

Class 11

2017-18



# CHEMISTRY

## FOR JEE MAIN & ADVANCED

SECOND  
EDITION



Topic Covered  
p-block Elements

Exhaustive Theory ◀  
(Now Revised)

Formula Sheet ◀

9000+ Problems ◀  
based on latest JEE pattern

2500 + 1000 (New) Problems ◀  
of previous 35 years of  
AIEEE (JEE Main) and IIT-JEE (JEE Adv)

5000+ Illustrations and Solved Examples ◀

Detailed Solutions ◀  
of all problems available

Planceess Concepts

Tips & Tricks, Facts, Notes, Misconceptions,  
Key Take Aways, Problem Solving Tactics

Planceessential

Questions recommended for revision

# 16. p - BLOCK ELEMENTS

## 1. GROUP 13 ELEMENTS (BORON FAMILY)

### 1.1 Introduction

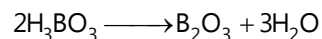
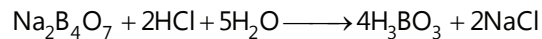
Elements of group 13 belong to p-block elements, since the last electron in them is present in the p-orbital. All these elements have three electrons in the outer most orbit: two in the s-orbital and one in the p-orbital. Thus, the electronic configuration of the outermost energy levels of these elements may be 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] $4f^{14} 5d^{10} 6s^2 6p^1$

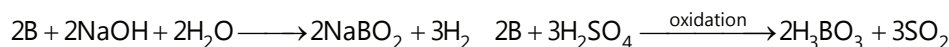
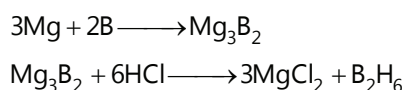
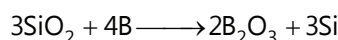
### 1.2 Boron

#### Preparation:

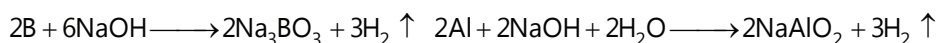


**Physical Properties:** Low electronegativity, hard, absorbs neutrons, steel grey in color. Some dissimilarities of boron with other elements of this group are:

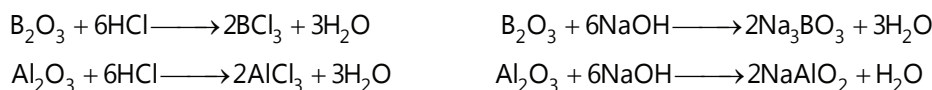
- (a) Boron does not form positive ions in aqueous solution and has low oxidation potential.
- (b) Boron always forms covalent compounds
- (c) Boron is non-metallic

**Chemical Properties****(a)** Reaction with  $O_2$  and  $N_2$ **(b)** Reaction with alkalis and acids**(c)** Boron reacts with Mg, which on hydrolysis give diborane.**(d)** Reaction with silica**PLANCESS CONCEPTS**

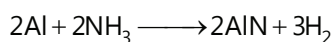
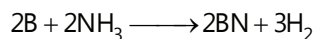
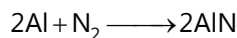
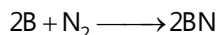
- Boron has high m.p. and b.p.  
Boron has a very high m. p. and b.p. because it exists as a giant covalent, polymeric structure both in solid as well as in liquid state.
- $B(OH)_3$  is an acid,  $Al(OH)_3$  is amphoteric and  $Tl(OH)_3$  is basic.  
The electropositive or metallic character of gp. 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.  $H_2SO_4$ :** Both react with conc.  $H_2SO_4$  to liberate  $SO_2$ .**(b) Action of alkalis:** Both liberate  $H_2$ .**(c) Formation of oxides:** Both form oxides when heated with oxygen at high temperature.

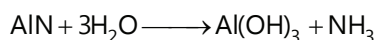
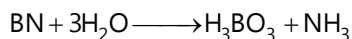
These oxides are amphoteric and dissolve in acids as well as in alkalis to form salts.



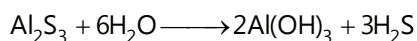
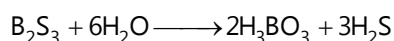
(d) **Formation of nitrides:** Both, when heated with nitrogen or ammonia, form nitrides.



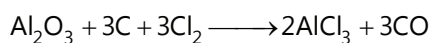
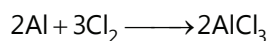
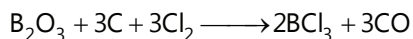
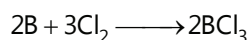
These nitrides are decomposed by steam to form ammonia.



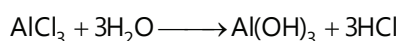
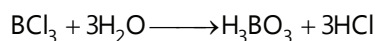
(e) **Formation of sulphides:** Both form sulphides on heating with sulphur at high temperatures. These are hydrolysed by water.



(f) **Formation of chlorides:** They form trichlorides by direct combination with  $\text{Cl}_2$  or by passing  $\text{Cl}_2$  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".

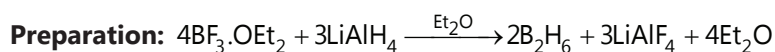
- From boron to thallium, +1 oxidation state becomes more stable.

Reason: inert pair effect.

GV Abhinav (JEE 2012, AIR 329)

### 1.2.2 Compounds of Boron

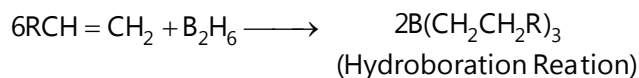
(a) Diborane ( $\text{B}_2\text{H}_6$ )



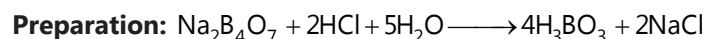
**Physical Properties:**

(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:

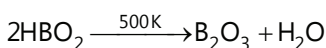
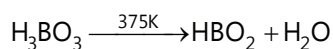


(b) **Boric Acid:** Orthoboric acid,  $\text{H}_3\text{BO}_3$  (commonly known as boric acid) and metaboric acid  $\text{HBO}_2$ , are two well-known, important oxoacids of boron.

**Properties:**

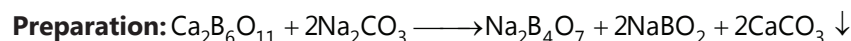
(i) It is moderately soluble in water.

(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.

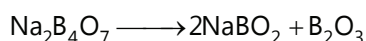


In solution, metaboric acid changes to orthoboric acid.

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

**Properties:**

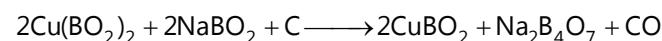
(i) On heating alone, it decomposes to form  $\text{NaBO}_2$  and  $\text{B}_2\text{O}_3$



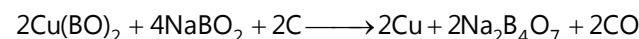
(ii) **Borax bead Test:** The formation of coloured metaborates by transition metal salts is used in the borax bead test as a qualitative analysis. The distinct colour of the bead depends on the oxidizing or reducing flame of the bunsen burner.

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:



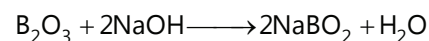
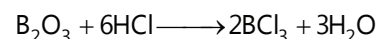
and to metallic copper and hence the bead becomes dull red and opaque.



**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.

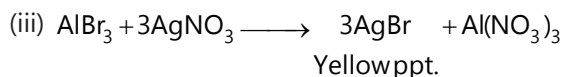
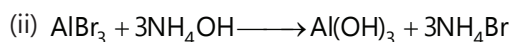
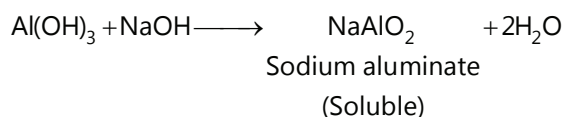
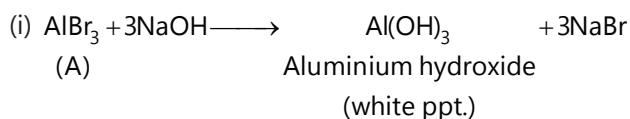
**(JEE MAIN)**

**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)

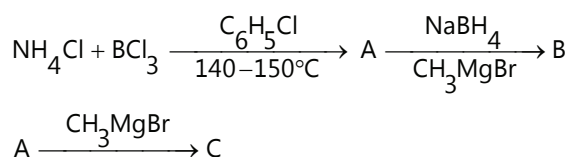
**(JEE ADVANCED)**

**Sol:** The given reactions are:

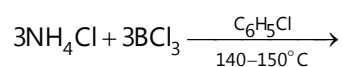
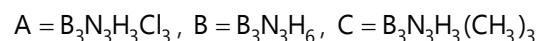


**Illustration 5:** Identify A, B and C in the given reaction sequence:

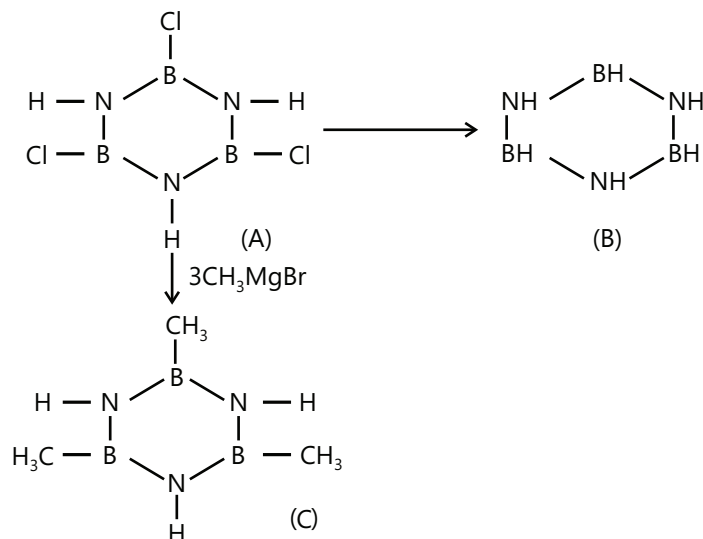
**(JEE ADVANCED)**



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

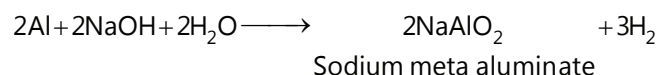


Reactions are:



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

**Sol:** Washing soda ( $\text{Na}_2\text{CO}_3$ ) reacts with water to form  $\text{NaOH}$  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,  $\text{B}=\text{N}$  bonds are polar and therefore, reactivity of borazole is more than benzene which possesses non-polar  $\text{C}=\text{C}$  and  $\text{C}-\text{C}$  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

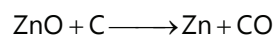
### 2.2.1 Allotropes of Carbon

- (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.

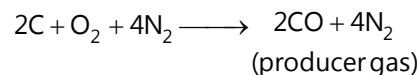
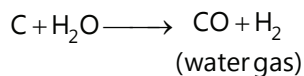
### 2.2.2 Important Compounds of Carbon

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

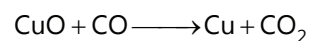
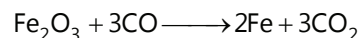
**Preparation:** (i) By heating oxides of heavy metals e. g. iron, zinc etc with carbon.



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

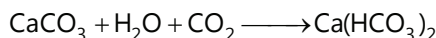
(b) A filter paper soaked in platinum or palladium chloride turns pink, green or black due to reduction of the chloride by carbon monoxide.

#### (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  $\text{VC}$ .

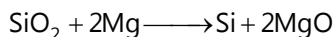
## 2.3 Silicon

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

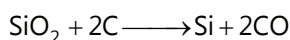
**Properties:** Silicon is obtained by the reduction of silica. It exists in two allotropic forms:

- (a) amorphous      (b) crystalline

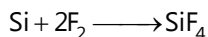
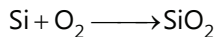
The amorphous variety is obtained by heating dry powdered silica with magnesium.



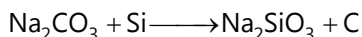
The crystalline variety is obtained by heating a finely powdered sand or quartz with carbon in an electric furnace where, a small amount of iron is added to prevent the formation of carborundum ( $\text{SiC}$ )



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.

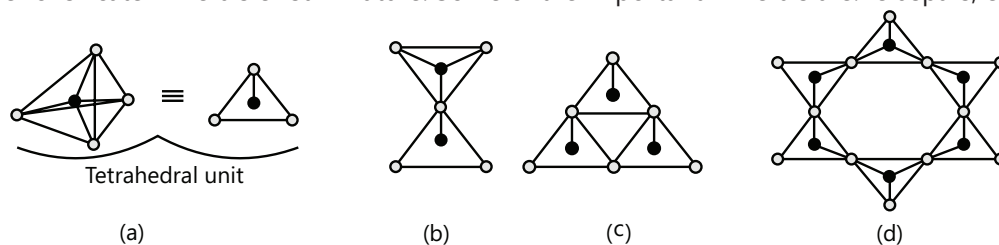


When amorphous silicon is strongly heated, it fuses and on cooling solidifies to the crystalline form. It forms a very hard crystalline silicon, which does not burn in oxygen but readily combines with fluorine. It dissolves in a mixture of  $\text{HNO}_3$  and  $\text{HF}$ . When fused with alkali, it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



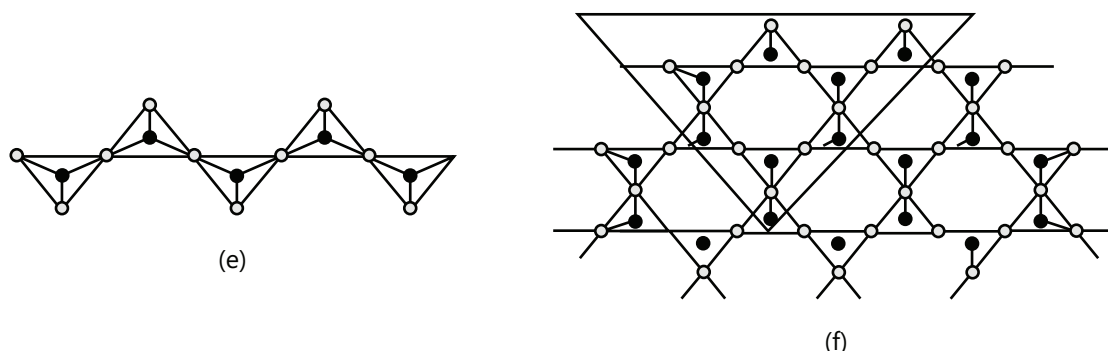
### 2.3.1 Silicates

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  $\text{Ca}_2[(\text{AlO}_2)_4(\text{SiO}_2)_8]\text{H}_2\text{O}$ , 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.

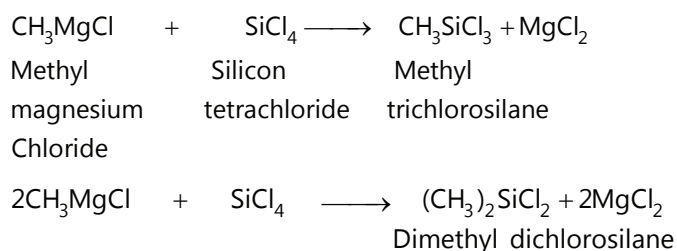


**Figure 16.2:** Normal orthosilicates

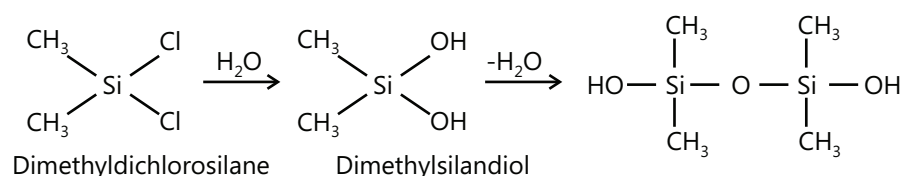
Normal orthosilicates (e.g.  $\text{Mg}_2\text{SiO}_4$ ) contain discrete  $\text{SiO}_4$  units. When two  $\text{SiO}_4$  tetrahedra share a corner (common oxygen atom), we get the  $(\text{Si}_2\text{O}_7)^{6-}$  unit and the silicates are called pyrosilicates. When  $\text{SiO}_4$  units share two 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

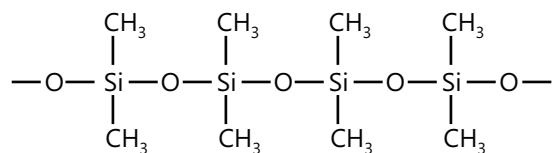
These are organosilicon polymers containing  $\text{Si}-\text{O}-\text{Si}$  linkages. They may be linear, cyclic or cross-linked polymers. These are prepared from alkyl- or aryl-chlorosilanes which in turn are obtained from Grignard reagent and silicon tetrachloride.



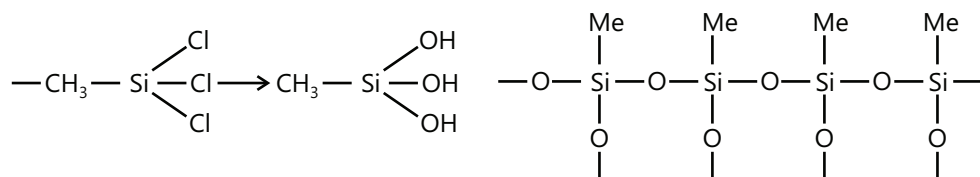
**Preparation:** Hydrolysis of the chlorides yields the corresponding silanols which polymerize by condensation by elimination of one water molecule from 2 molecules of alkyl silanols.



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.

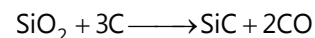
- (a) **Silica:** Sand of uniform size is used, i.e., neither too fine nor too coarse. Finer variety makes the reaction violent while coarse variety slows down the reaction. It should be free from iron oxide and organic matter.
- (b) **Boron Trioxide,  $\text{B}_2\text{O}_3$ :** This is introduced in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

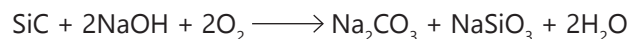
Lithium, sodium, potassium, calcium, barium, magnesium, lead and zinc oxides. Sodium is introduced in the form of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and carbon mixture. Potassium is added as potassium carbonate ( $\text{K}_2\text{CO}_3$ ) or potassium nitrate ( $\text{KNO}_3$ ). Calcium is 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:** 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 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,
  - Smaller size of F gives rise to less steric repulsion in  $\text{SiF}_6^{2-}$ .
  - 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)**

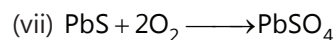
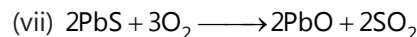
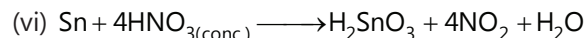
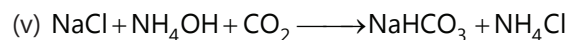
- Dilute nitric acid slowly reacts with tin.
- Carbon and steam are heated.
- Red lead is treated with nitric acid.
- Iodine is added to stannous chloride.
- Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia.
- Tin is treated with concentrated nitric acid.
- 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)  $\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$   
(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)  $2\text{SnCl}_2 + 2\text{I}_2 \longrightarrow \text{SnCl}_4 + \text{SnI}_4$

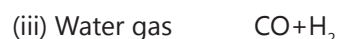


**Illustration 14:** Indicate the principal ingredients of the following:

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

**(JEE MAIN)**

**Sol:**

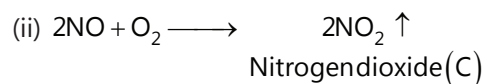
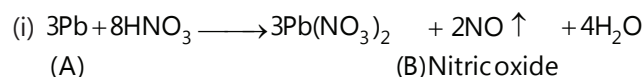


**Illustration 15:** A bluish metal (A) has a high density and readily dissolves in medium concentrated  $\text{HNO}_3$  and liberates a gas (B) which on mixing with air turns into red coloured gas (C). Metal is little affected by dil HCl or  $\text{H}_2\text{SO}_4$ . The solution containing bipositive 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.

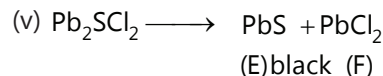
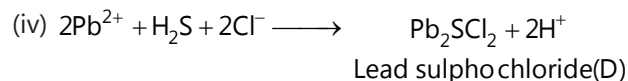
**(JEE ADVANCED)**

**Sol:** A=Pb;      B=NO;                      C=NO<sub>2</sub>;      D=Pb<sub>2</sub>SCl<sub>2</sub>;      E=PbS;                      F=PbCl<sub>2</sub>

Reactions are:



(iii) Metal is a little affected by dilute HCl or  $\text{H}_2\text{SO}_4$  due to the formation of insoluble PbCl<sub>2</sub> or PbSO<sub>4</sub> 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 CCl<sub>4</sub> is not possible but SiCl<sub>4</sub> is easily hydrolysed. Explain.

**(JEE ADVANCED)**

**Sol:** Silicon can accommodate OH<sup>-</sup> 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	7
P	15
As	33 $ns^2np^3$
Sb	51
Bi	83

(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  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$

(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.

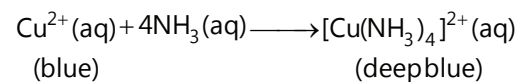
(iv) **Reactivity towards halogens:** These elements react to form two series of halides:  $EX_3$  and  $EX_5$

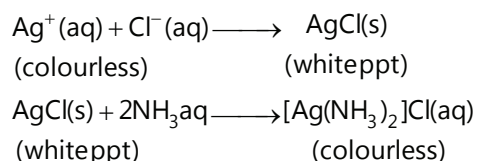
(v) **Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting -3 oxidation state.

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.





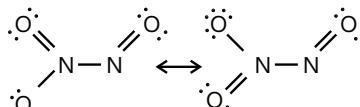
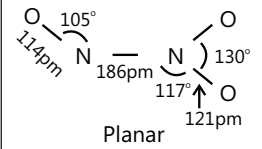
**Uses:** Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

### 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]	N <sub>2</sub> 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]	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]	N <sub>2</sub> O <sub>3</sub>	+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]	NO <sub>2</sub>	+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]	N <sub>2</sub> O <sub>4</sub>	+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]	N <sub>2</sub> O <sub>5</sub>	+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

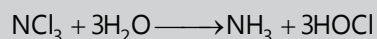
Formula	Resonance Structures	Bond Parameters
N <sub>2</sub> O	$:\text{N}=\text{N}=\ddot{\text{O}}: \leftrightarrow :\text{N}\equiv\text{N}-\ddot{\text{O}}:$	$\begin{array}{c} \text{N} - \text{N} - \text{O} \\ 113\text{pm} \quad 119\text{pm} \\ \text{Linear} \end{array}$
NO	$:\text{N}=\ddot{\text{O}}: \leftrightarrow :\dot{\text{N}}=\ddot{\text{O}}:$	$\begin{array}{c} \text{N} - \text{O} \\ 115\text{pm} \end{array}$
N <sub>2</sub> O <sub>3</sub>		



$\text{NO}_2$		
$\text{N}_2\text{O}_4$		
$\text{N}_2\text{O}_5$		

### PLANCESS CONCEPTS

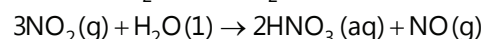
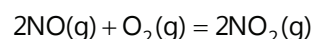
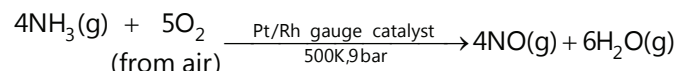
- NO is paramagnetic in its gaseous state but diamagnetic in its liquid or solid state, The NO molecule has eleven valence electrons and is thus paramagnetic in nature due to unpaired electron. In solution or solid state, it forms a loose dimer in such a way that magnetic field of unpaired electrons of two molecules cancel out it behaves as diamagnetic in nature
- $\text{NF}_3$  is stable but  $\text{NCl}_3$  and  $\text{NI}_3$  are readily hydrolysed and are explosives  $\text{NF}_3$  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 d-orbitals.



Vaibhav Gupta (JEE 2009, AIR 54)

### 3.2.4 Nitric Acid

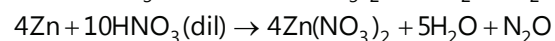
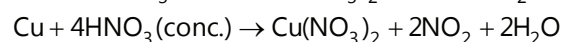
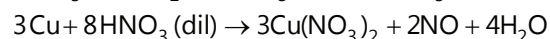
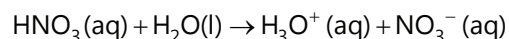
**Preparation:** By Ostwald's process:

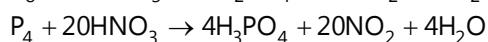
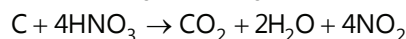
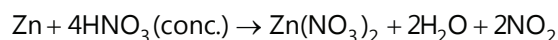


NO thus formed is recycled and the aqueous  $\text{HNO}_3$  can be concentrated by distillation upto ~68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated  $\text{H}_2\text{SO}_4$

**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  $\text{HNO}_3$  by mass and has a specific gravity of 1.504.

**Chemical reaction of  $\text{HNO}_3$  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.

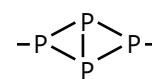


Figure 16.3: a Red

(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.

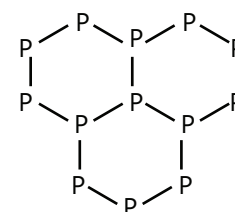


Figure 16.4: b Black

#### Uses:

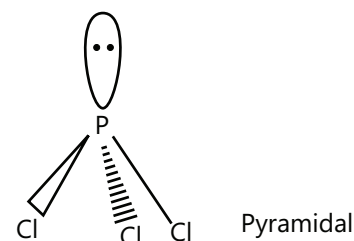
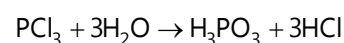
(a) Phosphorous is largely used in the matches industry.

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

#### 3.3.2 Some Important Compounds of Phosphorous

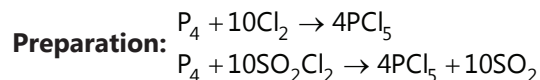
(a) **Phosphorus Trichloride:**  $\text{P}_4 + 8\text{SOCl}_2 \rightarrow 4\text{PCl}_3 + 4\text{SO}_4 + 2\text{S}_2\text{Cl}_2$

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



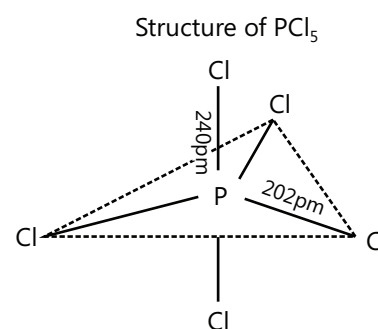
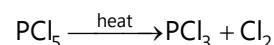
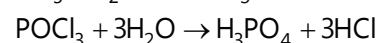
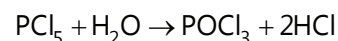
Pyramidal

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:**  $\text{PCl}_5$  is a yellowish white powder and in moist air, it hydrolyses to  $\text{POCl}_3$  and finally gets converted to phosphoric acid.



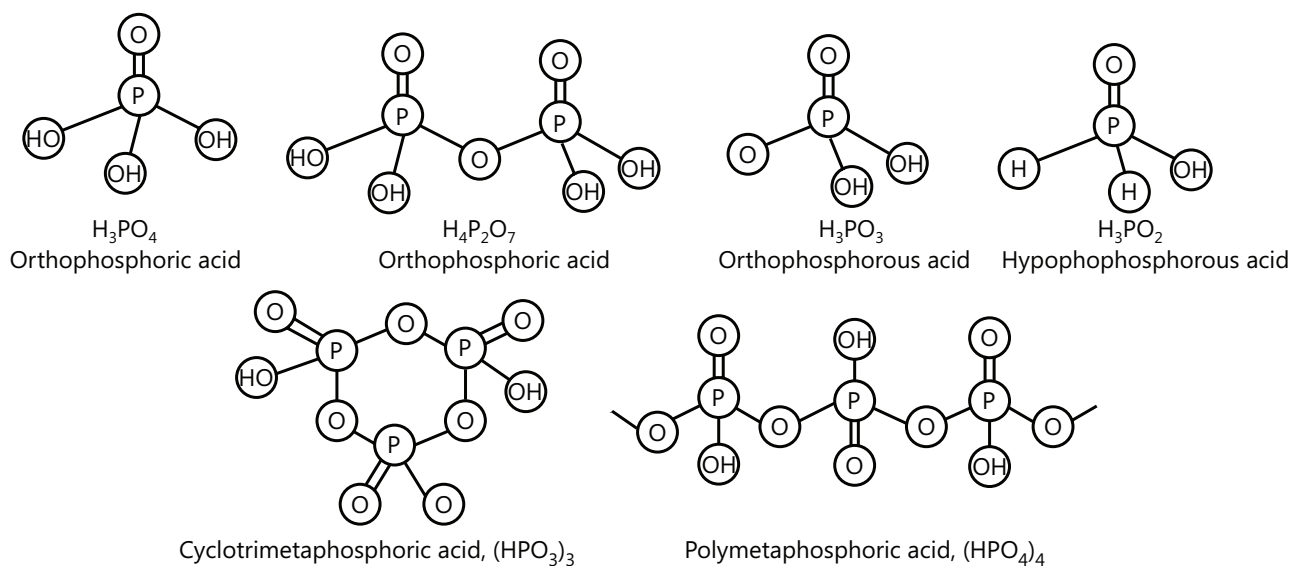
**Figure 16.6:** Structure of  $\text{PCl}_5$

**Note:** In the solid state it exists as an ionic solid,  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  in which the cation,  $[\text{PCl}_4]^+$  is tetrahedral and the anion,  $[\text{PCl}_6]^-$  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)	$\text{H}_3\text{PO}_2$	+1	One P-OH Two P-H One P=O	white $\text{P}_4$ + alkali
Orthophosphorous (Phosphonic)	$\text{H}_3\text{PO}_3$	+3	Two P-OH One P-H P-O-P One P=O	$\text{P}_2\text{O}_3 + \text{H}_2\text{O}$
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+3	Two P-OH Two P-H Two P=O	$\text{PCl}_3 + \text{H}_3\text{PO}_3$
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+4	Four P-OH Two P=O One P-P	red $\text{P}_4$ + alkali
Orthophosphoric	$\text{H}_3\text{PO}_4$	+5	Three P-OH One P=O	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+5	Four P-OH Two P=O One P-O-P	heat phosphoric acid
Metaphosphoric	$(\text{HPO}_3)_n$	+5	Three P-OH Three P=O Three P-O-P	Phosphorus acid + $\text{Br}_2$ , heat in a sealed tube

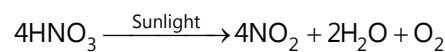


**Figure 16.7:** Halogen acids of Phosphorous

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

**(JEE MAIN)**

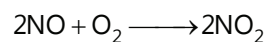
**Sol:**  $\text{HNO}_3$  is partially decomposed in sun light to produce  $\text{NO}_2$ . The  $\text{NO}_2$  formed dissolves in  $\text{HNO}_3$  to produce yellow colour.



**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?

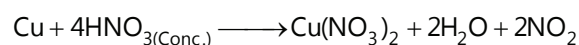
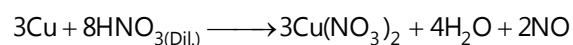
**(JEE MAIN)**

**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)  $N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$

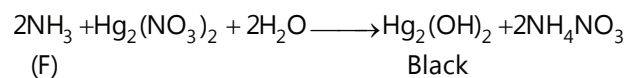
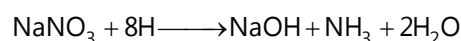
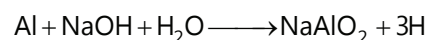
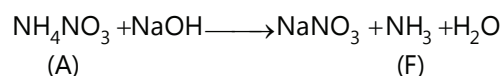
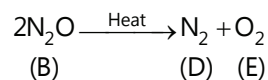
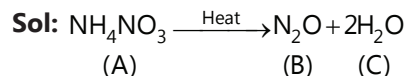
(ii)  $N_2H_4 + 2CuSO_4 + 4KOH \longrightarrow N_2 + 2Cu + 2K_2SO_4 + 4H_2O$

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

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

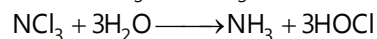
**Illustration 27:** An inorganic compound (A) when heated decomposes completely to give only two gases (B) and (C). (B) is a neutral gas, fairly soluble in water and itself decomposes on heating to two different gases (D) and (E).

(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}



- (a) **Electronic Configuration:**  $ns^2np^4$
- (b) **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.
- (c) **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.
- (d) **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

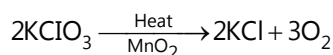
Due to its small size and high electronegativity, strong hydrogen bonding is observed in  $\text{H}_2\text{O}$  and not in  $\text{H}_2\text{S}$ .

- (a) **Reactivity with hydrogen:** All the elements of Group 16 form hydrides of the type  $\text{H}_2\text{E}$  ( $\text{E}=\text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$ ). 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  $\text{E}=\text{S}, \text{Se}, \text{Te}$  or  $\text{Po}$ .
- (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:

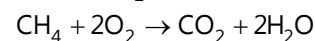
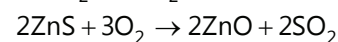
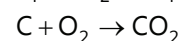
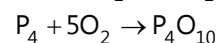
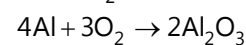
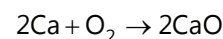
- (a) By heating oxygen containing salts such as chlorates, nitrates and permanganates.



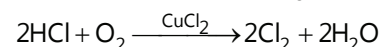
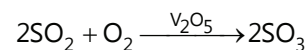
- (b) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.  $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
- (c) On a large scale, it can be prepared from water or air. Electrolysis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

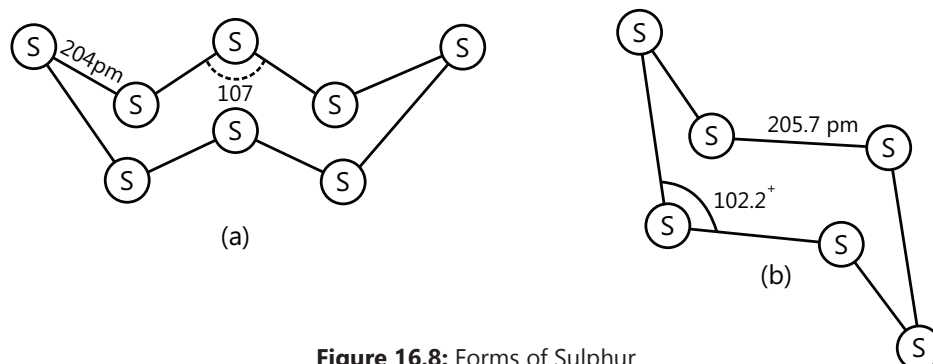


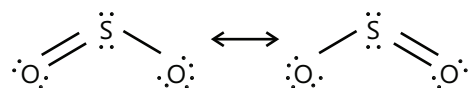
Figure 16.8: Forms of Sulphur

### 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

$\text{H}_2\text{SO}_3, \text{H}_2\text{S}_2\text{O}_3, \text{H}_2\text{S}_2\text{O}_4, \text{H}_2\text{S}_2\text{O}_5, \text{H}_2\text{S}_x\text{O}_6$  ( $x = 2$  to  $5$ ),  $\text{H}_2\text{SO}_4, \text{H}_2\text{S}_2\text{O}_7, \text{H}_2\text{SO}_5, \text{H}_2\text{S}_2\text{O}_8$

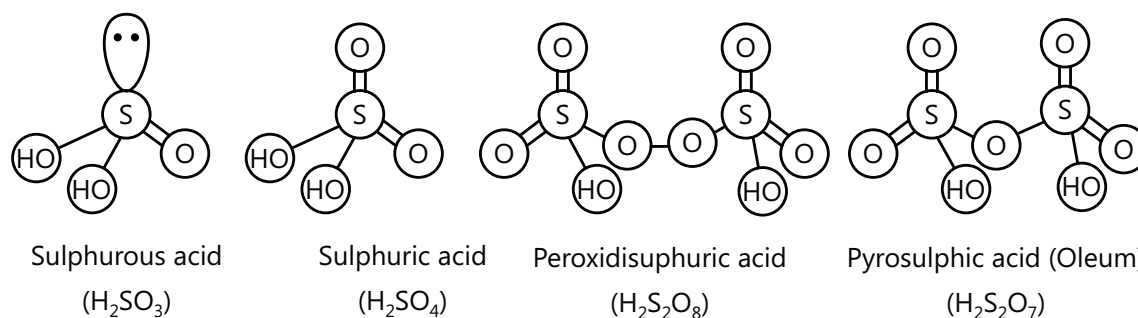


Figure 16.9: Oxoacids of Sulphur



### 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.

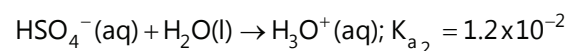
The key step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).



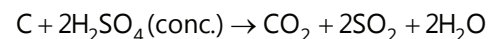
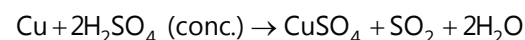
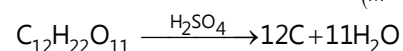
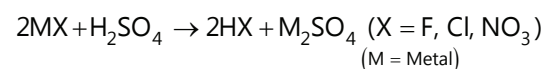
**Manufacture of Sulphuric Acid:** The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  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.

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

**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.

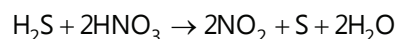
**(JEE MAIN)**

**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.



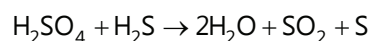
**Illustration 32:** Among H<sub>2</sub>O, HCl and NH<sub>3</sub>, H<sub>2</sub>O has the highest boiling point and HCl the lowest. **(JEE MAIN)**

**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)**

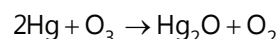
**Sol:** Conc. H<sub>2</sub>SO<sub>4</sub> oxidises H<sub>2</sub>S to S and thus cannot be used as for drying up H<sub>2</sub>S.



**Illustration 34:** Ozone destroys a mercury meniscus. Why?

**(JEE ADVANCED)**

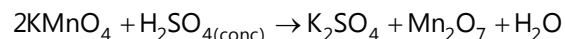
**Sol:** Ozone oxidises Hg to mercury suboxide which starts sticking to glass and loses its mobility. Hence, Hg loses its meniscus in contact with ozone. However, it can be regained by the action of H<sub>2</sub>O<sub>2</sub>.



**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>

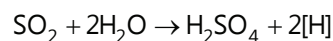


However it can be dissolved in dil. H<sub>2</sub>SO<sub>4</sub> to give nascent oxygen, if it is to be used as an oxidant

**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

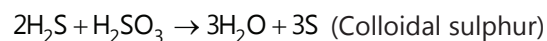
**Illustration 37:** An acidified  $K_2Cr_2O_7$  paper turns green when exposed to  $SO_2$ . Explain. **(JEE ADVANCED)**

**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)**

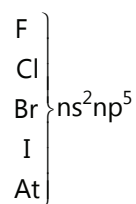
**Sol:** Aqueous solution of  $SO_2$  and  $H_2S$  undergoes redox changes to produce colloidal sulphur as white turbidity.



## 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)

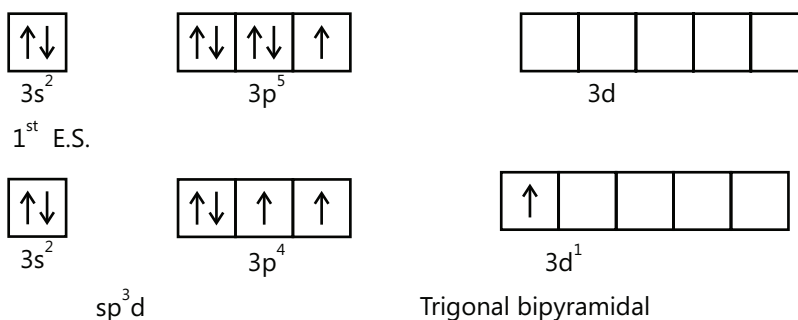
From F to Cl  $\rightarrow$  E.A increases.

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

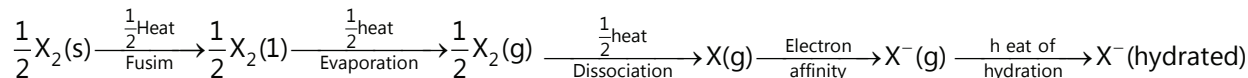
38 kcal/mol 57 kcal/mol 45.5 kcal/mol 35.6 kcal/mol  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

### 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.

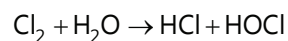
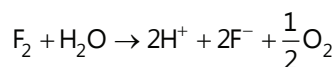


The heat of fusion, evaporation and dissociation are positive and electron affinity and heat of hydration are negative. The net energy (E) required for oxidizing reaction is given by-

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

Element	$E_{\text{net}}$ (kcal)
$\text{F}_2$	-186.5
$\text{Cl}_2$	-147.4
$\text{Br}_2$	-136.4
$\text{I}_2$	-122.4

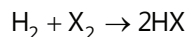
Thus oxidizing powers decrease on descending in group VII. Fluorine is a strong oxidising agent as seen in the reaction given below where oxygen in water has been oxidised. The oxidation of  $\text{H}_2\text{O}$  by  $\text{Cl}_2$  is thermodynamically possible but since the energy of activation is high, 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  $H_2$** 

(i) All halogens reacts with  $H_2$  to form hydrogen halides.

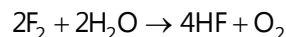


(ii) Reactivity of Halogens  $F > Cl > Br > I$

(iii)  $HCl$ ,  $HBr$ ,  $HI$  acts as reducing agent.

**(b) Reaction with  $H_2O$** 

(i)  $H_2O$  acts as reducing agent only with fluorine.



(ii)  $H_2O + I_2 \rightarrow$  No Reaction.

**(c) Displacement reaction**

(i)  $F_2 + 2NaX \rightarrow 2NaF + X_2$   $\{X = Cl, Br, I\}$

$Cl_2 + 2NaX \rightarrow 2NaCl + X_2$   $\{X = Br_2, I_2\}$

So order of displacement  $[F_2 > Cl_2 > Br_2 > I_2]$

(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.  $NF_3$ ,  $PCl_3$  etc.

**(f) Reaction with  $NH_3$** 

(i)  $3F_2 + NH_3 \rightarrow NF_3 + 3HF$

(ii)  $3Cl_2 + NH_3 \rightarrow NCl_3 + 3HCl$

**(g) Reaction with  $NaOH$** 

(i)  $F_2 + NaOH$  (dil.)  $\rightarrow 2NaF + OF_2 + H_2O$

(ii)  $2F_2 + 4NaOH$  (conc.)  $\rightarrow 4NaF + 2H_2O + O_2$

**(h) Formation of oxides**

(i) No oxides of F because of its maximum E.N. character.

(ii) Rest form

$X_2O$	$X_2O_3$	$X_2O_5$	$X_2O_7$
Eg. +1	+3	+5	+7
$Cl_2O$	$Cl_2O_3$	$Cl_2O_5$	$Cl_2O_7$

(iii) All these oxides are acidic

(iv) Acidity decreases down the group and maximum active oxide is  $Cl_2O_7$

**(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:

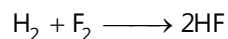
Fluorine differs considerably from other halogens due to its-

- 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

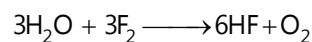
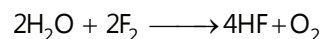
AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

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>)

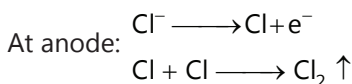
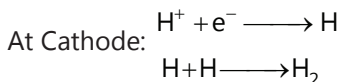
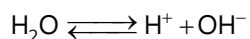
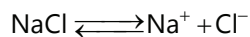
(i) Uses: It is used in the preparation of fluorine compounds such as.

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>

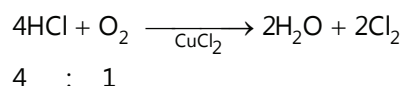
Teflon: (–F<sub>2</sub>C–CF<sub>2</sub>)<sub>n</sub> It is a new plastic.

**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:**



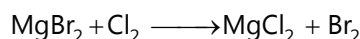
Chlorine gas thus obtained contains N<sub>2</sub> and O<sub>2</sub> and is used for the manufacture of bleaching powder by Hasenclever's process

(c) **Uses:**

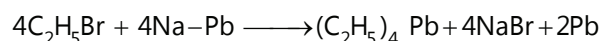
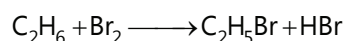
- (i) As a germicide and disinfectant.
- (ii) Domestic antiseptic solution (NaOCl)

**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.

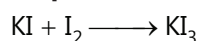


(b) **Uses:** (a) It is used in preparation of ethyl bromide which is used in the manufacturing of tetraethyl lead (TEL) as an important anti-knock compound in the petroleum industry.

**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
+3	HClO <sub>2</sub>	-	-	Halous	Halite	Increases but
+5	HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>	Halic	Halate	Oxidizing power
+7	HClO <sub>4</sub>	HBrO <sub>4</sub>	HIO <sub>4</sub>	Perhalic	Perhalate	decreases

**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-

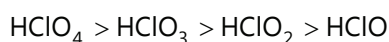


↓



Hypochlorites are the strongest oxidizing agents.

(e) Relative acidity  $\propto$  oxidation no.

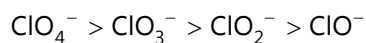


**Note:** (i) In all these acids and salts halogen is in  $\text{sp}^3$  hybridised state.

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



Thus,  $\text{ClO}_4^-$  is the weakest base and  $\text{HClO}_4$  (conjugate acid of  $\text{ClO}_4^-$ ) is the strongest acid.



←—————

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  $\text{KClF}_2$  or  $\text{KBrF}_2$  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  $\text{KClF}_2$  or  $\text{KBrF}_2$  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>	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$	$\uparrow$
			Covalence = 1
<b>II excited state</b>	$\uparrow\downarrow$	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow$
			Covalence = 3
<b>III excited state</b>	$\uparrow$	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow \uparrow$
			Covalence = 5
			Covalence = 7

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.

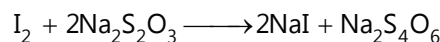
(JEE ADVANCED)

**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)

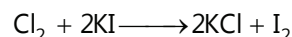
**Sol:** Hypo reacts with iodine to form water soluble sodium tetrathionate and sodium iodide.



**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  $[K^+ \text{ and } F^- \cdots H-F^-]$  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.

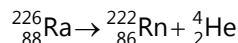
(a) They exist in gaseous state.

(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.

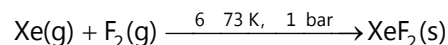
**(h) Adsorption of inert gases:**

- (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.

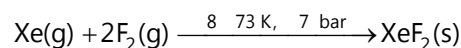
**Family members of noble gases:**

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.

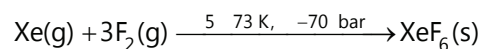
**Xenon (Xe):** It is the only element that forms true compounds and that too with highly reactive elements  $\text{F}_2$ . Xenon forms three binary fluorides,  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  by the direct union of elements under appropriate sunlight or light from a high pressure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



(xenon in excess)

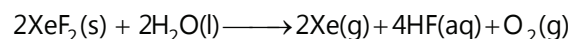


(1:5 ratio)

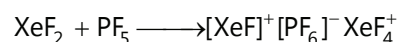


(1:20 ratio)

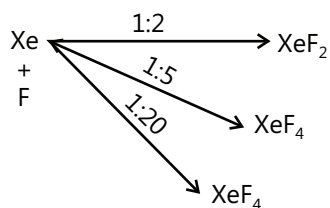
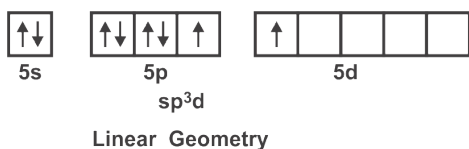
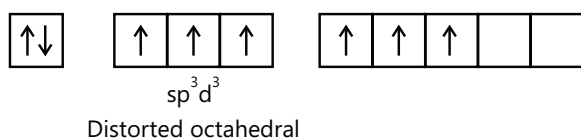
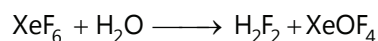
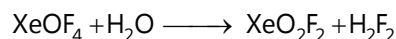
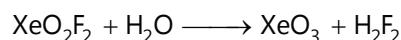
$\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  are colourless solids subliming readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed by even traces of water. The hydrolysis of  $\text{XeF}_2$  can be represented by the equation:



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)  $\text{XeF}_2$ :(b)  $\text{XeF}_4$ :(c)  $\text{XeF}_6$ :(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)

- (i)  $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow$   
 (ii)  $\text{XeF}_2 + \text{H}_2 \longrightarrow$   
 (iii)  $\text{XeF}_6 + \text{SiO}_2 \longrightarrow$   
 (iv)  $\text{XeF}_6 + \text{NH}_3 \longrightarrow$   
 (v)  $\text{XeF}_6 + \text{SbF}_5 \longrightarrow$   
 (vi)  $\text{XeF}_4 + \text{KI} \longrightarrow$   
 (vii)  $\text{XeF}_4 + \text{BCl}_3 \xrightarrow{-78^\circ\text{C}}$   
 (viii)  $\text{XeF}_2 + \text{HClO}_4 \longrightarrow$

**Sol:**

- (i)  $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$   
 (ii)  $\text{XeF}_2 + \text{H}_2 \longrightarrow \text{Xe} + 2\text{HF}$   
 (iii)  $2\text{XeF}_6 + \text{SiO}_2 \longrightarrow 2\text{XeOF}_4 + \text{SiF}_4$   
 $2\text{XeOF}_4 + \text{SiO}_2 \longrightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$   
 $2\text{XeO}_2\text{F}_2 + \text{SiO}_2 \longrightarrow 2\text{XeO}_3 + \text{SiF}_4$   
 Explosive  
 (iv)  $\text{XeF}_6 + 8\text{NH}_3 \longrightarrow \text{Xe} + 6\text{NH}_4\text{F} + \text{N}_2$   
 (v)  $\text{XeF}_6 + \text{SbF}_5 \longrightarrow [\text{XeF}_5]^+ [\text{SbF}_6]^-$   
 [Addition ionic product is formed]  
 (vi)  $\text{XeF}_4 + 4\text{KI} \longrightarrow \text{Xe} + 4\text{KF} + 2\text{I}_2$   
 (vii)  $3\text{XeF}_4 + 4\text{BCl}_3 \xrightarrow{-78^\circ\text{C}} 4\text{BF}_3 + 3\text{Xe} + 6\text{Cl}_2$   
 (viii)  $\text{XeF}_2 + 2\text{HClO}_4 \longrightarrow \text{Xe}(\text{O} - \text{ClO}_3)_2 + 2\text{HF}$

**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.  
 $2.00\text{ \AA} > 1.95\text{ \AA} > 1.89\text{ \AA}$