thus, paramagnetic in nature due to the unpaired electron. In solution or solid state, it forms a loose dimer in such a way that the magnetic field of unpaired electrons of two molecules cancel out and it behaves as diamagnetic in nature.

**Illustration 24:** Which among  $P_4O_{10}$ ,  $Cl_2O_7$ ,  $I_2O_5$  has the greatest affinity for water? **(JEE ADVANCED)**

**Sol:**  $P_4O_{10}$ , one of the most powerful dehydrating agents known.  $Cl_2O_7$  is the product of dehydration of  $HClO_4$  by  $P_4O_{10}$ .  $12HClO_4 + P_4O_{10} \longrightarrow 6Cl_2O_7 + 4H_3PO_4$

Also,  $I_2O_5$  is obtained by heating  $HIO_3$  and thus, it cannot have too great affinity for water.

**Illustration 25:** Describe the action of heat on the following compounds: **(JEE ADVANCED)**

- |                         |   |
|-------------------------|---|
| (i) Ammonium nitrate    | (ii) Ammonium nitrite                   |
| (iii) Ammonium Chloride | (iv) A mixture of $NaNO_2$ and $NH_4Cl$ |
| (v) Ammonium dichromate | (vi) Orthophosphoric acid               |
| (vii) Phosphorous acid  | (viii) Hypophosphorous acid             |
| (ix) Copper nitrate     | (x) Silver Nitrate                      |

**Sol:** (i)  $NH_4NO_3 \longrightarrow N_2O + 2H_2O$

(ii)  $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(iii)  $NH_4Cl \rightleftharpoons NH_3 + HCl$

(iv)  $NaNO_2 + NH_4Cl \longrightarrow N_2 + NaCl + 2H_2O$

(v)  $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

(vi)  $2H_3PO_4 \xrightarrow{205^\circ C} H_4P_2O_7 + H_2O$

$H_3PO_4 \xrightarrow{600^\circ C} HPO_3 + H_2O$

$4H_3PO_4 \xrightarrow{\text{Red heat}} P_4O_{10} + 6H_2O$

(vii)  $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$

(viii)  $2H_3PO_2 \longrightarrow H_3PO_4 + PH_3$

(ix)  $2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

(x)  $2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

**Illustration 26:** What happens when an aqueous solution of hydrazine reacts with:

- An aqueous solution  $I_2$ .
- An alkaline solution of copper sulphate.
- An aqueous alkaline solution of potassium ferricyanide.
- An ammoniacal solution of silver nitrate.

**(JEE ADVANCED)**

**Sol:** (i)  $N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$

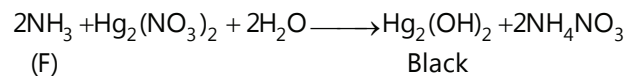
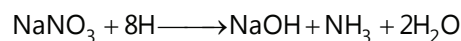
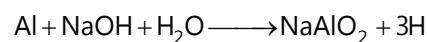
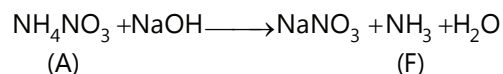
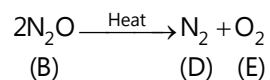
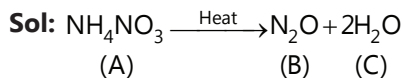
(ii)  $N_2H_4 + 2CuSO_4 + 4KOH \longrightarrow N_2 + 2Cu + 2K_2SO_4 + 4H_2O$

(iii)  $4K_3[Fe(CN)_6] + 4KOH + N_2H_4 \longrightarrow 4K_4[Fe(CN)_6] + 4H_2O + N_2$

(iv)  $N_2H_4 + 2NH_4OH + 2AgNO_3 \longrightarrow N_2 + 2Ag + 2NH_4NO_3 + 2H_2O$

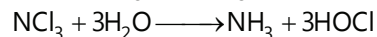
**Illustration 27:** An inorganic compound (A) when heated decomposes completely to give only two gases (B) and (C). (B) is a neutral gas, fairly soluble in water and itself decomposes on heating to two different gases (D) and (E).

(A) When warmed with NaOH gives another gas (F) which turns mercurous nitrate paper black. After sometime, the gas (F) ceases to evolve, however its supply is restored by treating residual solution with aluminium powder. Identify (A) to (F) and give necessary equations. **(JEE ADVANCED)**



**Illustration 28:**  $\text{NF}_3$  is stable but  $\text{NCl}_3$  and  $\text{NI}_3$  are readily hydrolysed and are explosives. Explain. **(JEE ADVANCED)**

**Sol:**  $\text{NF}_3$  is not hydrolysed because neither N nor F can expand their octet by using d-orbitals. On the other hand,  $\text{NCl}_3$  and  $\text{NI}_3$  hydrolyse violently because Cl and I can expand their octet by using their d-orbitals.



## 4. GROUP 16 ELEMENTS (OXYGEN FAMILY)

### 4.1 Introduction

These are called chalcogen. Because these are ore forming elements {Chalco=ore}



- Electronic Configuration:**  $ns^2np^4$
- Atomic and Ionic Radii:** Due to the increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.
- Electron Gain Enthalpy:** Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative up to polonium.
- Physical Properties:** Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life= 13.8 days).

The melting and boiling points increase with an increase in atomic number down the group.

### 4.1.1 Anomalous Behaviour of Oxygen

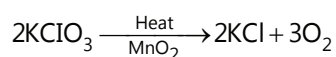
Due to its small size and high electronegativity, strong hydrogen bonding is observed in  $\text{H}_2\text{O}$  and not in  $\text{H}_2\text{S}$ .

- (a) **Reactivity with hydrogen:** All the elements of Group 16 form hydrides of the type  $\text{H}_2\text{E}$  (E=O, S, Se, Te, Po). Their acidic character increases from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Te}$ . The increase in acidic character can be explained in terms of a decrease in bond enthalpy for the dissociation of H-E bond down the group. Owing to the decrease in enthalpy for the dissociation of H-E bond, down the group, the thermal stability of hydrides also decreases from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Po}$ . All the hydrides except water possess reducing property and this character increases from  $\text{H}_2\text{S}$  to  $\text{H}_2\text{Te}$ .
- (b) **Reactivity with oxygen:** All these elements form oxides of the  $\text{EO}_2$  and  $\text{EO}_3$  types where E=S, Se, Te or Po.
- (c) **Reactivity towards the halogens:** Elements of group 16 form a large number of halides of the type,  $\text{EX}_6$ ,  $\text{EX}_4$  and  $\text{EX}_2$  where E is an element of the group and X is a halogen. The stability of the halides decreases in the order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ .

## 4.2 Dioxygen

**Preparation:** Dioxygen can be obtained in the laboratory by the following ways:

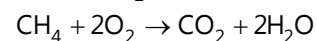
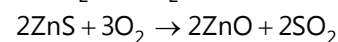
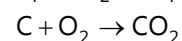
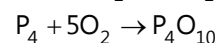
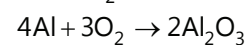
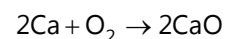
- (a) By heating oxygen containing salts such as chlorates, nitrates and permanganates.



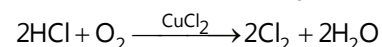
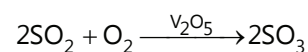
- (b) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.  $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
- (c) On a large scale, it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

**Properties:** Dioxygen is a colourless and odourless gas. Its solubility in water is to the extent of  $3.08 \text{ cm}^3$  in  $100 \text{ cm}^3$  water at 293 K which is just sufficient for the vital support of marine and aquatic life.

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:



Some compounds are catalytically oxidized. For e.g.



## 4.3 Sulphur

- (a) **Rhombic sulphur ( $\alpha$ -sulphur):** This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in  $\text{CS}_2$ . It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in  $\text{CS}_2$ .
- (b) **Monoclinic sulphur ( $\beta$ -sulphur):** This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling. Till a crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of  $\beta$ -sulphur are formed. It is stable above 369 K and

transforms into  $\alpha$ -sulphur below it. Its m.p. is 393 K and specific gravity 1.98. It is soluble in  $\text{CS}_2$ . Conversely,  $\alpha$ -sulphur is stable below 369 K and transforms into  $\beta$ -sulphur above this temperature. At 369 K both the forms are stable. This temperature is called transition temperature. Both rhombic and monoclinic sulphur have  $\text{S}_8$  molecules. These  $\text{S}_8$  molecules are packed to give different crystal structures.

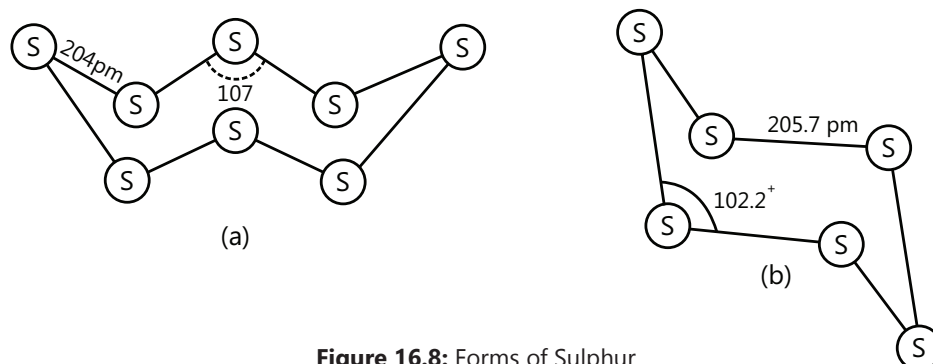


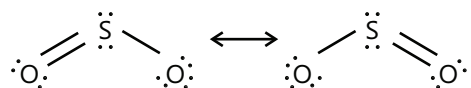
Figure 16.8: Forms of Sulphur

### 4.3.1 Sulphur Dioxide

**Preparation:** When sulphur is burnt in air or oxygen to form  $\text{SO}_2$   $\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$

**Properties:** Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.

**Structure of  $\text{SO}_2$  molecules**



The molecule of  $\text{SO}_2$  is angular. It is a resonance hybrid of the two canonical forms.

**Uses:** Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide.

### 4.3.2 Oxoacids of Sulphur

Sulphur forms a number of oxoacids such as

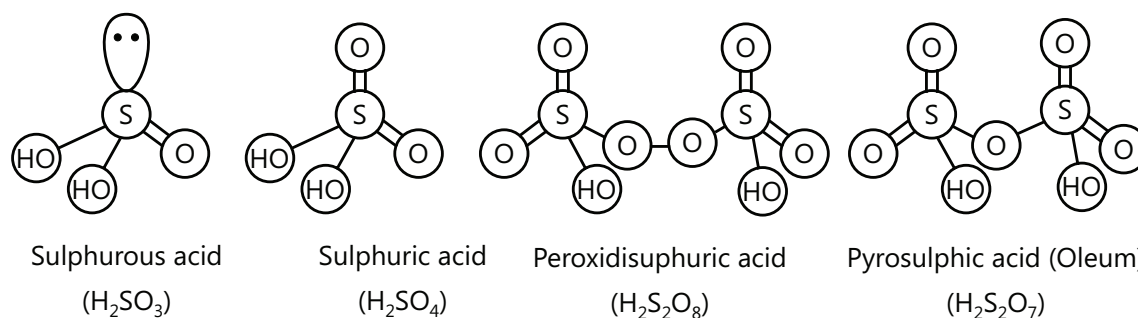
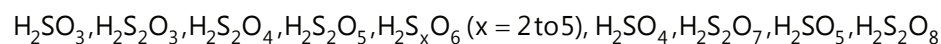


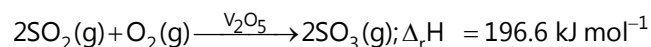
Figure 16.9: Oxoacids of Sulphur

### 4.3.3 Sulphuric Acid

**Manufacture:** Sulphuric acid is one of the most important industrial chemicals worldwide. Sulphuric acid is manufactured by the Contact Process which involves three steps:

- Burning of sulphur or sulphide ores in air to generate  $\text{SO}_2$
- Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction with oxygen in the presence of a catalyst ( $\text{V}_2\text{O}_5$ ), and
- Absorption of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ). The  $\text{SO}_2$  produced is purified by removing dust and other impurities such as arsenic compounds.

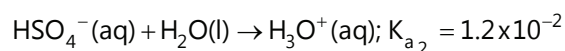
The key step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).



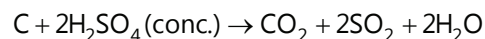
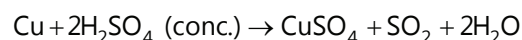
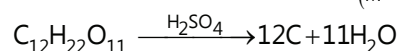
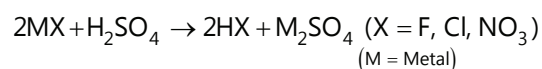
**Manufacture of Sulphuric Acid:** The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration. In the industry, two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7$  (Oleum). The sulphuric acid obtained by Contact process is 96-98% pure.

**Properties:** Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. It dissolves in water with the evolution of a large quantity of heat. While preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring. The chemical reaction of sulphuric acid is as a result of the following characteristics: (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidizing agent.



#### Chemical Reactions:



#### PLANCESS CONCEPTS

- Among  $\text{H}_2\text{O}$ ,  $\text{HCl}$  and  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  has the highest boiling point and  $\text{HCl}$  the lowest.  $\text{H}_2\text{O}$  is capable of showing more stronger H-bonding than  $\text{NH}_3$ , while  $\text{HCl}$  has no H-bonding. The b.p. order is  $\text{H}_2\text{O} > \text{NH}_3 > \text{HCl}$ .
- $\text{H}_2\text{S}$  acts only as a reducing agent while  $\text{SO}_2$  can act both as a reducing agent and oxidizing agent. S in  $\text{SO}_2$  has a oxidation state of +4. It lies between the minimum oxidation state (-2) and maximum oxidation (+6) of S. Thus, S in  $\text{SO}_2$  can show an increase in its oxidation number (i.e., act as a reductant) or can show a decrease in its oxidation number (i.e., it acts as an oxidant). On the other hand, in  $\text{H}_2\text{S}$ , S is in -2 oxidation state and can only increase its oxidation state to act as a reductant.



**Illustration 29:** What are the oxidation states of S in the following compounds: **(JEE MAIN)**

(a) PbS      (b) SO<sub>2</sub>    (c) SF<sub>6</sub>      (d) Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>    (e) H<sub>2</sub>SO<sub>3</sub>

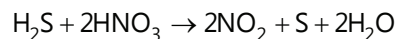
**Sol:** (a) -2, (b) +4, (c) +4, (d) +2, (e) +4

**Illustration 30:** H<sub>2</sub>S acts only as reducing agent while SO<sub>2</sub> can act both as reducing agent and oxidising agent. Explain. **(JEE MAIN)**

**Sol:** S in SO<sub>2</sub> has oxidation state +4. It lies between the minimum oxidation state (-2) and maximum oxidation state (+6) of S. Thus S in SO<sub>2</sub> can show an increase in its ox. no. (i.e., act as reductant) or can show a decrease in its ox. no. (i.e., act as oxidant). On the other hand, in H<sub>2</sub>S, S is in -2 oxidation state and can only increase its oxidation state to act as reductant.

**Illustration 31:** Nitric acid cannot be used to prepare H<sub>2</sub>S. Explain. **(JEE MAIN)**

**Sol:** Nitric acid is an oxidizing agent. It will oxidise H<sub>2</sub>S.

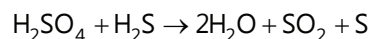


**Illustration 32:** Among H<sub>2</sub>O, HCl and NH<sub>3</sub>, H<sub>2</sub>O has the highest boiling point and HCl the lowest. **(JEE MAIN)**

**Sol:** H<sub>2</sub>O is capable of showing more stronger H-bonding than NH<sub>3</sub>, while HCl has no H-bonding. The b.p. order is H<sub>2</sub>O > NH<sub>3</sub> > HCl

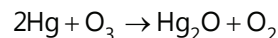
**Illustration 33:** Conc. H<sub>2</sub>SO<sub>4</sub> cannot be used for drying up H<sub>2</sub>S. Explain **(JEE MAIN)**

**Sol:** Conc. H<sub>2</sub>SO<sub>4</sub> oxidises H<sub>2</sub>S to S and thus cannot be used as for drying up H<sub>2</sub>S.



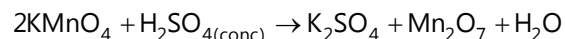
**Illustration 34:** Ozone destroys a mercury meniscus. Why? **(JEE ADVANCED)**

**Sol:** Ozone oxidises Hg to mercury suboxide which starts sticking to glass and loses its mobility. Hence, Hg loses its meniscus in contact with ozone. However, it can be regained by the action of H<sub>2</sub>O<sub>2</sub>.



**Illustration 35:** KMnO<sub>4</sub> should not be dissolved in conc. H<sub>2</sub>SO<sub>4</sub>. Explain. **(JEE ADVANCED)**

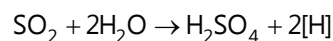
**Sol:** KMnO<sub>4</sub> forms explosive covalent compound, Mn<sub>2</sub>O<sub>7</sub> with conc. H<sub>2</sub>SO<sub>4</sub>



However it can be dissolved in dil. H<sub>2</sub>SO<sub>4</sub> to give nascent oxygen, if it is to be used as an oxidant

**Illustration 36:** SO<sub>2</sub> acts as bleaching agent. Explain. **(JEE ADVANCED)**

**Sol:** SO<sub>2</sub> in presence of water is oxidized to H<sub>2</sub>SO<sub>4</sub> liberating nascent hydrogen, which reduces/bleaches the colouring matter.



Colouring matter + 2[H] → Colourless compound

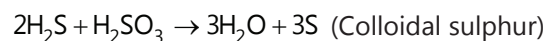
**Illustration 37:** An acidified  $K_2Cr_2O_7$  paper turns green when exposed to  $SO_2$ . Explain. **(JEE ADVANCED)**

**Sol:**  $SO_2$  reduces  $K_2Cr_2O_7$  to green chromium sulphate.



**Illustration 38:** A white turbidity is obtained by passing  $H_2S$  in aqueous solution of  $SO_2$ . Why? **(JEE ADVANCED)**

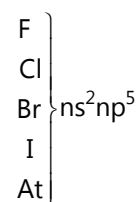
**Sol:** Aqueous solution of  $SO_2$  and  $H_2S$  undergoes redox changes to produce colloidal sulphur as white turbidity.



## 5. GROUP 17 ELEMENTS (HALOGEN FAMILY)

### 5.1 Introduction

Named because they are sea - salts forming elements.



#### General Properties:

##### (a) State and Nature

- (i) F and Cl are Gas
- (ii) Br: Liquid
- (iii) I, At is solid
- (iv) All are non metallic. But non metallic character decreases down the group.
- (v) I has metallic lustre on heating and undergoes sublimation.

**(b) Atomic Radii, Ionic Radii, B.P. and M.P., Density:** All these characters increase down the group

**(c) Ionization Potential and Electronegativity:** Decreases down the group

##### (d) Electron Affinity (E.A)

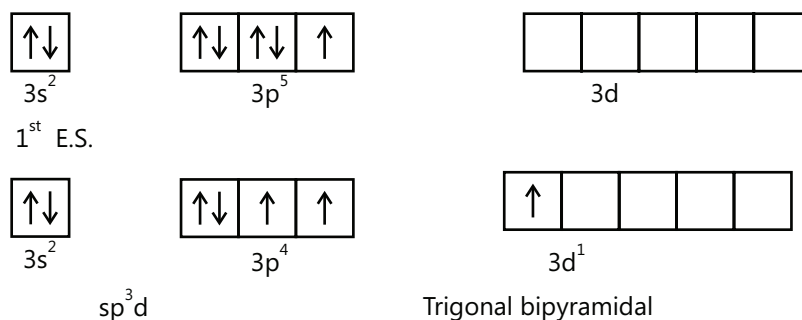
From F to Cl  $\rightarrow$  E.A increases.

Due to the availability of a vacant d-orbital in Cl and then E.A. decreases

So, order is  $Cl > F > Br > I$ .

##### (e) Valency and Oxidation State:

- (i)  $ns^2 np^5$
- (ii) Valency = 1  
If halogens combines with more E.N. elements, then O.S. = +1.
- (iii) For Cl, Ground State:  
Valency = 1



(f) **Bond Energy:** F – F bond dissociation energy is less than that of Cl-Cl and Br-Br. It is due to larger inter electronic (electron-electron) repulsion between the non-bonding electrons in the 2p orbitals of fluorine atom than in the 3p orbitals of chlorine atoms.

F-F Cl-Cl Br-Br I-I

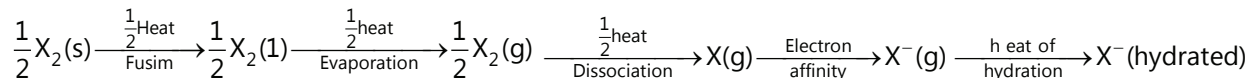
38 kcal/mol 57 kcal/mol 45.5 kcal/mol 35.6 kcal/mol  $Cl_2 > Br_2 > F_2 > I_2$

### 5.1.1 Oxidising Power

The electron affinity, or tendency to gain electrons reaches a maximum at chlorine. Oxidation may be regarded as the removal of electrons so that an oxidizing agent gains electrons.

Thus halogens act as oxidizing agents.

The strength of an oxidizing agent (i.e. oxidation potential) depends upon several energy terms and is represented by following diagram.

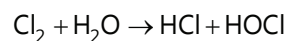
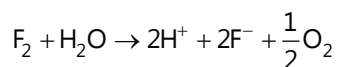


The heat of fusion, evaporation and dissociation are positive and electron affinity and heat of hydration are negative. The net energy (E) required for oxidizing reaction is given by-

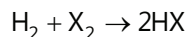
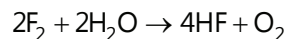
$$E_{(\text{net})} = \frac{1}{2}H_f + \frac{1}{2}H_v + \frac{1}{2}H_d - E.A. - H_{(\text{hyd})}$$

Element	$E_{\text{net}}$ (kcal)
$F_2$	-186.5
$Cl_2$	-147.4
$Br_2$	-136.4
$I_2$	-122.4

Thus oxidizing powers decrease on descending in group VII. Fluorine is a strong oxidising agent as seen in the reaction given below where oxygen in water has been oxidised. The oxidation of  $H_2O$  by  $Cl_2$  is thermodynamically possible but since the energy of activation is high, this reaction does not occur.



Iodine is even weaker where the free energy change indicates that for oxidation of water, it needs a supply of energy.

**Chemical Properties****(a) Reaction with H<sub>2</sub>****(i)** All halogens reacts with H<sub>2</sub> to form hydrogen halides.**(ii)** Reactivity of Halogens F > Cl > Br > I**(iii)** HCl, HBr, HI acts as reducing agent.**(b) Reaction with H<sub>2</sub>O****(i)** H<sub>2</sub>O acts as reducing agent only with fluorine.**(ii)** H<sub>2</sub>O + I<sub>2</sub> → No Reaction.**(c) Displacement reaction****(i)**  $\text{F}_2 + 2\text{NaX} \rightarrow 2\text{NaF} + \text{X}_2$  {X = Cl, Br, I} $\text{Cl}_2 + 2\text{NaX} \rightarrow 2\text{NaCl} + \text{X}_2$  {X = Br<sub>2</sub>, I<sub>2</sub>}So order of displacement [F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>]**(ii)** If Halogen is in -ve O.S., then it is replaced by more E.N. element.**(iii)** If Halogen is +ve O.S., then it is replaced by less E.N. element.**(d) Reaction with metals: Metal halides are formed F > Cl > Br > I****(e) Reaction with non-metals:** Non-metallic halides are formed.Eg. NF<sub>3</sub>, PCl<sub>3</sub> etc.**(f) Reaction with NH<sub>3</sub>****(i)**  $3\text{F}_2 + \text{NH}_3 \rightarrow \text{NF}_3 + 3\text{HF}$ **(ii)**  $3\text{Cl}_2 + \text{NH}_3 \rightarrow \text{NCl}_3 + 3\text{HCl}$ **(g) Reaction with NaOH****(i)**  $\text{F}_2 + \text{NaOH (dil.)} \rightarrow 2\text{NaF} + \text{OF}_2 + \text{H}_2\text{O}$ **(ii)**  $2\text{F}_2 + 4\text{NaOH (conc.)} \rightarrow 4\text{NaF} + 2\text{H}_2\text{O} + \text{O}_2$ **(h) Formation of oxides****(i)** No oxides of F because of its maximum E.N. character.**(ii)** Rest form

X <sub>2</sub> O	X <sub>2</sub> O <sub>3</sub>	X <sub>2</sub> O <sub>5</sub>	X <sub>2</sub> O <sub>7</sub>
Eg. +1	+3	+5	+7
Cl <sub>2</sub> O	Cl <sub>2</sub> O <sub>3</sub>	Cl <sub>2</sub> O <sub>5</sub>	Cl <sub>2</sub> O <sub>7</sub>

**(iii)** All these oxides are acidic**(iv)** Acidity decreases down the group and maximum active oxide is Cl<sub>2</sub>O<sub>7</sub>**(i) Formation of oxyacids****(i)** F does not form any oxyacid due to High E.N.

(ii) Rest oxyacids are

HXO	HXO <sub>2</sub>	HXO <sub>3</sub>	HXO <sub>4</sub>
+1	+3	+5	+7
Hypohalous acid	Halous acid	Halic acid	Perhalic acid

(j) **Interhalogens**

Products are obtained by uniting two halogen compounds:



Where A = less E.N. Halogen

B = More E.N. Halogen

	ClF	ClF <sub>3</sub>	BrF <sub>5</sub>	IF <sub>7</sub>
Eg.	BrCl	BrCl <sub>3</sub>	ICl <sub>5</sub>	
	IBr	IBr <sub>3</sub>		

These interhalogens have polarity because of different E.N.

**Note:** Abnormal behaviour of Fluorine as compared to Other Members:

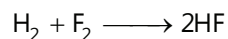
Fluorine differs considerably from other halogens due to its-

- Small size
- High electronegativity.
- Non availability of d – orbitals in its valence shell.
- Low bond dissociation energy of F – F bond.
- Boiling point of HF is the highest and then it increases down the group.
- Due to hydrogen bonding, HF is a liquid while HCl, HBr and HI are gases.
- Solubility of salts

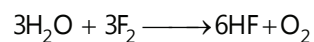
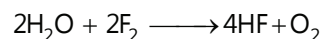
AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

It combines with hydrogen explosively at a low temperature and even in the dark.

None of the other halogens combine so readily.



(i) It liberates oxygen as well as ozone with water.



**Family Members of Halogen**

(a) **Fluorine (F<sub>2</sub>)**

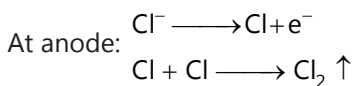
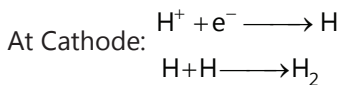
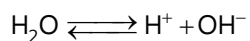
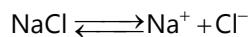
(i) Uses: It is used in the preparation of fluorine compounds such as.

Freon: Freon – 12 i.e. CF<sub>2</sub>Cl<sub>2</sub> as used in refrigeration and air conditioning in place of NH<sub>3</sub> and SO<sub>2</sub>

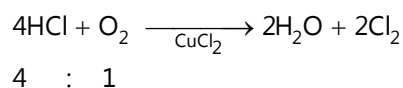
Teflon: (–F<sub>2</sub>C–CF<sub>2</sub>)<sub>n</sub> It is a new plastic.

**Chlorine (Cl<sub>2</sub>)**

(a) **Preparation:** By the electrolysis of brine (Aq. Solution of NaCl) in nelson cell. This is the cheapest method



(b) **Deacon's process:**



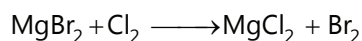
Chlorine gas thus obtained contains N<sub>2</sub> and O<sub>2</sub> and is used for the manufacture of bleaching powder by Hasenclever's process

(c) **Uses:**

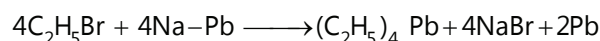
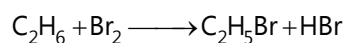
- (i) As a germicide and disinfectant.
- (ii) Domestic antiseptic solution (NaOCl)

**Bromine (Br<sub>2</sub>)**

(a) **Preparation:** (a) Bittern: Mother liquor contains about 0.25% of bromine or MgBr<sub>2</sub> and is known as bittern. Bittern is treated with Chlorine gas.

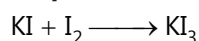


(b) **Uses:** (a) It is used in preparation of ethyl bromide which is used in the manufacturing of tetraethyl lead (TEL) as an important anti-knock compound in the petroleum industry.

**Iodine (I<sub>2</sub>)**

(a) I<sub>2</sub> is the rarest of all the halogens. Its main source is kelp (varee).

(b) **Properties:** (a) It is only sparingly soluble in water but readily in NaOK iodide due to formation of triiodide.



However, this solution behaves as a simple mixture of KI and free I<sub>2</sub>.

**Note:** Tincture of iodine contains  $\frac{1}{2}$  ounce I<sub>2</sub>,  $\frac{1}{4}$  ounce KI and 1 pinch of rectified spirit.

**Table 16.6:** Oxy acids of Halogens

Oxidation state	Chlorine	Bromine	Iodine	Name of acid	Name of salt of halogens	
+1	HClO	HBrO	HIO	Hypohalous	Hypohalite	Stability and acidity increases but oxidizing power decreases
+3	HClO <sub>2</sub>	-	-	Halous	Halite	
+5	HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>	Halic	Halate	
+7	HClO <sub>4</sub>	HBrO <sub>4</sub>	HIO <sub>4</sub>	Perhalic	Perhalate	

**Oxy Acids of Halogens:**

(a) Fluorine does not form any oxy-acids because it is more electronegative than oxygen.

(b) Other halogens form four series of oxy acids with formulae

HXO → Hypohalous

HXO<sub>2</sub> → Halous

HXO<sub>3</sub> → Halic

HXO<sub>4</sub> → Perhalic acids or Halic (I), Halic (III), Halic (V) and Halic (VII)

(c) Thermal stability – Stability increases and oxidizing power decreases

(d) Oxidising power-

ClO<sup>-</sup>

↓

ClO<sub>4</sub><sup>-</sup>

Hypochlorites are the strongest oxidizing agents.

(e) Relative acidity ∝ oxidation no.

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

**Note:** (i) In all these acids and salts halogen is in sp<sup>3</sup> hybridised state.

(ii) Stronger the acid, the weaker will be its conjugate base and vice-versa.

ClO<sub>4</sub><sup>-</sup> < ClO<sub>3</sub><sup>-</sup> < ClO<sub>2</sub><sup>-</sup> < ClO<sup>-</sup> (relative basic character)

Thus, ClO<sub>4</sub><sup>-</sup> is the weakest base and HClO<sub>4</sub> (conjugate acid of ClO<sub>4</sub><sup>-</sup>) is the strongest acid.

ClO<sub>4</sub><sup>-</sup> > ClO<sub>3</sub><sup>-</sup> > ClO<sub>2</sub><sup>-</sup> > ClO<sup>-</sup>

←—————

Relative stability of Cl–O bonds

### PLANCESS CONCEPTS

- Fluorine exhibits a covalence of one only whereas other halogens show a covalence ranging from 1 to 7. Because in fluorine vacant d-orbitals are not present and so the electron can't be unpaired by electronic excitation. On the other hand, rest all halogens show covalence from 1 to 7 by the excitation of their p-electrons to d-subshells.
- $\text{KHF}_2$  is well known, whereas  $\text{KCl}_2$  or  $\text{KBr}_2$  does not exist.  $\text{H}_2\text{F}_2$  exists as dimeric molecule due to H-bonding and thus, shows dibasic nature. Hence, it gives two series of salts  $\text{KHF}_2$  [ $\text{K}^+$  and  $\text{F}^- \cdots \cdots \text{H} - \text{F}^-$ ] and  $\text{KF}$  [ $\text{K}^+$  and  $\text{F}^-$ ] whereas  $\text{HCl}$  and  $\text{HBr}$  do not show hydrogen bonding and thus formation of  $\text{KCl}_2$  or  $\text{KBr}_2$  is not possible.

**Chinmay S Purandare (JEE 2012, AIR 698)**

**Illustration 39:** Pure HI kept in a bottle acquires a brown colour after some time. Explain. **(JEE MAIN)**

**Sol:** HI is strong reducing agent and is oxidized by oxygen to  $\text{I}_2$ . The liberated iodine is dissolved there and imparts a brown colour to the solution.  $4\text{HI} + \text{O}_2 \longrightarrow 2\text{H}_2\text{O} + 2\text{I}_2$

**Illustration 40:** Iodine dissolves more in KI solution, than in pure water. Explain **(JEE MAIN)**

**Sol:**  $\text{I}_2$  is non-polar in nature and thus its solubility in water (a polar solvent) is less which however becomes more if KI is present due to a complex formation.  $\text{I}_2 + \text{KI} \longrightarrow \text{KI}_3$  (soluble complex)

**Illustration 41:** Chlorine is a gas while iodine is a solid under ordinary conditions. Explain. **(JEE MAIN)**

**Sol:** Due to high mol. wt., Van der Waals' forces of attraction are stronger in  $\text{I}_2$ .

**Illustration 42:** Fluorine exhibits a covalence of one only whereas other halogens show a covalence ranging from 1 to 7. **(JEE MAIN)**

**Sol:** Because in fluorine, vacant d-orbitals are not present and so electrons can't be unpaired by electronic excitation. On the other hand, rest all halogens show covalence from 1 to 7 by excitation of their s and p-electrons to d-subshells.

Halogens (Cl, Br, I)	ns	np	nd
<b>Ground state</b>	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow$	
<b>I excited state</b>	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$	$\uparrow$ <span style="float: right;">Covalence = 1</span>
<b>II excited state</b>	$\uparrow\downarrow$	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow$ <span style="float: right;">Covalence = 3</span>
<b>III excited state</b>	$\uparrow$	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow \uparrow$ <span style="float: right;">Covalence = 5</span>
			$\uparrow \uparrow \uparrow \uparrow$ <span style="float: right;">Covalence = 7</span>

Fluorine is the most electronegative element and thus shows only negative oxidation state. Furthermore, it has  $2s^2 2p^5$  configuration and thus shows only -1 oxidation state in order to complete its octet. Also like other halogens, it does not have vacant d-orbitals in its valence shell.



**Illustration 43:** Fluorine is a non-metal whereas iodine shows some metallic properties as well. Explain.

(JEE MAIN)

**Sol:** Owing to small size and high I.E., F has no tendency to lose electron. I is large and has lower I.E. So, it may lose an electron.

**Illustration 44:** Why are halogens coloured and on moving from  $F_2$  to  $I_2$ , the colour of halogens becomes dark, why?

(JEE ADVANCED)

**Sol:** Because energy required in electronic excitation and de-excitation lies in visible region. On moving from  $F_2$  to  $I_2$ , the size of atom increases and so energy levels become closer and so promotion energy becomes less. So, colour deepens.

**Illustration 45:** Dry chlorine does not act as bleaching agent.

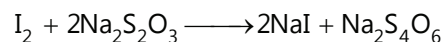
(JEE ADVANCED)

**Sol:** The bleaching action of  $Cl_2$  is due to its reaction with  $H_2O$  to liberate nascent oxygen.

**Illustration 46:** Iodine stains on cloths can be removed by hypo.

(JEE ADVANCED)

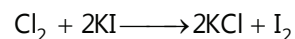
**Sol:** Hypo reacts with iodine to form water soluble sodium tetrathionate and sodium iodide.



**Illustration 47:** Colour of KI solution containing starch turns blue when chlorine water is added to it. Explain.

(JEE ADVANCED)

**Sol:**  $Cl_2$  replaces  $I_2$  from its aqueous solution due to its higher standard reduction potential than iodine.



**Illustration 48:**  $KHF_2$  is well known, whereas  $KHBr_2$  does not exist. Explain.

(JEE ADVANCED)

**Sol:**  $H_2F_2$  exists as dimeric molecule due to H—bonding and thus shows dibasic nature. Hence it gives two series of salts  $KHF_2$  as  $[K^+ \text{ and } F^- \dots\dots H-F^-]$  and  $KF [K^+ \text{ and } F^-]$  whereas HCl and HBr do not show hydrogen bonding and thus formation of  $KHCl_2$  or  $KHBr_2$  is not possible.

## 6. NOBLE GASES OR RARE GASES

### 6.1 Introduction

They occur in the atmosphere infrequently and are hence also referred to as the rare gases.

He 2  $1s^2$

Ne 10	}	$ns^2np^6$
Ar 18		
Kr 36		
Xe 54		
Rn 86		

All have octet configuration except He having duplet configuration.

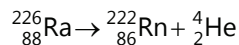
(a) They exist in gaseous state.

(b) Rn is produced by the disintegration of radium and is radioactive itself.

- (c) Ramsay discovered these gases.
- (d) The first inert gas to be discovered by Ramsay was argon.

**Occurance:** Group 18 of the periodic table consists of six elements – helium, neon, argon, krypton, xenon and radon which are collectively known as the Noble Gases.

All the noble gases except radon occur in the atmosphere. Their total abundance in dry air is 1% by volume of which argon is the major component. Neon, argon, krypton and xenon are obtained as by-products of liquefaction of air and separation of its constitution by fractional distillation. The main commercial source of helium is natural gas. Helium is the second most abundant element in the universe (23% compared to 76% hydrogen) although its terrestrial abundance is very low. Radon is obtained as the decay product of  $^{226}\text{Ra}$ .



**Isolation:** Except He, non-radioactive noble gases are commercially isolated from air by two methods.

- (a) **Fractional distillation of liquid air (claude's method):** Due to the difference in b.p. the various constituents of air are separated from each other.
- (b) **Dewar's coconut charcoal adsorption method:**
- (i)  $\text{O}_2$  and  $\text{N}_2$  are removed by means of compound formation.
  - (ii) The principle of this method is that the adsorption capacity of these gases at low temperature by coconut charcoal increase with the increase in their atomic weights.
  - (iii) Thus He has the lowest and Xe has the maximum adsorption capacity.

### General Properties

- (a) **Atomic radii, melting point and boiling point, density:**
- (i) All increases down the group.
  - (ii) He is the only element having two boiling point i.e. 4.1 K and 2.5 K.
  - (iii) It is the only element which exists in two liquid phases i.e. He and  $\text{He}_2$ .
- (b) **Ionisation energy:**
- (i) They possess very high ionisation energy.
  - (ii) Ionisation energy of Xe is nearly equal to that of molecular oxygen.
- (c) **Electron affinity:** Due to complete octet, noble gas atoms are unable to take extra electrons.
- (d) **Monatomicity:** Due to very high I.E. and nearly zero E.A. noble gas atoms are not capable of combining and their value of  $\gamma = \frac{C_p}{C_v}$  is close to 1.66.
- (e) **Force of attraction between atoms of noble Gases:**  
Vander Waal's force between the atoms increases from He to Xe.
- (f) **Solubility in water:** Slightly soluble in water and solubility in water increases with the increase in atomic number.
- (g) **Chemical nature:**
- (i) Noble gases are almost chemically inert.
  - (ii) But Kr, Xe and Rn are slightly reactive because of the radioactive nature of these gases.

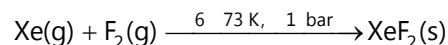
**(h) Adsorption of inert gases:**

- (i) Done on coconut. Gas particles are adsorbed at the surface of coconut charcoal
- (ii) Larger the size, more will be the adsorption. So, maximum adsorption of Xe at highest temp.
- (iii) First gas discovered was Argon. (Ar Lazy gas)
- (iv) The other inert gas isolated was Neon.
- (v) The other inert gas which remained a hidden gas krypton (Kryptos = Hidden)
- (vi) Then Xenon (Xenon = danger) was discovered
- (vii) Rn emits  $\alpha$ ,  $\beta$ ,  $\gamma$  radiations.
- (viii) Discovery of the by Lockyer on sun's atmosphere.

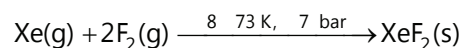
**Family members of noble gases:**

Noble gas compounds proved elusive for many years. The real chemistry of noble gases began in 1962 with the isolation of an orange yellow solid by Neil Bartlett from the reaction of xenon with  $\text{PtF}_6$ . Bartlett had noticed that  $\text{PtF}_6$  reacts with oxygen to form  $\text{O}_2^+[\text{PtF}_6]^-$  and since the ionization enthalpies of  $\text{O}_2$  and Xe are close to each other [ $\text{Xe}=1170$ ;  $\text{O}_2=1175 \text{ kJ mol}^{-1}$ ], he reasoned that  $\text{PtF}_6$  would react with xenon to form  $\text{Xe}^+[\text{PtF}_6]^-$ . Since this exciting discovery, several other xenon compounds, mainly with the most electronegative elements—fluorine and oxygen, have been synthesised. The compounds of krypton are fewer, only the difluoride ( $\text{KrF}_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified by radiotracer techniques. No true compounds of Ar, Ne or He are known.

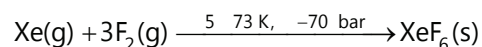
**Xenon (Xe):** It is the only element that forms true compounds and that too with highly reactive elements  $\text{F}_2$ . Xenon forms three binary fluorides,  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  by the direct union of elements under appropriate sunlight or light from a high pressure mercury arc lamp:



(xenon in excess)

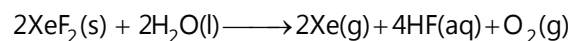


(1:5 ratio)

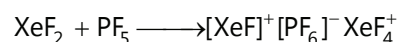


(1:20 ratio)

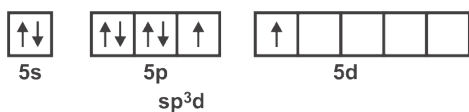
$\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  are colourless solids subliming readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed by even traces of water. The hydrolysis of  $\text{XeF}_2$  can be represented by the equation:



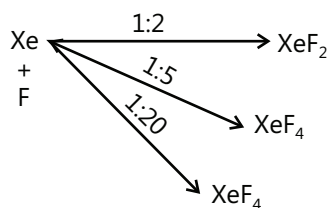
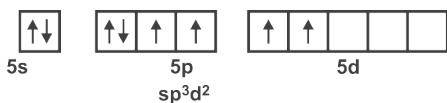
The structures of the three xenon fluorides can be deduced from VSEPR theory (Valence shell electron pair theory).  $\text{XeF}_2$  and  $\text{XeF}_4$  have linear and square planar structures, respectively.  $\text{XeF}_6$  has seven electron pairs (6 bonding pairs and one lone pair) and would thus have a distorted octahedral structure as found experimentally in the gas phase. In the solid state,  $\text{XeF}_6$  contains tetrameric and hexameric units in which acceptors form cationic species and fluoride ion donors form fluoroanions.



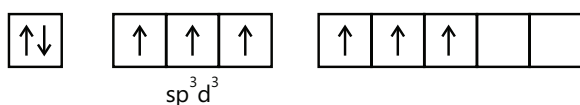
[M = Na, K, Rb or Cs]

(a)  $\text{XeF}_2$ :

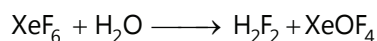
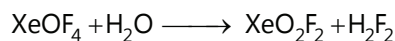
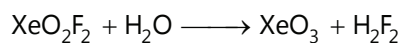
Linear Geometry

(b)  $\text{XeF}_4$ :

Square Planar

(c)  $\text{XeF}_6$ :

Distorted octahedral

(d) Reaction with  $\text{H}_2\text{O}$ : $sp^3d^2$  (Square Pyramidal)Xenon dioxy difluoride ( $sp^3d$ ) i.e. Trigonal bipyramidExplosive Xenon trioxide ( $sp^3$ )**Neon and Argon:**

- (a) Gets trapped in the interstitial spaces of  $\text{H}_2\text{O}$  or alcohols and this type of mixture resulted in what is called as a clathrate compound.
- (b) These compounds are not formed by He.

**Uses:**

- (a) Noble gases are widely used to provide inert atmospheres in metallurgical process
- (b) He is used as a cooling medium in gas cooled atomic reactions because of its high thermal conductivity, low viscosity and low density.
- (c) Liquid He is used in gas thermometers required for low temperature measurement.
- (d) Neon in neon lamps.
- (e) Neon is used in neon tubes for rectifiers, voltage regulators etc.
- (f) Argon is used in filling incandescent lamps.
- (g) Xe is used in the discharge tube for quick photography.
- (h) Rn is used in the treatment of cancer (Radiotherapy)

## PLANCESS CONCEPTS

- Noble gases have zero electron affinity. Noble gases have stable electronic configuration. Hence, it is difficult to add the electron
- Atomic size of noble gases is maximum in their period. For noble gases only, Van der Waals' radii can be obtained. For rest of the elements, covalent or ionic radii are obtained. Van der Waals' radii are always larger than covalent radii.
- Decreasing order of Xe-F bond length in  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$   
 $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$   
 $2.00\text{\AA} \quad 1.95\text{\AA} \quad 1.89\text{\AA}$   
 Bond shortening may be accounted in terms of an increase in the charge on a xenon atom.

Vaibhav Gupta (JEE 2009, AIR 54)

**Illustration 49:** Helium and neon do not form compounds with fluorine. Explain. (JEE MAIN)

**Sol:** They are chemically unreactive, owing to small size and high I.E.

**Illustration 50:** Why do noble gases have zero electron affinity? (JEE MAIN)

**Sol:** Noble gases have stable electronic configuration. Hence, it is difficult to add the electron resulting in zero electron affinity.

**Illustration 51:** Why are noble gases less reactive? (JEE MAIN)

**Sol:** Due to completely filled outermost shell.

**Illustration 52:** Atomic size of noble gases is maximum in their period. Explain. (JEE MAIN)

**Sol:** For noble gases only Van der Waals' radii can be obtained. For rest all elements, covalent or ionic radii are obtained. Van der Waals' radii are always larger than covalent radii.

**Illustration 53:** Noble gases have maximum ionization energy in their period. (JEE MAIN)

**Sol:** Due to a more effective nuclear charge which increases along the period.

**Illustration 54:** The b.p. of noble gases increases with the increase in at. no. Explain. (JEE ADVANCED)

**Sol:** As at. wt. increases, Van der Waals' forces of attraction becomes strong.

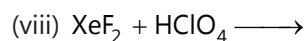
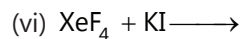
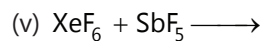
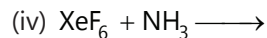
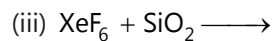
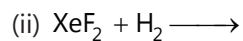
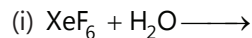
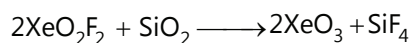
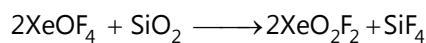
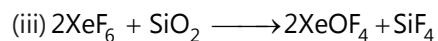
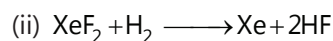
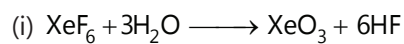
**Illustration 55:** Why is helium molecule, ( $\text{He}_2$ ) not formed? (JEE ADVANCED)

**Sol:** For  $\text{He}_2$ , bond order is zero.

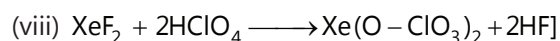
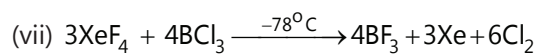
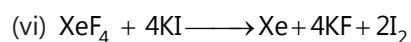
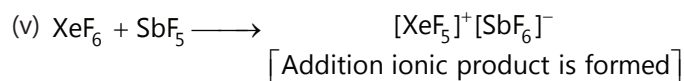
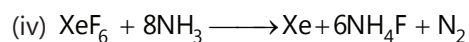
**Illustration 56:** Xenon has a closed shell configuration but forms compounds with fluorine. Explain. (JEE ADVANCED)

**Sol:** Gases and thus the outermost shell electrons of Xe are excited to d-subshell.

**Illustration 57:** Complete the following reactions. (JEE ADVANCED)

**Sol:**

Explosive

**Illustration 58:** Arrange the  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$  in decreasing order of Xe-F bond length give reason also.**(JEE ADVANCED)****Sol:**  $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$ , bond shortening may be accounted for in terms of increase in the charge on a xenon atom.

2.00 Å 1.95 Å 1.89 Å

## POINTS TO REMEMBER

- Elements of group 15 exhibit two important oxidation states +3 and +5 but +3 oxidation state is formed because of inert pair effect.
- In hydrides of group V:
  - Bond angle :  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$  Basic character :  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$
  - Boiling point :  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$  Stability :  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
  - Reducing character :  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3$
- Phosphorus exists as  $\text{P}_4$  in elemental state and exists in several allotropic forms.
- The oxoacids having P-H bonds are good reducing agents.
- $\text{N}_2\text{O}$  is called laughing gas and is obtained by heating  $\text{NH}_4\text{NO}_3$ .
- Sulphur exists as  $\text{S}_8$  and has plucked ring structure.
- Group 16 elements are called chalcogens. These consists of O, S, Se, Te and Po.
- Allotropic forms of oxygen is  $\text{O}_3$ , which is highly oxidising agent.
- The highest oxidation state of S is +6 in  $\text{SF}_6$ .
- In hydrides of group VI
  - Bond angle :  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$  Acidic character :  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$
  - Volatility :  $\text{H}_2\text{O} < \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$ .
- Halogens are most electronegative elements. Among these iodine has some electropositive character and exists as +1 and +3.
- Reducing Power :  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
- Oxidising power :  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Acidic strength in water :  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ . HF weaker base because of its highest bond dissociation energy
- Acidic character :  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$
- $\text{HClO} > \text{HBrO} > \text{HIO}$ .
- Oxidation power :  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$
- Fluorine shows only -1 oxidation state while other halogens show variable oxidation states from +1 to +7.

## JEE Main/Boards

### Exercise 1

**Q.1** How is ammonia manufactured industrially?

**Q.2** The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

**Q.3** Write main differences between the properties of white phosphorus and red phosphorus.

**Q.4** Why does nitrogen show catenation properties less than phosphorus?

**Q.5** Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

**Q.6** Knowing the electron gain enthalpy values for  $\text{O} \rightarrow \text{O}^-$  and  $\text{O} \rightarrow \text{O}_2^-$  as  $-141$  and  $702 \text{ kJ mol}^{-1}$

respectively, how can you account for the formation of a large number of oxides having  $O^{2-}$  species and not  $O^-$ ?

**Q.7** Which aerosols deplete ozone?

**Q.8** Describe the manufacture of  $H_2SO_4$  by contact process?

**Q.9** Why are halogens strong oxidizing agents?

**Q.10** Explain why in spite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

**Q.11** How can you prepare  $Cl_2$  from  $HCl$  and  $HCl$  from  $Cl_2$ ? Write reactions only.

**Q.12** What are the oxidation states of phosphorus in the following:

- (i)  $H_3PO_3$                       (ii)  $PCl_3$                       (iii)  $Ca_3P_2$   
(iv)  $Na_3PO_4$                     (v)  $POF_3$

**Q.13** Write balanced equation for the following:

- (i)  $NaCl$  is heated with sulphuric acid in the presence of  $MnO_2$ .  
(ii) Chlorine gas is passed into a solution of  $NaI$  in water.

**Q.14** How are xenon fluorides  $XeF_2$ ,  $XeF_4$  and  $XeF_6$  obtained?

**Q.15** With what neutral molecule is  $ClO^-$  isoelectronic? Is that molecule a Lewis base?

**Q.16** How are  $XeO_3$  and  $XeOF_4$  prepared?

**Q.17** Why do noble gases have comparatively large atomic sizes?

**Q.18** List the uses of neon.

**Q.19** Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionization enthalpy and electronegativity.

**Q.20** Give the formula and describe the structure of a noble gas species which is isostructural with:

- (i)  $ICl_4^-$  (ii)  $IBr_2^-$                       (iii)  $BrO_3^-$

**Q.21** Draw the structure of the following molecules:

- (i)  $XeF_4$                                       (ii)  $BrF_3$

**Q.22** Account for the following:

- (i)  $H_2S$  acts only as a reducing agent but  $SO_2$  acts both as a reducing agent as well as an oxidising agent.  
(ii)  $SF_6$  is known but  $SH_6$  is not known.  
(iii) Compounds of fluorides of oxygen and not the oxides of fluorine.

**Q.23** (i) Complete the following reaction equations:

- (A)  $XeF_2 + PF_5 \rightarrow$   
(B)  $Cl_2(g) + NaOH(aq) \rightarrow$   
(hot and conc.)

(ii) Explain the following observations:

- (a) +3 oxidation state becomes more and more stable from As to Bi in the group.  
(b) Sulphur in the vapour state exhibits para magnetism

**Q.24** (i) Draw the structure of the following:

- (a)  $H_3PO_2$                                       (b)  $BrF_3$

(ii) How would you account for the following observations:

- (A) Phosphorus has a greater tendency for catenation than nitrogen.  
(B) Bond dissociation energy of fluorine is less than that of chlorine.  
(C) No chemical compound of helium is known.

**Q.25** Explain the following:

- (A) Ammonia has a higher boiling point than phosphine.  
(B) Helium does not form any chemical compound.  
(C) Bi (V) is a stronger oxidising agent than Sb(V).

**Q.26** (i) Complete the following reaction equations.

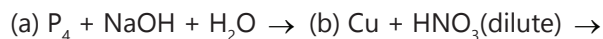
- (a)  $PCl_5 + H_2O(\text{excess}) \rightarrow$   
(b)  $F_2 + H_2O \rightarrow$

(ii) Explain the following observations:

- (a) Phosphorus has a greater tendency for catenation than nitrogen.  
(b) In solution of  $H_2SO_4$  in water, the second dissociation constant  $k_{a2}$ , is less than first dissociation constant  $k_{a1}$ .



**Q.27** (i) Complete the following reaction equations



(ii) Explain why

(a)  $H_2O$  is a liquid while, inspite of a higher molecular mass  $HS_2$  is a gas

(b) Helium is used in diving equipment.

**Q.28**  $PCl_5$  is well known while  $PI_5$  is unknown. Why?

**Q.29** Urea is better nitrogenous fertilizer than ammonium sulphate. Explain.

**Q.30** HF is stored in wax coated glass bottles. Why?

**Q.31**  $KHF_2$  is well known, whereas  $KHCl_2$  or  $KHBr_2$  does not exist. Explain

**Q.32** Halogens are strong oxidants. Why?

**Q.33** Chlorine displaces iodine from aqueous solution of KI. Why?

**Q.34** Account for the following observation

(i) Iodine is liberated in the reaction between KI and  $Cu^{2+}$  but chlorine is not liberated when KCl is added to  $Cu^{2+}$ .

(ii) In the contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is catalyst used in the oxidation of  $SO_2$ ?

**Q.35** Explain the following

(i) An orange potassium dichromate paper turns green on exposure to sulphur dioxide.

(ii) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction.

**Q.36** Explain it with reason:  $SO_2$  can function both as a reducing or oxidizing agent while  $SO_3$  can function only as an oxidizing agent and  $H_2S$  can function as reducing agent only

**Q.37** Explain why?

(i) Orthophosphoric acid is tribasic but phosphorus acid is dibasic.

(ii) It is advisable to grow a leguminous crop on a soil every three or four years

**Q.38** Zinc reacts with dil.  $H_2SO_4$  to give  $H_2$ . It also reacts with conc.  $H_2SO_4$  to give  $SO_2$ . Make difference between these two reactions.

## Exercise 2

### Single Correct Choice Type

**Q.1**  $H_3PO_3 \xrightarrow{\Delta} (x) + PH_3$ ; is

(A) Dehydration reaction

(B) Oxidation reaction

(C) Disproportionation reaction

(D) Dephosphorylation reaction

**Q.2** Which of the following species is not a pseudohalide?

(A)  $CNO^-$  (B)  $RCOO^-$

(C)  $OCN^-$  (D)  $N_3^-$

**Q.3** First compound of inert gases was prepared by scientist Neil Barthlete in 1962. This compound is

(A)  $XePtF_6$  (B)  $XeO_3$  (C)  $XeF_6$  (D)  $XeOF_4$

**Q.4** Boron forms  $BX_3$  type of halides. The correct increasing order of Lewis-acid strength of these halides is

(A)  $BF_3 > BCl_3 > BBr_3 > BI_3$  (B)  $BI_3 > BBr_3 > BCl_3 > BF_3$

(C)  $BF_3 > BI_3 > BCl_3 > BBr_3$  (D)  $BF_3 > BCl_3 > BI_3 > BBr_3$

**Q.5.** The compound  $(SiH_3)_3N$  is

(A) Pyramidal and more basic than  $(CH_3)_3N$

(B) Planar and less basic than  $(CH_3)_3N$

(C) Pyramidal and less basic than  $(CH_3)_3N$

(D) Planar and more basic than  $(CH_3)_3N$

**Q.6.** In a molecule of phosphorus (V) oxide, there are

(A) 4P-P, 10P-O and 4P=O bonds.

(B) 12P-O and 4P=O bonds

(C) 2P-O and 4P=P bonds

(D) 6P-P, 12P-O and 4P=P bonds

**Q.7.** When oxalic acid reacts with conc.  $H_2SO_4$ , two gases produced are neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases.

The product formed during this absorption and the gas which absorbed are respectively.

- (A)  $K_2CO_3$  and  $CO_2$       (B)  $KHCO_3$  and  $CO_2$   
 (C)  $K_2CO_3$  and  $CO$       (D)  $KHCO_3$  and  $CO$

**Q 8.** Which of the following is the correct order of acidic strength?

- (A)  $Cl_2O_7 > SO_2 > P_4O_{10}$       (B)  $CO_2 > N_2O_5 > SO_3$   
 (C)  $Na_2O > MgO > Al_2O_3$       (D)  $K_2O > CaO > MgO$

**Q 9.**  $Ca + C_2 \xrightarrow{\quad} CaC_2 \xrightarrow{N_2} A$  Compound (A) is used as a/an

- (A) Fertilizer      (B) Dehydrating agent  
 (C) Oxidizing agent      (D) Reducing agent

**Q 10.** A gas which exists in three allotropic forms  $\alpha, \beta,$  and  $\gamma$  is

- (A)  $SO_2$       (B)  $SO_3$       (C)  $CO_2$       (D)  $NH_3$

**Q 11.** When an inorganic compound reacts with  $SO_2$  in aqueous medium, produces (A). (A) on reaction with  $Na_2CO_3$ , gives compound (B) which with sulphur, gives a substance (C) used in photography. Compound C is

- (A)  $Na_2S$       (B)  $Na_2S_2O_7$       (C)  $Na_2SO_4$       (D)  $Na_2S_2O_3$

**Q 12.** Borax is actually made of two tetrahedral and two triangular units joined together and should be written as:  $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ . Consider the following statements about borax:

- (a) Each boron atom has four B-O bonds  
 (b) Each boron atom has three B-O bonds  
 (c) Two boron atoms have four B-O bonds while other two have three B-O bonds.  
 (d) Each boron atom has one -OH groups

Select correct statement(s)

- (A) a, b      (B) b, c      (C) c, d      (D) a, c

**Q.13** When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidizing agent, then X, Y and Z will be

- (A)  $X = HI, Y = I_2$  and  $Z = HIO_3$   
 (B)  $X = KI, Y = I_2$  and  $Z = HIO_3$   
 (C)  $X = KI, Y = I_2$  and  $Z = HIO_4$   
 (D)  $X = HI, Y = I_2$  and  $Z = HIO_4$

## Previous Years' Questions

**Q.1** Aluminium chloride exists as dimer,  $Al_2Cl_6$  in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives **(2004)**

- (A)  $[Al(OH)_6]^{3-} + 3HCl$       (B)  $[Al(H_2O)_6]^{3+} + 3Cl^-$   
 (C)  $Al^{3+} + 3Cl^-$       (D)  $Al_2O_3 + 6HCl$

**Q.2** In the extraction of aluminium the electrolyte is. **(1989)**

- (A) Fused cryolite with feldspar  
 (B) Fused cryolite with fluorspar  
 (C) Pure alumina in molten cryolite  
 (D) Pure alumina with bauxite and molten cryolite

**Q.3** Boron cannot form which one of the following anions. **(2011)**

- (A)  $BF_6^{3-}$       (B)  $BH_4^-$       (C)  $B(OH)_4^-$       (D)  $BO_2^-$

**Q.4** Heating an aqueous solution of aluminium chloride to dryness will give **(2005)**

- (A)  $AlCl_3$       (B)  $Al_2Cl_6$       (C)  $Al_2O_3$       (D)  $Al(OH)Cl_2$

**Q.5** The structure of diborane ( $B_2H_6$ ) contains. **(2009)**

- (A) Four 2c-2e bonds and two 3c-2e bonds  
 (B) Two 2c-2e bonds and four 3c-2e bonds  
 (C) Two 2c-2e bonds and two 3c-3e bonds  
 (D) Four 2c-2e bonds and four 3c-2e bonds

**Q.6** The stability of dihalides of Si, Ge, Sn and Pb increases steadily in sequence **(2007)**

- (A)  $GeX_2 \ll SiX_2 \ll SnX_2 \ll PbX_2$   
 (B)  $SiX_2 \ll GeX_2 \ll PbX_2 \ll SnX_2$   
 (C)  $SiX_2 \ll GeX_2 \ll SnX_2 \ll PbX_2$   
 (D)  $PbX_2 \ll SnX_2 \ll GeX_2 \ll SiX_2$

**Q.7** In silicon dioxide, **(2005)**

- (A) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms  
 (B) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bounded to two silicon atoms

- (C) Silicon atom is bonded to two oxygen atoms  
 (D) There are double bonds between silicon and oxygen atoms

**Q.8** In which of the following arrangements the sequence is not strictly according to the property written against it. **(2009)**

- (A)  $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$ : Increasing oxidizing power  
 (B)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ : Increasing acid strength  
 (C)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$ : Increasing basic strength  
 (D)  $\text{B} < \text{C} < \text{O} < \text{N}$ : Increasing first ionization enthalpy

**Q.9** The percentage of p-character in the orbitals forming P-P bonds in  $\text{P}_4$  is **(2007)**

- (A) 25      (B) 33      (C) 50      (D) 75

**Q.10** Which of the following statement is wrong **(2011)**

- (A) The stability of hydrides increase from  $\text{NH}_3$  to  $\text{BiH}_3$  in group 15 of the periodic table  
 (B) Nitrogen cannot form  $d\pi - p\pi$  bond  
 (C) Single N - N bond is weaker than the single P - P bond  
 (D)  $\text{N}_2\text{O}_4$  has two resonance structure

**Q.11** What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid **(2003)**

- (A)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed  
 (B)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed  
 (C)  $\text{CrO}_4^{2-}$  is reduced to +3 state of Cr  
 (D)  $\text{CrO}_4^{2-}$  is oxidized to +7 state of Cr

**Q.12** In case of nitrogen,  $\text{NCl}_3$  is possible but not  $\text{NCl}_5$  while in case of phosphorous,  $\text{PCl}_3$  as well as  $\text{PCl}_5$  are possible. It is due to **(2004)**

- (A) Availability of vacant d-orbital in P but not in N  
 (B) Lower electronegativity of P than N  
 (C) Lower tendency of H bond formation in P than N  
 (D) Occurrence of P in solid while N in gaseous state at room temperature

**Q.13** What may be expected to happen when phosphine gas is mixed with chlorine gas **(2003)**

- (A) The mixture only cools down  
 (B)  $\text{PCl}_3$  and  $\text{HCl}$  are formed and the mixture warms up  
 (C)  $\text{PCl}_5$  and  $\text{HCl}$  are formed and mixture cools down  
 (D)  $\text{PCl}_3$  and  $\text{Cl}_2$  is formed with warming up

**Q.14** Which of the following statements regarding sulphur is incorrect? **(2011)**

- (A)  $\text{S}_2$  molecule is paramagnetic  
 (B) The vapour at  $200^\circ\text{C}$  consists mostly of  $\text{S}_8$  rings  
 (C) At  $600^\circ\text{C}$ , the gas mainly consists of  $\text{S}_2$  molecules  
 (D) The oxidation state of sulphur is never less than +4 in its compounds

**Q.15** The correct order of the thermal stability of hydrogen halides ( $\text{H} - \text{X}$ ) is **(2010)**

- (A)  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$     (B)  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$   
 (C)  $\text{HCl} < \text{HF} < \text{HBr} < \text{HI}$     (D)  $\text{HI} > \text{HCl} < \text{HF} < \text{HBr}$

**Q.16** Identify the incorrect statement among the following **(2007)**

- (A) Ozone reacts with  $\text{SO}_2$  to give  $\text{SO}_3$   
 (B) Silicon reacts with  $\text{NaOH}_{(\text{aq})}$  in the presence of air to give  $\text{Na}_2\text{SiO}_3$  and  $\text{H}_2\text{O}$   
 (C)  $\text{Cl}_2$  reacts with excess of  $\text{NH}_3$  to give  $\text{N}_2$  and  $\text{HCl}$   
 (D)  $\text{Br}_2$  reacts with hot and strong  $\text{NaOH}$  solution to give  $\text{NaBr}$ ,  $\text{NaBrO}_4$  and  $\text{H}_2\text{O}$

**Q.17** Which one of the following reactions of Xenon compounds is not feasible? **(2009)**

- (A)  $\text{XeO}_3 + 6\text{HF} \rightarrow \text{XeF}_6 + 3\text{H}_2\text{O}$   
 (B)  $3\text{XeF}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{Xe} + \text{XeO}_3 + 12\text{HF} + 1.5\text{O}_2$   
 (C)  $2\text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2$   
 (D)  $\text{XeF}_6 + \text{RbF} \rightarrow \text{Rb}[\text{XeF}_7]$

**Q.18** The number of hydrogen atom(s) attached to phosphorus atom in hypophosphorous acid is **(2005)**

- (A) Zero                                      (B) Two  
 (C) One                                        (D) Three

**Q.19** The decreasing bond angles from  $\text{NH}_3$  ( $106^\circ$ ) to  $\text{SbH}_3$  ( $101^\circ$ ) down group-15 of the periodic table is due to **(2006)**

- (A) Increasing bp-bp repulsion
- (B) Increasing p-orbital character in  $\text{sp}^3$
- (C) Decreasing lp-bp repulsion
- (D) Decreasing electronegativity

**Q.20** In  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ , the number of lone pairs on Xe is respectively **(2002)**

- (A) 2, 3, 1
- (B) 1, 2, 3
- (C) 4, 1, 2
- (D) 3, 2, 1

**Q.21** Which one of the following statements regarding helium is incorrect? **(2004)**

- (A) It is used to produce and sustain powerful superconducting magnets
- (B) It is used as a cryogenic agent for carrying out experiments at low temperatures
- (C) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable
- (D) It is used in gas-cooled nuclear reactors

**Q.22** Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that **(2003)**

- (A) Concentrated hydrochloric acid emits strongly smelling HCl gas all the time
- (B) Oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas
- (C) Strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke
- (D) Due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence the cloud.

**Q.23** Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar? **(2013)**

- (A)  $\text{Ca} < \text{S} < \text{Ba} < \text{Se} < \text{Ar}$
- (B)  $\text{S} < \text{Se} < \text{Ca} < \text{Ba} < \text{Ar}$
- (C)  $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$
- (D)  $\text{Ca} < \text{Ba} < \text{S} < \text{Se} < \text{Ar}$

**Q.24** Which one of the following properties is **not** shown by  $\text{NO}$ ? **(2014)**

- (A) It combines with oxygen to form nitrogen dioxide
- (B) Its bond order is 2.5
- (C) It is diamagnetic in gaseous state
- (D) It is a neutral oxide

**Q.25 Assertion:** Nitrogen and Oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen. **(2015)**

**Reason:** The reaction between nitrogen and oxygen requires high temperature.

- (A) Both assertion and reason are correct, and the reason is the correct explanation for the assertion
- (B) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion
- (C) The assertion is incorrect, but the reason is correct
- (D) Both the assertion and reason are incorrect

**Q.26** The species in which the N atom is in a state of  $\text{sp}$  hybridization is: **(2016)**

- (A)  $\text{NO}_2^+$
- (B)  $\text{NO}_2^-$
- (C)  $\text{NO}_3^-$
- (D)  $\text{NO}_2$

**Q. 27** The pair in which phosphorous atoms have a formal oxidation state of + 3 is : **(2016)**

- (A) Orthophosphorous and pyrophosphorous acids
- (B) Pyrophosphorous and hypophosphoric acids
- (C) Orthophosphorous and hypophosphoric acids
- (D) Pyrophosphorous and pyrophosphoric acids

## JEE Advanced/Boards

### Exercise 1

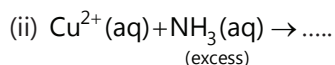
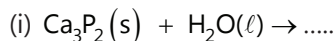
**Q.1** Arrange the following in the order of property indicated for each set:

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

**Q.2** Which one of the following does not exist?

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

**Q.3** Complete the following chemical equations:



**Q.4** A solution of ferric chloride acidified with HCl is unaffected when hydrogen is bubbled through it, but gets reduced when zinc is added to some acidified solution. Why?

**Q.5** Aqua-regia dissolves noble metals in it. Explain.

**Q.6** Pure  $PH_3$  does not burn in air, but impure sample of  $PH_3$  burns in air. Why?

**Q.7** Precipitation of second group sulphides in qualitative analysis is carried out with  $H_2S$  in presence of HCl and not nitric acid. Why?

**Q.8**  $KMnO_4$  should not be dissolved in conc.  $H_2SO_4$ . Why?

**Q.9** Account for the following observations

- (i) Bleaching of flowers by  $Cl_2$  is permanent, while by  $SO_2$  it is temporary.
- (ii) The brown colour of an acidified dilute solution of iodine in aqueous potassium iodide is intensified by the addition of a nitrite but is discharged by the addition of a sulphite.

**Q.10** Explain the following

Silver nitrate solution when treated with a very dilute solution of hypo gives black precipitate but when it is treated with a concentrated solution of hypo it does not form any ppt.

**Q.11** Explain it with reason

- (i) Concentrated nitric acid turns yellow in sunlight.
- (ii) Nitrous oxide supports combustion more vigorously than air.

**Q.12** Explain why?

(i) Yellow phosphorous is kept under water but not the red phosphorous.

**Q.13** What happens when .....(Give relevant equation)

- (i) Hypophosphorous acid is heated.
- (ii) Sodium iodate is treated with sodium bisulphite solution.
- (iii) Chlorine gas is passed through dry and aqueous  $SO_2$  gas.
- (iv) Potassium dichromate and concentrated hydrochloric acid are heated together.

**Q.14** Brief it with relevant equation

- (i) A few drops of bismuth oxide solution in conc. HCl are added to excess of water.
- (ii) Iodine is added to a solution of potassium iodide.
- (iii) Hydriodic acid is added to copper sulphate solution.
- (iv) Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.

**Q.15** Explain it (Give relevant equation)

- (i) Sulphur dioxide is bubbled through aq. Solution of  $CuSO_4$  in presence of potassium thiocyanate.
- (ii) Ozone is treated with ethylene.
- (iii) Sulphur is boiled with caustic soda solution.

## Exercise 2

### Single Correct Choice Type

**Q.1** Which is incorrectly matched

- (A)  $\text{CsBr}_3 \rightarrow \text{Cs}^+ + \text{Br}_3^-$   
 (B)  $\text{I}_4\text{O}_9 \rightarrow \text{I}^{3+} + (\text{IO}_3^-)_3$   
 (C)  $\text{AgBrO}_3 \rightarrow \text{Ag}^+ + \text{BrO}_3^-$   
 (D)  $\text{I}_2\text{O}_4 \rightarrow \text{IO}_2^- + \text{IO}_2^-$

**Q.2** An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatment with Mg, produces a white solid substance.....

- (A)  $\text{Mg}_3\text{N}_2$  (B) MgO (C)  $\text{Mg}_2\text{O}_3$  (D)  $\text{MgCl}_2$

**Q.3** An inorganic salt (A) is decomposed at about 523 K to give products (B) and (C). Compound (C) is a liquid at room temperature and is neutral to litmus paper while oxide (B) on burning with white phosphorous, given a dehydrating agent (D).

Compounds (A), (B), (C) and (D) will be identified as

- (A)  $\text{NH}_4\text{NO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{P}_2\text{O}_5$   
 (B)  $\text{NH}_4\text{NO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_2$   
 (C)  $\text{CaCO}_3$ , CaO,  $\text{H}_2\text{O}$ ,  $\text{CaCl}_2$   
 (D)  $\text{CaCO}_3$ , CaO,  $\text{H}_2\text{O}$ ,  $\text{Ca}(\text{OH})_2$

**Q.4** An inorganic compound (A) made of two most occurring elements into the earth crust, having a polymeric tetra-headral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be

- (A)  $\text{SiO}_2$ ,  $\text{CO}_2$  (B)  $\text{SiO}_2$ , CO  
 (C) SiC, CO (D)  $\text{SiO}_2$ ,  $\text{N}_2$

**Q.5** A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide

(D) Gas (B) turns  $\text{K}_2\text{Cr}_2\text{O}_7$  paper green while gas (C) forms a trimer in which there is no S-S bond. Compound (D) with HCl, forms a Lewis base (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively

- (A)  $\text{FeSO}_4$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$   
 (B)  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeCl}_3$   
 (C) FeS,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$   
 (D) FeS,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Fe}_2(\text{PO}_4)_3$ ,  $\text{FeCl}_2$

**Q.6** A tetra-atomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C). (B) is a dehydrating agent in its monomeric gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be

- (A)  $\text{P}_4$ ,  $\text{P}_4\text{O}_1$ ,  $\text{N}_2$  (B)  $\text{P}_4$ ,  $\text{N}_2\text{O}_5$ ,  $\text{N}_2$   
 (C)  $\text{P}_4$ ,  $\text{P}_2\text{O}_3$ , Ar (D)  $\text{P}_4$ ,  $\text{P}_2\text{O}_3$ ,  $\text{H}_2$

**Q.7** Which one of the following compounds on strong heating evolves ammonia gas?

- (A)  $(\text{NH}_4)_2\text{SO}_4$  (B)  $\text{HNO}_3$   
 (C)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (D)  $\text{NH}_3\text{NO}_3$

**Q.8** The correct order of acidic strength of oxy-acids of chlorine is

- (A)  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$   
 (B)  $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$   
 (C)  $\text{HClO} > \text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2$   
 (D)  $\text{HClO}_4 < \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

**Q.9** Concentrated  $\text{HNO}_3$  reacts with iodine to give

- (A) HI (B) HOI (C)  $\text{HOIO}_2$  (D)  $\text{HOIO}_3$

**Q.10** Conc.  $\text{H}_2\text{SO}_4$  cannot be used to prepare HBr from NaBr because it

- (A) Reacts slowly with NaBr  
 (B) Oxides HBr  
 (C) Reduces HBr  
 (D) Disproportionates HBr

**Q.11** Compound (X) is  $\text{CH}_2$   $\begin{cases} \text{COOH} \\ \text{COOH} \end{cases} \xrightarrow{\text{P}_4\text{O}_{10}, 150^\circ\text{C}}$  X

- (A) Malonic acid (B) Carbon suboxide  
 (C) Tartaric acid (D) Acetic acid

**Q.12** Molecular shapes of  $\text{SF}_4$ ,  $\text{CF}_4$  and  $\text{XeF}_4$  are

- (A) The same, with 2, 0 and 1 lone pairs of electrons respectively  
 (B) The same, with 2, 0 and 1 lone pairs of electrons respectively  
 (C) The different, with 0, 1 and 2 lone pairs of electrons respectively  
 (D) The different, with 1, 0 and 2 lone pairs of electrons respectively

**Q.13** When  $\text{AgNO}_3$  is heated strongly, the products formed are

- (A)  $\text{NO}$  and  $\text{NO}_2$  (B)  $\text{NO}_2$  and  $\text{O}_2$   
 (C)  $\text{NO}_2$  and  $\text{N}_2\text{O}$  (D)  $\text{NO}$  and  $\text{O}_2$

**Q.14**  $\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow \text{HPO}_3 + \text{A}$ ; the product A is

- (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{NO}_2$  (D)  $\text{N}_2\text{O}_5$

**Q.15**  $\text{B}(\text{OH})_3 + \text{NaOH} \longrightarrow \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$

How can these reaction is made to proceed in forward direction?

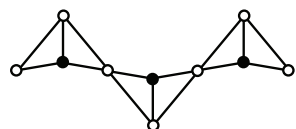
- (A) Addition of cis 1, 2 diol (B) Addition of borax  
 (C) Addition of trans 1, 2 diol (D) Addition of  $\text{Na}_2\text{HPO}_4$

### Comprehension Type

**Paragraph 1:** Read the following short write-up and answer the questions at the end of it.

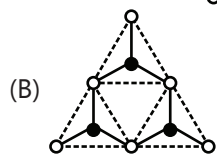
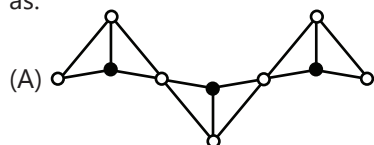
The name 'silica' covers an entire group of minerals, which have general formula  $\text{SiO}_2$ , the most common of which is quartz. Quartz is a framework silicate with  $\text{SiO}_4$  tetrahedra arranged in spirals. The spirals can turn in a clockwise or anticlockwise direction- a feature that results in there being two mirror images, optically active, varieties of quartz.

**Q.16** The following pictures represent various silicate anions. Their formulae are respectively:



- (A)  $\text{SiO}_3^{2-}$   $\text{Si}_3\text{O}_7^{2-}$  (B)  $\text{SiO}_4^{4-}$   $\text{Si}_3\text{O}_{10}^{8-}$   
 (C)  $\text{SiO}_4^{2-}$   $\text{Si}_3\text{O}_9^{2-}$  (D)  $\text{SiO}_3^{4-}$   $\text{Si}_3\text{O}_7^{8-}$

**Q.17**  $\text{Si}_3\text{O}_9^{6-}$  (having three tetrahedral) is represented as:



- (C) Both (A) and (B)  
 (D) None of these

**Q.18** The silicate anion in the mineral kinoite is a chain of three  $\text{SiO}_4$  tetrahedra that share corners with adjacent tetrahedral. The mineral also contains  $\text{Ca}^{2+}$  ions,  $\text{Cu}^{2+}$  ions, and water molecules in 1:1:1 ratio mineral is represented as:

- (A)  $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$  (B)  $\text{CaCuSi}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$   
 (C)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  (D) None of these.

**Paragraph 2:** There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$ , and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorus.

**Q.19** Among the following, the correct statement is

- (A) Phosphorus have no biological significance in humans.  
 (B) Between nitrates and phosphates, phosphates are less abundant in earth's crust.  
 (C) Between nitrates and phosphates, nitrates are less abundant in earth's crust.  
 (D) Oxidation of nitrates is possible in soil.

**Q.20** Among the following, the correct statement is

- (A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical  $\text{sp}^3$  orbital and is less directional  
 (B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is more directional  
 (C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is more directional  
 (D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical  $\text{sp}^3$  orbital and is less directional

**Q.21**  $\text{PH}_3$  as one of the products. This is a

- (A) Dimerization reaction.  
 (B) Disproportionation reaction  
 (C) Condensation reaction  
 (D) Precipitation reaction

**Assertion Reasoning Type**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following responses:

- (A) If both (A) and (R) are true and (R) is correct explanation of (A)  
 (B) If both (A) and (R) are true but (R) is not correct explanation of (A)  
 (C) If (A) is true but (R) is false  
 (D) If (A) is false but (R) is true

**Q.22 Assertion:** Borax bead test is applicable only to coloured salt.

**Reason:** In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

**Q.23 Assertion:** Conc.  $\text{H}_2\text{SO}_4$  cannot be used to prepare pure HBr from NaBr

**Reason:** It reacts slowly with NaBr.

**Q.24 Assertion:** Silicones are very inert polymers.

**Reason:** Both Si-O and Si-C bond energies are very high.

**Q.25 Assertion:** Chlorine gas disproportionates in hot and conc. NaOH solution.

**Reason:** NaCl and NaOCl are formed in the above reaction.

**Multiple Correct Choice Type**

**Q.26** The correct statement(s) related to allotropes of carbon is/are

- (A) Graphite is the most stable allotropes of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon ( $sp^2$ ).  
 (B) Diamond is the hardest allotrope of carbon and having a three dimensional network structure of C ( $sp^3$ )  
 (C) Fullerene ( $\text{C}_{60}$ ) is recently discovered non-crystalline allotrope of carbon having a football like structure.  
 (D) Vander waal's force of attraction acts between the layers of graphite 6.14 Å away from each other.

**Q.27**  $\text{Al}_2(\text{SO}_4)_3 + \text{NH}_4\text{OH} \longrightarrow \text{X}$ , then

- (A) X is a white coloured compound  
 (B) X is insoluble in excess of  $\text{NH}_4\text{OH}$   
 (C) X is soluble in NaOH  
 (D) X cannot be used as an antacid.

**Q.28** Which of the following is/are correct for group 14 elements?

- (A) The stability of dihalides are in the order  $\text{CX}_2 < \text{SiX}_2 < \text{GeX}_2 < \text{SnX}_2 < \text{PbX}_2$   
 (B) The ability to form  $p\pi - p\pi$  multiple bonds among themselves increases down the group.  
 (C) The tendency for catenation decreases down the group.  
 (D) They all form oxides with the formula  $\text{MO}_2$ .

**Q.29**  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  The dimerization of  $\text{NO}_2$  is accompanied with

- (A) Decrease in paramagnetism  
 (B) Change in colour  
 (C) Increase in temperature  
 (D) Increase in paramagnetism

**Q.30**  $\text{C}(\text{OH})_4$  is unstable because a carbon atom cannot hold more than one -OH groups but  $\text{Si}(\text{OH})_4$

is stable compound because

- (A) C-O bond energy is low.  
 (B) C-O bond energy is high.  
 (C) Si-O bond energy is low.  
 (D) Si-O bond energy is high.

**Q.31** Which of the following statements is/are correct regarding inter-halogen compound  $\text{AB}_x$  types?

- (A) x may be 1, 3, 5 and 7  
 (B) A is more electronegative halogen than B  
 (C)  $\text{FBr}_3$  cannot exist  
 (D) the structure of  $\text{ClF}_3$  and  $\text{IF}_7$  show deviation from normal structures and could be explained on the basis of VSEPR theory.



**Q.32** Select correct statement(s)

- (A) Borax is used as buffer  
 (B) 1 M borax solution reacts with equal volumes of 2M HCl solution  
 (C) Titration of borax can be made using methyl orange as the indicator.  
 (D) Coloured bead obtained in borax-bead test contains metaborate.

**Q.33** Select correct statement about  $B_2H_6$

- (A) Bridging groups are electron-deficient with 12 valence electrons  
 (B) It has 2c-2e B-H bonds  
 (C) It has 3c-2e B-H-B bonds  
 (D) All above are correct statements.

### Match the Columns

**Q.34** Match the following

Column I	Column II
(A) $Bi^{3+} \rightarrow (BiO)^+$	(p) Heat
(B) $[AlO_2]^- \rightarrow Al(OH)_3$	(q) Hydrolysis
(C) $SiO_4^{4-} \rightarrow Si_2O_7^{6-}$	(r) Acidification
(D) $(B_4O_7^{2-}) \rightarrow [B(OH)_3]$	(s) Dilution by water

## Previous Years' Questions

**Q.1**  $H_3BO_3$  is (2003)

- (A) Monobasic acid and weak Lewis acid  
 (B) Monobasic and weak Bronsted acid  
 (C) Monobasic and strong Lewis acid  
 (D) Tribasic and weak Bronsted acid

**Q.2**  $B(OH)_3 + NaOH \longrightarrow NaBO_2 + Na[B(OH)_4] + H_2O$   
 How can one proceed this reaction in the forward direction? (2006)

- (A) Addition of cis 1, 2 diol  
 (B) Addition of borax  
 (C) Addition of trans 1, 2 diol  
 (D) Addition of  $Na_2HPO_4$

**Q.3** In the reaction,  $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+ [BH_4]^-$ , the amine (s) X is (are) (2009)

- (A)  $NH_3$  (B)  $CH_3NH_2$   
 (C)  $(CH_3)_2NH$  (D)  $(CH_3)_3N$

Read the following questions and answer as per the direction given below:

- (a) Statement-I is true; statement-II is true; statement-II is the correct explanation of statement-I.  
 (b) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement-I.  
 (c) Statement-I is true; statement-II is false.  
 (d) Statement-I is false; statement-II is true.

**Q.4 Statement-I:** In water, orthoboric acid behaves as a weak monobasic acid.

**Statement-II:** In water, orthoboric acid acts as a proton donor. (2007)

**Q.5 Statement-I:** Between  $SiCl_4$  and  $CCl_4$ , only  $SiCl_4$  reacts with water.

**Statement-II:**  $SiCl_4$  is ionic and  $CCl_4$  is covalent. (2001)

**Q.6** The two types of bonds present in  $B_2H_6$  are covalent and ..... (1994)

**Q.7** Extra pure  $N_2$  can be obtained by heating (2011)

- (A)  $NH_3$  with CuO (B)  $NH_4NO_3$   
 (C)  $(NH_4)_2Cr_2O_7$  (D)  $Ba(N_3)_2$

**Q.8** The reaction of  $P_4$  with X leads selectively to  $P_4O_6$ . The X, is (2009)

- (A) Dry  $O_2$   
 (B) A mixture of  $O_2$  and  $N_2$   
 (C) Moist  $O_2$   
 (D)  $O_2$  in the presence of aqueous NaOH

**Q.9** The set with correct order of acid strength is (2001)

- (A)  $HClO < HClO_2 < HClO_3 < HClO_4$   
 (B)  $HClO_4 < HClO_3 < HClO_2 < HClO$   
 (C)  $HClO < HClO_4 < HClO_3 < HClO_2$   
 (D)  $HClO_4 < HClO_2 < HClO_3 < HClO$

**Q.10** Nitrogen (I) oxide is produced by (1989)

- (A) Thermal decomposition of  $\text{NH}_4\text{NO}_3$   
 (B) Disproportionation of  $\text{N}_2\text{O}_4$   
 (C) Thermal decomposition of  $\text{NH}_4\text{NO}_2$   
 (D) Interaction of hydroxylamine and nitrous acid

**Q.11** White phosphorus ( $\text{P}_4$ ) has (1998)

- (A) Six P—P single bonds  
 (B) Four P—P single bonds  
 (C) Four lone pairs of electrons  
 (D) PPP angle of  $60^\circ$

**Paragraph:** The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6.  $\text{XeF}_4$  reacts violently with water to give  $\text{XeO}_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. (2007)

**Q.12** Argon is used in arc welding because of its

- (A) Low reactivity with metal  
 (B) Ability to lower the melting point of metal  
 (C) Flammability  
 (D) High calorific value

**Q.13** The structure of  $\text{XeO}_3$  is

- (A) Linear (B) Planer (C) Pyramidal (D) T-shaped

**Q.14**  $\text{XeO}_4$  and  $\text{XeO}_6$  are expected to be

- (A) Oxidizing (B) Reducing  
 (C) Unreactive (D) Strongly basic

**Q.15** White phosphorus on reaction with NaOH gives  $\text{PH}_3$  as one of the products. This is a (2008)

- (A) Dimerisation reaction  
 (B) Disproportionation reaction  
 (C) Condensation reaction  
 (D) Precipitation reaction

**Q.16** All the compounds listed in column I react with water. Match the result of the respective with the appropriate option listed in column II. (2010)

Column I	Column II
(A) $(\text{CH}_3)_2\text{SiCl}_2$	(p) Hydrogen halide formation
(B) $\text{XeF}_4$	(q) Redox reaction
(C) $\text{Cl}_2$	(r) Reacts with glass
(D) $\text{VCl}_2$	(s) Polymerization
	(t) $\text{O}_2$ formation

**Q.17** The basicity of phosphorus acid ( $\text{H}_3\text{PO}_3$ ) is ..... (1990)

**Q.18** Among the following, the number of compounds than can react with  $\text{PCl}_5$  to give  $\text{POCl}_3$  is  $\text{O}_2, \text{CO}_2, \text{SO}_2, \text{H}_2\text{SO}_4, \text{P}_4\text{O}_{10}$  (2011)

**Q.19** Extra pure  $\text{N}_2$  can be obtained by heating (2011)

- (A)  $\text{NH}_3$  with  $\text{CuO}$  (B)  $\text{NH}_4\text{NO}_3$   
 (C)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (D)  $\text{Ba}(\text{N}_3)_2$

**Q.20** The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively (2012)

- (A) Redox reaction ; 3 and 5  
 (B) Redox reaction; +3 and +5  
 (C) Disproportionation reaction ; -3 and + 5  
 (D) Disproportionation reaction ; 3 and + 3

**Q.21** Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is (2012)

- (A)  $\text{Cl}_2\text{O}$  (B)  $\text{Cl}_2\text{O}_7$  (C)  $\text{ClO}_2$  (D)  $\text{Cl}_2\text{O}_6$

**Q.22** With respect to graphite and diamond, which of the statement(s) given below is (are) correct? (2012)

- (A) Graphite is harder than diamond.  
 (B) Graphite has higher electrical conductivity than diamond.  
 (C) Graphite has higher thermal conductivity than diamond.  
 (D) Graphite has higher C - C bond order than diamond.



# PlancEssential Questions

## JEE Main/Boards

### Exercise 1

Q.12      Q.22      Q.23  
Q.34      Q.36      Q.37

### Exercise 2

Q.7      Q.12

### Previous Years' Questions

Q.1      Q.8      Q.12  
Q.14      Q.21

## JEE Advanced/Boards

### Exercise 1

Q.3      Q.9      Q.13  
Q.14      Q.16

### Exercise 2

Q.1      Q.3      Q.11  
Q.15      Q.27      Q.28  
Q.29      Q.30      Q.32  
Q.33

### Previous Years' Questions

Q.3      Q.5      Q.6

## Answer Key

## JEE Main/Boards

### Exercise 2

#### Single Correct Choice Type

Q.1 C      Q.2 B      Q.3 A      Q.4 B      Q.5 B      Q.6 B  
Q.7 A      Q.8 A      Q.9 A      Q.10 B      Q.11 D      Q.12 C  
Q.13 A

### Previous Years' Questions

Q.1 D      Q.2 C      Q.3 A      Q.4 C      Q.5 A      Q.6 C  
Q.7 A      Q.8 C      Q.9 D      Q.10 A      Q.11 B      Q.12 A  
Q.13 C      Q.14 D      Q.15 B      Q.16 D      Q.17 A      Q.18 B  
Q.19 D      Q.20 D      Q.21 C      Q.22 B      Q.23 C      Q.24. C  
Q.25 A      Q.26 A      Q.27 A

## JEE Advanced/Boards

### Exercise 2

#### Single Correct Choice Type

Q.1 D	Q.2 B	Q.3 A	Q.4 B	Q.5 A	Q.6 A
Q.7 A	Q.8 A	Q.9 C	Q.10 B	Q.11 B	Q.12 D
Q.13 B	Q.14 D	Q.15 A			

#### Comprehension Type

Q.16 B	Q.17 B	Q.18 C	Q.19 C	Q.20 C	Q.21 B
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#### Assertion Reasoning Type

Q.22 A	Q.23 C	Q.24 A	Q.25 C
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#### Multiple Correct Choice Type

Q.26 A, B	Q.27 A, B, C	Q.28 A, C, D	Q.29 A, B	Q.30 A, D	Q.31 A, C
Q.32 A, B, C, D	Q.33 B, C				

#### Match the Columns

Q.34 A → q, s; B → r; C → r; D → q, r

#### Previous Years' Questions

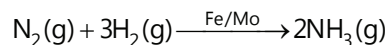
Q.1 A	Q.2 A	Q.3 A, B, C	Q.4 C	Q.5 C	Q.6 Banana Bond
Q.7 D	Q.8 B	Q.9 A	Q.10 A, D	Q.11 A, C, D	Q.12 A
Q.13 C	Q.14 A	Q.15 B	Q.16 A → p, s; B → p, q, r, t; C → p, q, t; D → p		
Q.17 B	Q.18 D	Q.19 D	Q.20 C	Q.21 A	Q.22 B, C, D
Q.23 B	Q.24 B	Q.25 A, C, D	Q.26 A	Q.27 C	Q.28 6
Q.29 B, C	Q.30 D	Q.31 B	Q.32 A, C, D	Q.33 B, D	

## Solutions

### JEE Main/Boards

#### Exercise 1

**Sol 1:** Ammonia is manufactured industrially by using Haber's process.



2. In  $\text{NH}_3$ , N is  $sp^3$  hybridised and one lone pair of electrons is present on N atom. Due to lone pair – bond pair repulsions, the H-atoms are pushed closer and the bond angles decrease from  $109^\circ$  to  $107^\circ$ . In  $\text{HPH}$  or  $\text{HAsH}$  or  $\text{HSbH}$ , the central atom uses only pure p-atomic orbital in the bond formation. As p-atomic orbitals are mutually perpendicular to each other, the bond angle is close to  $90^\circ$

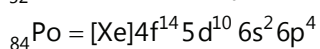
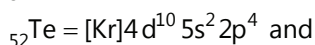
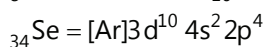
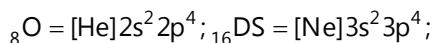
**Sol 2:** On moving down the group, size of central atom increases and its electronegativity decreases. As a result, bond pairs lie away from central atom resulting in decreases in bond angle.

**Sol 3:**

White phosphorus	Red phosphorus
(i) It consists of discrete $\text{P}_4$ tetrahedral.	(i) It consists of polymer of $\text{P}_4$ tetrahedral units
(ii) It glows in dark and is soluble in $\text{CS}_2$	(ii) It does not glow in the dark and is insoluble in $\text{CS}_2$
(iii) It is highly reactive due to strained $\text{P}_4$ tetrahedral	(iii) It is much less reactive due to polymerization
(iv) It dissolves in $\text{NaOH}$ to give $\text{PH}_3$	(iv) It is insoluble in $\text{NaOH}$

**Sol 4:** The bond dissociation energy of N-N bond is less than that of P-P due to strong lone pair-lone pair repulsions.

**Sol 5:** (i) Electronic configuration:



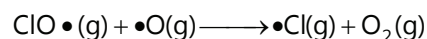
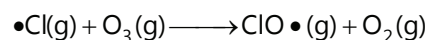
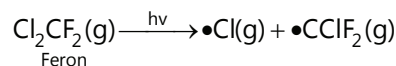
All these elements have same  $ns^2 np^4$  ( $n = 2$  to  $6$ ) valence shell electronic configuration and hence are justified to be placed in group 16 of the periodic table.

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

(iii) Formation of hydrides: All the elements complete their respective octets by sharing two of their valence electrons with 1s-orbital of hydrogen to form hybrids of the general formula  $\text{EH}_2$  i.e.,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$  and  $\text{H}_2\text{Po}$ . Therefore, on the basis of formation of hydride of the general formula,  $\text{EH}_2$ , these elements are justified to be placed in group 16 of the periodic table.

**Sol 6:** Although the formation of  $\text{O}^{2-}$  from O is endothermic but still almost all elements form oxides and this is due to high lattice energy of the oxides. This is due to small size and high charge of  $\text{O}^{2-}$ .

**Sol 7:** Aerosols such as chlorofluorocarbons (CFCs), i.e., freon ( $\text{CCl}_2\text{F}_2$ ) depletes the  $\text{O}_3$  layer by supplying Cl free radicals which convert  $\text{O}_3$  to  $\text{O}_2$  as shown below:



**Sol 8:** Sulphuric acid is manufactured by the Contact Process which involves three steps:

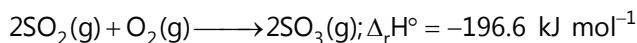
(i) Burning of sulphur or sulphide ores in air to produce  $\text{SO}_2$ .

(ii) Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction with oxygen in the presence of a catalyst ( $\text{V}_2\text{O}_5$ ), and

(iii) absorption of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ).

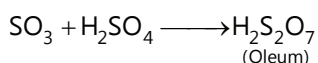
The  $\text{SO}_2$  produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).



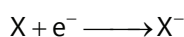
The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise the rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The  $\text{SO}_3$  gas oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration.



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

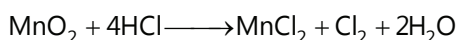
**Sol 9:** Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.



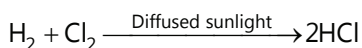
Thus, halogens act as strong oxidising agents. Their oxidising power, however, decreases from  $\text{F}_2$  to  $\text{I}_2$ .

**Sol 10:** Although O and Cl have about the same electronegativity, yet their atomic size (covalent radii) are much different : O = 66 pm and Cl = 99 pm. Thus, electron density per unit volume on oxygen atom is much higher than that on chlorine atom. Hence, oxygen forms hydrogen bonds while chlorine does not though both have approx. The same electronegativity.

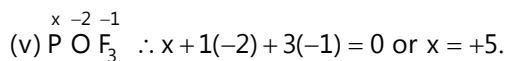
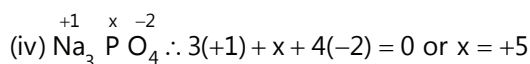
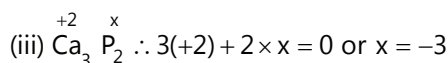
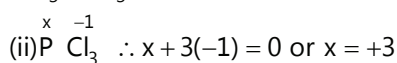
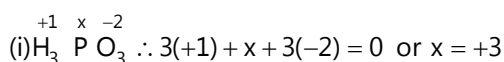
**Sol 11:** HCl can be oxidized to  $\text{Cl}_2$  by a number of oxidising agents like  $\text{MnO}_2$ ,  $\text{KMnO}_4$  and  $\text{K}_2\text{CrO}_7$



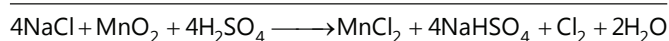
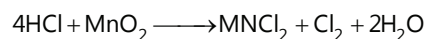
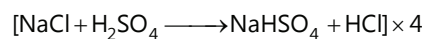
$\text{Cl}_2$  can be reduced to HCl by reaction of  $\text{H}_2$  in the presence of diffused sunlight.



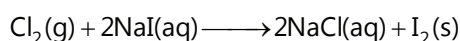
**Sol 12:** Let the oxidation state of P be x.



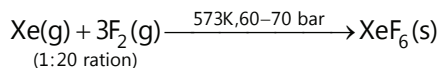
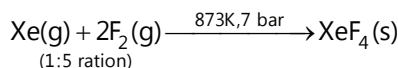
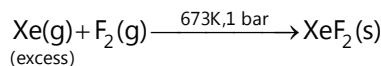
**Sol 13:**  $\text{Cl}_2$  is produced



(ii)  $\text{Cl}_2$  being an oxidising agent oxidises  $\text{NaI}$  to  $\text{I}_2$ .

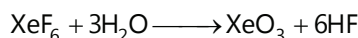


**Sol 14:** These xenon fluorides are prepared by direct reaction between Xe and  $\text{F}_2$  under different conditions as shown below:

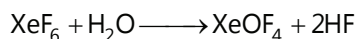


**Sol 15:** Replace  $\text{O}^-$  (9 electrons) in  $\text{ClO}^-$  by F (9 electrons). The resulting neutral molecule is ClF. Since ClF can combine further with F to form  $\text{ClF}_3$ , so, ClF is a Lewis base.

**Sol 16:** Hydrolysis of  $\text{XeF}_4$  and  $\text{XeF}_6$  with water gives  $\text{XeO}_3$ .



In contrast, partial hydrolysis of  $\text{XeF}_6$  gives  $\text{XeOF}_4$



**Sol 17:** Noble gases have only van der Waals' radii while others have covalent radii. Van der Waals' radii are larger than covalent radii. Hence, noble gases have comparatively large atomic sizes.

**Sol 18:** Uses of Neon:

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

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

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

**Sol 19: Electronic configuration:** The valence shell electronic configuration of these elements are  $ns^2 np^3$ . The s-orbital in these elements is completely filled and p-orbitals are half-filled, making their electronic configuration extra stable.

**Oxidation states:** The common oxidation states of these elements are -3, +3, and +5. The tendency to exhibit -3 oxidation, state decreases down the group due to increase in size and metallic character. In fact last member of the group, bismuth hardly forms any compounds in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterized Bi (v) compound is  $\text{BiF}_3$ . The stability of +5 oxidation state decreases and that of +3 oxidation state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.

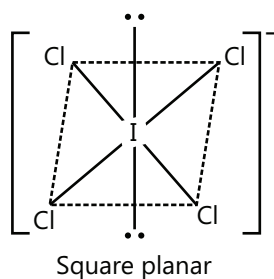
Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

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

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

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

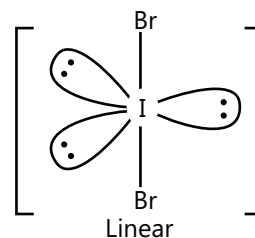
**Sol 20: (i) Structure of  $\text{ICl}_4^-$ :**



I in  $\text{ICl}_4^-$  has four bond pairs and two lone pairs. Therefore, according to VSEPR theory, it should be square planar as shown.

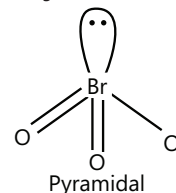
Here,  $\text{ICl}_4^-$  has  $(7 + 4 \times 7 + 1) = 36$  valence electrons. A noble gas species having 36 valence electrons is  $\text{XeF}_4$  ( $8 + 4 \times 7 = 36$ ). Therefore, like  $\text{ICl}_4^-$ ,  $\text{XeF}_4$  is also square planar.

**(ii) Structure of  $\text{IBr}_2^-$ :**



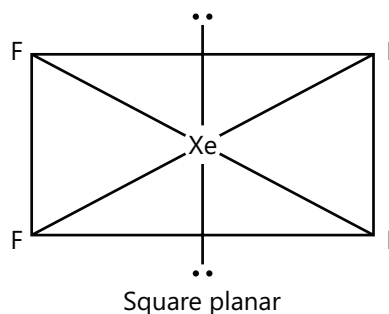
I in  $\text{IBr}_2^-$  has two bond pairs and three lone pairs. So, according to VSEPR theory, it should be linear. Here,  $\text{IBr}_2^-$  has  $22(7 + 2 \times 7 + 1)$  valence electrons. A noble gas species having 22 valence electrons is  $\text{XeF}_2$  ( $8 + 2 \times 7 = 22$ ). Thus, like  $\text{IBr}_2^-$ ,  $\text{XeF}_2$  is also linear:

**(iii) Structure of  $\text{BrO}_3^-$ :**

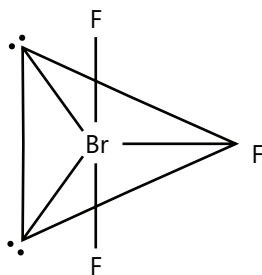


The central atom Br has seven electrons. Four of these electrons form two double bonds or coordinate bonds with two oxygen atoms while the fifth electron forms a single bond with  $\text{O}^-$  ion. The remaining two electrons form one lone pair. Hence, in all there are three bond pairs and one lone pair around Br atom in  $\text{BrO}_3^-$ . Therefore, according to VSEPR theory,  $\text{BrO}_3^-$  should be pyramidal. Here,  $\text{BrO}_3^-$  has  $26(7 + 3 \times 6 + 1 = 26)$  valence electrons. A noble gas species having 26 valence electrons is  $\text{XeO}_3$  ( $8 + 3 \times 6 + 1 = 26$ ). Thus, like  $\text{BrO}_3^-$ ,  $\text{XeO}_3$  is also pyramidal.

**Sol 21:  $\text{XeF}_4$**





BrF<sub>3</sub>

T-Shaped

**Sol 22:** (i) The minimum oxidation number (O.N.) of S is -2 while its maximum O.N. is +6. In SO<sub>2</sub>, the O.N. is +4, here, it can not only increase its O.N. by losing electrons but also reduce its O.N. by gaining electrons. Thus, it acts both as a reducing agent as well as an oxidising agent. In contrast, in H<sub>2</sub>S, S has an O.N. of -2. Thus, it can only increase its O.N. by losing electrons and hence acts only as a reducing agent.

(ii) Fluorine being the strongest oxidising agent oxidises sulphur to its maximum oxidation state of +6 and thus forms SF<sub>6</sub>. In contrast H<sub>2</sub> being a very weak oxidising agent cannot oxidise S to its maximum oxidation state of +6 and hence does not form SH<sub>6</sub>.

(iii) This is because fluorine is more electronegative than oxygen.

**Sol 23:** (i) (a)  $\text{XeF}_2 + \text{PF}_5 \longrightarrow [\text{XeF}]^+ [\text{PF}_6]^-$  :

(b)  $2\text{AgNO}_3 \xrightarrow{\Delta} 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$

(ii) (a) +3 oxidation state becomes more stable from As to Bi in the group due to inert pair effect. The reluctance of the s electrons to take part in the chemical bonding due to which the lower oxidation state become more stable on descending down the group of p-block elements is known as inert pair effect.

(b) Sulphur in vapour state exhibits paramagnetic behaviour because it forms S<sub>2</sub> molecules like O<sub>2</sub> which contains two unpaired electrons.

**Sol 24:** (ii) (a) Because P-P bond is stronger than N-N bond.

(b) pπ-pπ bonding is available in case of fluorine whereas in case of chlorine, dπ-pπ is seen.

(c) Ionization energy is quite high.

**Sol 25:** (ii) a Hydrogen bonding in NH<sub>3</sub>

(b) same as 24(c).

(c) Due to the inert pair effect, Sb and Bi are more stable in +3 oxidation state as compared to the +5 state. But due to the presence of f orbital electrons in Bi, its +3 is more stable than Sb(+3). That is why, Bi(V) tends to achieve Bi(III) state (i.e. reduction of Bi) for greater stability easily as compared to the Sb. since Bi (V) is undergoing self reduction, hence it is a stronger oxidising agent than Sb(V).

**Sol 26:**

(i) (a)  $\text{PCl}_5 + \text{H}_2\text{O} \rightarrow \text{Cl} + \text{H}_3\text{PO}_4$

(b)  $\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{HF} + \text{O}_2$

(ii) (a) Presence of d-orbitals in P.

(b) Formation of bisulfate anion (HSO<sub>4</sub><sup>-</sup>) by loss of one proton gives a bigger K<sub>a1</sub>.

**Sol 27:** (i) (a)  $\text{P}_4 + 4\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 2\text{Na}_2\text{HPO}_3$

(b)  $3\text{Cu} + 8\text{HNO}_3 (\text{dilute}) \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$

(ii)(a) Oxygen has small size and more electronegativity in comparison to sulphur and thus H<sub>2</sub>O molecules exists as associated molecule to form liquid state because of H-bonding. H<sub>2</sub>S does not show H-bonding and thus exists as unassociated molecules to have gaseous state.

ii) (b) Deep sea divers can remain at depth only for controlled periods and must come up slowly and even remain at specified depths to avoid the bends. When ordinary air is used for diving the oxygen in the air is used up by the body but the nitrogen builds up to a new equilibrium state at the higher pressure required at great depths. The excess nitrogen would then come out of tissues and form bubbles (like the fizz in a opened can of soda) in the blood causing the bends and great pain with possible death. During controlled decompression the helium would also diffuse out of tissues and the lungs more easily than nitrogen avoiding the bends.

**Sol 28:** In PCl<sub>5</sub>, due to small size and high electronegativity of Cl, hybridisation is possible. But in PI<sub>5</sub>, hybridisation is restricted due to large size and less electronegativity.

**Sol 29:** Urea releases nitrogen readily as compared to ammonium sulphate and moreover, urea contains the highest percentage of nitrogen.

**Sol 30:** HF has a corrosive action on glass.

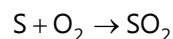
**Sol 31:**  $\text{H}_2\text{F}_2$  exists as dimeric molecule due to H-bonding and thus shows dibasic nature. Hence it gives two series of salts  $\text{KHF}_2$  as  $[\text{K}^+\text{andF}^- \dots \text{H}-\text{F}^-]$  and  $\text{KF}[\text{K}^+\text{andF}^-]$  whereas  $\text{HCl}$  and  $\text{HBr}$  do not show hydrogen bonding and thus formation of  $\text{KHCl}_2$  or  $\text{KHBBr}_2$  is not possible.

**Sol 32:** Halogens have variable oxidation states, +1, +3, +5 and +7.

**Sol 33:** Chlorine can displace iodine since it is above I in the group.

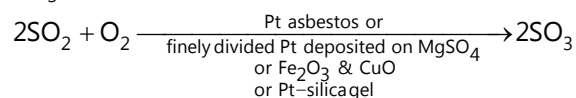
**Sol 34:** (i) Ionization energy of Cl is greater than Iodine. Thus  $\text{I}_2$  can be readily displaced.

ii)  $\text{SO}_2$  is obtained by burning sulphur in air.



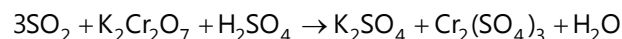
The  $\text{SO}_2$  so obtained is impure. Dust present in sulphur is removed by allowing the gas to expand, when some dust settles, as well as by passing through electrostatic precipitators and finally washing with water. The moistened gas is now treated with conc.  $\text{H}_2\text{SO}_4$  to dry  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  is kept in use until its concentration falls to 94%.

The  $\text{SO}_2$  so obtained then catalytically converted to  $\text{SO}_3$



**Sol 35:** (i)

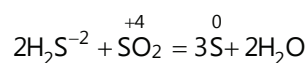
$\text{SO}_2$  reduces  $\text{K}_2\text{Cr}_2\text{O}_7$  to green chromium sulphate.



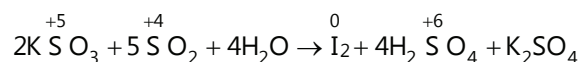
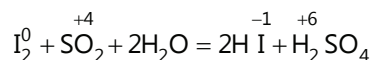
ii)  $\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{S} \uparrow$   
foul odour

**Sol 36:** The oxidation number of sulphur in sulphur dioxide is +4 which lies between its maximum value (+6) and minimum value (-2). Hence sulphur dioxide can both be oxidized and reduced and  $\text{SO}_2$  can act both as a reducer and oxidizer respectively

As oxidizer



As reducer-

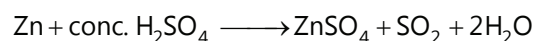
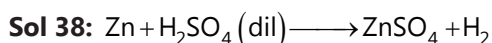


Sulphur is placed below oxygen in the same group in the periodic table.

Thus  $\text{H}_2\text{S}$  acts as a reducing agent only.

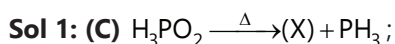
**Sol 37:** (i)  $\text{H}_3\text{PO}_4$ , orthophosphoric acid, can be written  $\text{O}=\text{P}(\text{OH})_3$ . It has three acidic protons (attached to oxygen) and is therefore tribasic. But Phosphorous acid,  $\text{H}_3\text{PO}_3$ , is diprotic (readily ionizes two protons), not triprotic as might be suggested by the formula.

ii) to restore the fertility of the soil. These plants have the ability to fix atmospheric nitrogen to form nitrogen compounds through the help of certain bacteria present in their root. These nitrogen compounds go into the soil and make it more fertile.



## Exercise 2

### Single Correct Choice Type



Disproportionation reaction

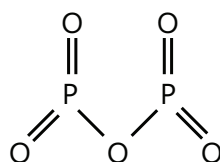
**Sol 2: (B)** (b) **Pseudohalogen molecules:** (meaning "fake" halogens) are inorganic molecules of the general forms  $\text{Ps-Ps}$  or  $\text{Ps-X}$ , where Ps is a **pseudohalogen group** such as cyanide, cyanate, thiocyanate and others, and X is a "true" halogen.

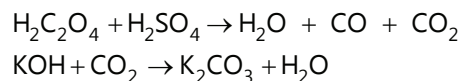
**Sol 3: (A)** Fact.

**Sol 4: (B)** (b) Depends on the sizes of the halogens

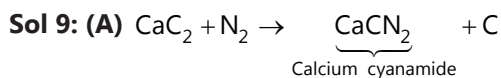
**Sol 5: (B)** (b) It has a lone pair in 2p orbital which is transferred to the empty d-orbital of Si atom resulting  $d\pi-p\pi$  bonding.

**Sol 6: (B)**



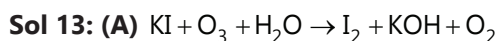
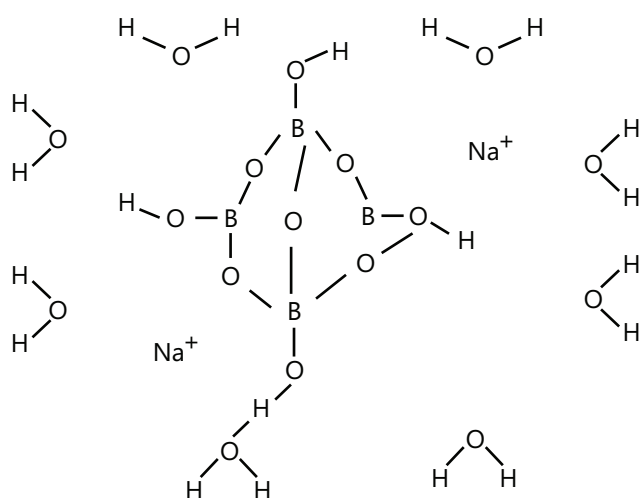
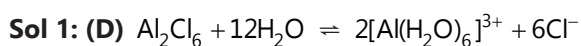
**Sol 7: (A)**

**Sol 8: (A)** Acidic strengths increases as electronegativity of atom increases So,  $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$



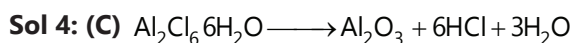
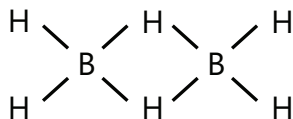
**Sol 10: (B)** Fact.

**Sol 11: (D)** Self explanatory

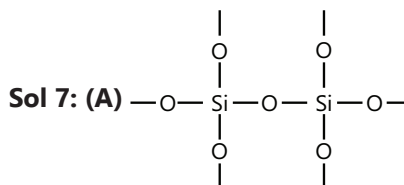
**Sol 12: (C)****Previous Years' Questions**

**Sol 2: (C)** Fact.

**Sol 3: (A)** Boron does not have d orbitals in its valence shell and so, maximum covalency of Boron cannot exceed 4. So, its cannot form  $\text{BF}_6^{-3}$ .

**Sol 5: (A)**

**Sol 6: (C)** Stability of dihalides increases down the group.

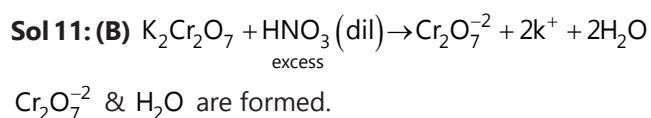


**Sol 8: (C)** Down the group, acidic character increases.

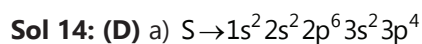
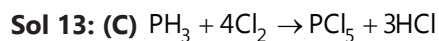
**Sol 9: (D)** In  $\text{P}_4$ , P – P bond is  $\text{sp}^3$  hybridised

$$\therefore \% \text{ p character} = 75$$

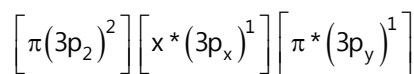
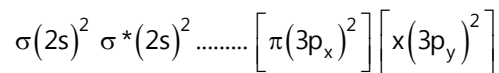
**Sol 10: (A)** Down the group, stability of hydrides decreases.



**Sol 12: (A)** Nitrogen does not have vacant d-orbitals.



$$\text{S}_2 = \text{total } 32 \text{ e}^-$$

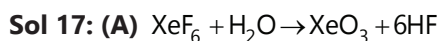
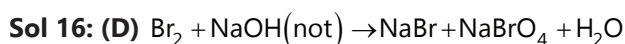


b) Vapour at 200 -  $\text{S}_8$

c) Vapour at 600 -  $\text{S}_2$

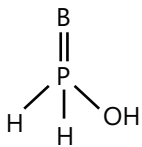
d) Oxidation state of S in  $\text{S}_2$  is 0.

**Sol 15: (B)**  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$  (Thermal stability).

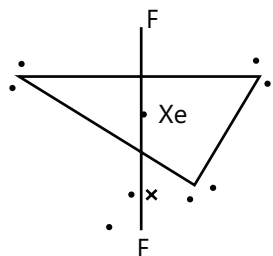
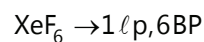
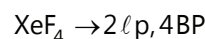


Reaction is not reversible.

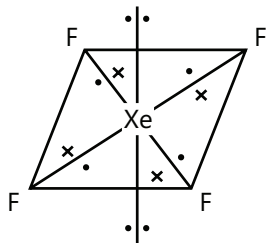
**Sol 18: (B)**



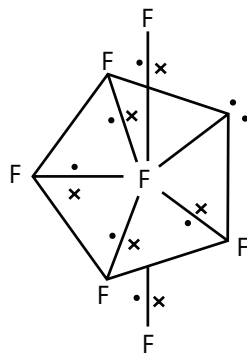
**Sol 19: (D)** Decrease in Electronegativity down the group causes decreases in bond angles.



$sp^3$  hybridization



$sp^3d^2$  hybridization



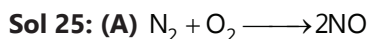
$sp^3d^2$  hybridization

**Sol 21: (C)** Helium is twice as heavy as hydrogen, its lifting power is 92% of that of hydrogen. Helium has the lowest melting and boiling point of any element which makes liquid helium an ideal coolant for many extremely low temperature application such as super conducting magnet and cryogenic research where temperature close to absolute zero are needed.

**Sol 22: (B)** HCl is a gas.

**Sol 23: (C)** Factual.

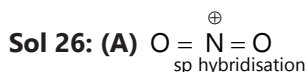
**Sol 24: (C)** NO is paramagnetic in gaseous state and diamagnetic in solid state.



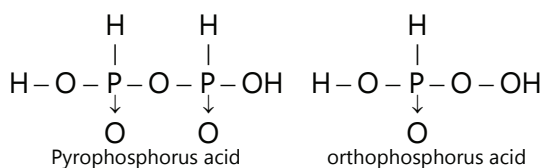
$$\Delta G = \Delta H - T\Delta S$$

$\Delta H$  &  $\Delta S$  As are positive.

So reaction is thermodynamically favourable at high temperature.

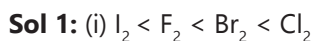


**Sol 27: (A)** Phosphorus acid series contain phosphorus in the oxidation state (+ III).

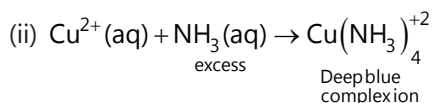
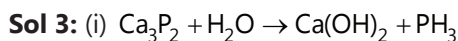


## JEE Advanced/Boards

### Exercise 1



**Sol 2:**  $\text{NeF}_2$  does not exist.



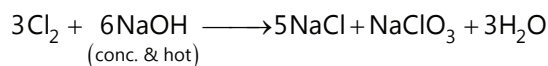
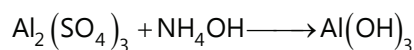
**Sol 4:** Reaction of Zinc and HCl produces nascent hydrogen which is more reactive than molecular hydrogen.

**Sol 5:** Aquaregia is a mixture of 1 part conc.  $\text{HNO}_3$  and 3 part conc. HCl. The mixture liberate nascent chlorine which dissolves noble metals.

**Sol 6:** The impurity in  $\text{PH}_3$  is  $\text{P}_2\text{H}_4$ , the liquid hydride present in phosphine catches fire as soon as it contact with air and forms vortex rings of smoke.





**Sol 25: (C)****Multiple Correct Choice Type****Sol 26: (A, B)** Fact.**Sol 27: (A, B, C)**

- (a) White coloured  
 (b) Insoluble in  $\text{NH}_4\text{OH}$   
 (c) Soluble in  $\text{NaOH}$

**Sol 28: (A, C, D)** Stability of dihalides increase down the group.

Ability of forming  $p\pi-p\pi$  multiple bonds decreases down the group.

They all form oxides ( $\text{MO}_2$ ).

**Sol 29: (A, B)**  $\text{NO}_2$  is paramagnetic, but  $\text{N}_2\text{O}_4$  is diamagnetic.

$\text{NO}_2$  is brown and  $\text{N}_2\text{O}_4$  is colourless.

**Sol 30: (A, D)** C – O bond energy is less than SiO bond energy.

**Sol 31: (A, C)**  $\text{IF}_3$ ,  $\text{IF}_5$ ,  $\text{IF}_7$ ,  $\text{BrCl}$

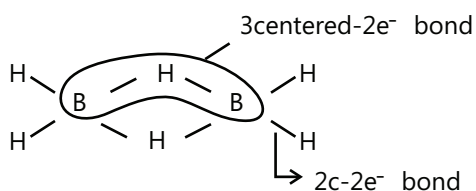
B is more Electronegative than A

$\text{FBr}_3$  does not exist.

There is no deviation in structure of  $\text{ClF}_3$  and  $\text{IF}_7$ .

**Sol 32: (A, B, C, D)** Fact.

**Sol 33: (B, C)**

**Match the Columns**

**Sol 34:** A  $\rightarrow$  q, s; B  $\rightarrow$  r; C  $\rightarrow$  r; D  $\rightarrow$  q, r

A.  $\text{Bi}^{3+} + \text{H}_2\text{O} \longrightarrow \text{BiO}^+ + 2\text{H}^+$  thus (q) and (s)

B.  $\text{AlO}_2^- + \text{H}_3\text{O}^+ \longrightarrow \text{Al}(\text{OH})_3 \downarrow$  thus (r)

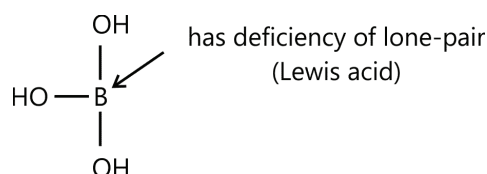
C.  $2\text{SiO}_4^{4-} + 2\text{H}^+ \longrightarrow \text{Si}_2\text{O}_7^{6-}$  thus (r)

D.  $\text{B}_4\text{O}_7^{2-} \xrightarrow{\text{H}^+} \text{B}(\text{OH})_3$

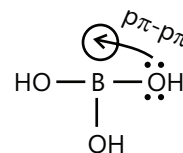
$\text{B}_4\text{O}_7^{2-} \xrightarrow{\text{H}_2\text{O}} \text{B}(\text{OH})_3$ . Thus, (q) are (r)

**Previous Years' Questions**

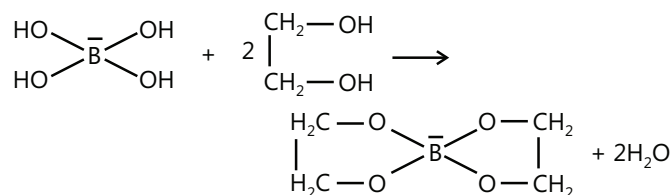
**Sol 1: (A)** Orthoboric acid is a weak, monobasic, Lewis acid.



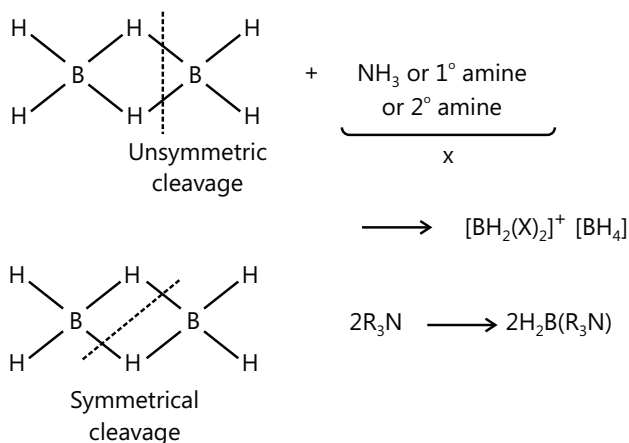
$p\pi-p\pi$  back-bonding between 'B' and 'O' decreases acid strength greatly:



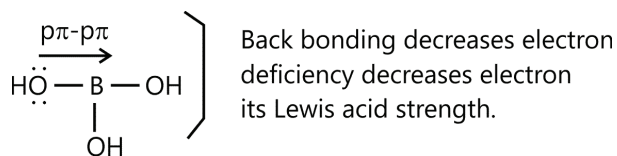
**Sol 2: (A)** Orthoboric acid is a very weak acid, direct neutralization does not complete. However, addition of cis-diol allow the reaction to go to completion by forming a stable complex with  $[\text{B}(\text{OH})_4]^-$  as:



**Sol 3: (A, B, C)** Diborane ( $\text{B}_2\text{H}_6$ ) undergo unsymmetric cleavage with  $\text{NH}_3$ , primary and secondary amine while tertiary amine brings about symmetrical cleavage of  $\text{B}_2\text{H}_6$  as:



**Sol 4: (C)** Orthoboric acid is a weak, monobasic, Lewis acid and the poor acidic character is due to  $p\pi-p\pi$  back bondings as

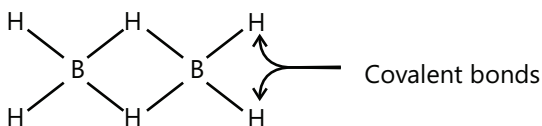


**Sol 5: (C)**  $\text{SiCl}_4$  reacts with water due to vacant d-orbitals available with Si as:



No such vacant d-orbitals are available with carbon, hence  $\text{CCl}_4$  does not react with water. Otherwise, both  $\text{SiCl}_4$  and  $\text{CCl}_4$  are covalent.

**Sol 6:** Three centred two electron bonds.

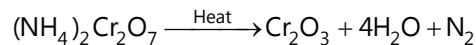
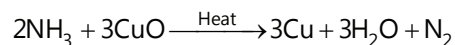


Three centred two electron bridged B—H—B bonds

**Sol 7: (D)**  $\text{Ba}(\text{N}_3)_2 \xrightarrow{\text{Heat}} \text{Ba}(\text{s}) + 3\text{N}_2(\text{g})$

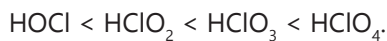
Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as by product along with gaseous nitrogen, hence no additional step of separation is required.

Other reactions are:

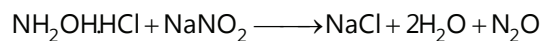
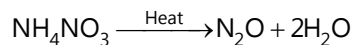


**Sol 8: (B)** In limited supply of oxygen, phosphorus is oxidized to its lower oxide  $\text{P}_4\text{O}_6$  while excess of oxygen gives  $\text{P}_4\text{O}_{10}$ . A mixture of  $\text{O}_2$  and  $\text{N}_2$  is used for controlled oxidation of phosphorus into  $\text{P}_4\text{O}_6$ .

**Sol 9: (A)** Amongst oxyacids of a given halogen, higher the oxidation number of halogen, stronger the acid. Hence,

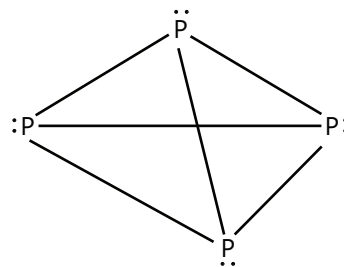


**Sol 10: (A, D)**



However,  $\text{NH}_4\text{NO}_2$  on heating gives  $\text{N}_2$ .

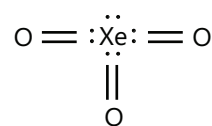
**Sol 11: (A, C, D)** The structure of  $\text{P}_4$  is



It has six P-P single bonds. There are four lone pairs of electrons on four phosphorus. P-P-P bond angle are  $60^\circ$ .

**Sol 12: (A)** Ar, being inert, provide inert atmosphere in arc welding, and prevent from undesired oxidation.

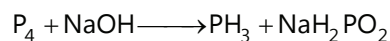
**Sol 13: (C)** Xe is  $sp^3$  hybridised with one lone pair. Hence, molecule of  $\text{XeO}_3$  has pyramidal shape.



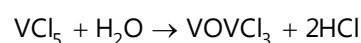
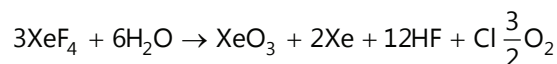
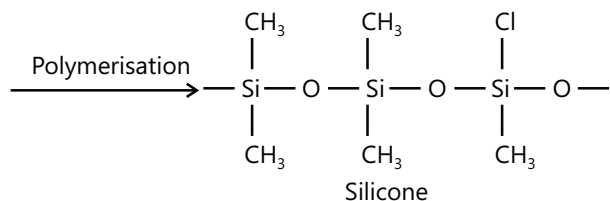
**Sol 14: (A)** Both  $\text{XeF}_4$  and  $\text{XeF}_6$  are strong oxidising agent.



**Sol 15: (B)** White phosphorus undergo disproportionation in alkaline medium.

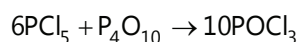
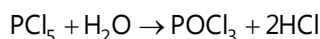


**Sol 16:** A  $\rightarrow$  p, s; B  $\rightarrow$  p, q, r, t; C  $\rightarrow$  p, q, t; D  $\rightarrow$  p

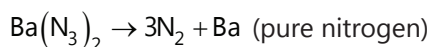
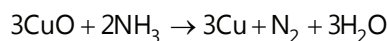
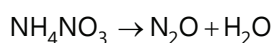


**Sol 17: (B)**  $H_3PO_3 [O = PH(OH)_2]$  is a dibasic acid.

**Sol 18: (D)**  $PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$



**Sol 19: (D)**  $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$



**Sol 20: (C)**  $P_4$  (white) + NaOH +  $3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

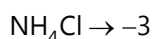
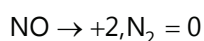
$PH_3$  has  $-3$  and  $NaH_2PO_3$  has  $+5$ .

**Sol 21: (A)** Bleaching powder contains salt HCl

It is obtained by adding  $H_2O$  to  $Cl_2O$

**Sol 22: (B, C, D)** Graphite is  $sp^2$  hybridized and contains Vander Wall Force. While diamond is  $sp^3$  hybridized.

**Sol 23: (B)**  $HNO_3 \rightarrow +5$

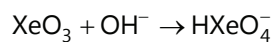


**Sol 24: (B)**  $4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$

**Sol 25: (A, C, D)** Exothermic.

**Sol 26: (A)**  $SOCl_2 + P_4 \longrightarrow PCl_3 + SO_2 + S_2Cl_2$

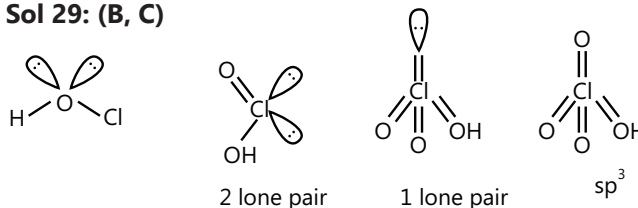
**Sol 27: (C)**  $XeF_6 + 3H_2O \rightarrow XeO_3 + 3H_2F_2$



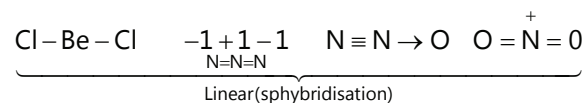
**Sol 28:**  $B_2H_6 + 6MeOH \rightarrow 2B(OMe)_3 + 6H_2$

Diborane reacts with methanol to give hydrogen and trimethoxyborate ester.

**Sol 29: (B, C)**



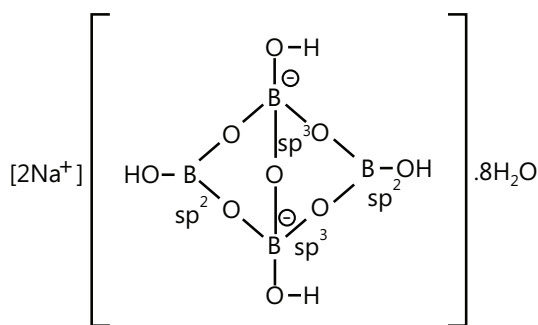
**Sol 30: (D)**



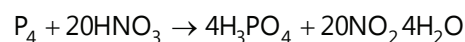
**Sol 31: (B)**  $Ga < Al < In < Tl$

On moving down the group, atomic radii increases except Ga to poor screening effect.

**Sol 32: (A, C, D)**



**Sol 33: (B, D)**  $4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$



$O = \text{N} - \text{O} - \text{N} = \text{O}$  is diamagnetic

