CHAPTER 16

P-BLOCK ELEMENTS

16.1 GROUP 13 (BORON FAMILY)

General electronic configuration of this group is $ns^2\ np^1$ and except B all are metals; B exist in crystalline and amorphous forms with icosahedral geometry with B at all 12 corners. Properties of Al are different form Ga, In and Tl due to intervening transition metals.

Ionization energy: Decreases down the group but ionization energy of Ga is more than Tl due to intervening (n – l)d orbitals and that of Tl is more than In, due to poor shielding effect of (n – 2) f orbital. First ionization energy is in the order:

$$B > Tl > Ga > Al > In$$

Oxidation state: All the element exhibit +3 oxidation state. On moving down the group, +1 oxidation state becomes dominant due to inert pair effect. Inert pair effect increases after In. Tl (III) is a strong oxidizing agent > 4 and increases with the increasing value of n. Reducing character of the elements increases as we move down the group.

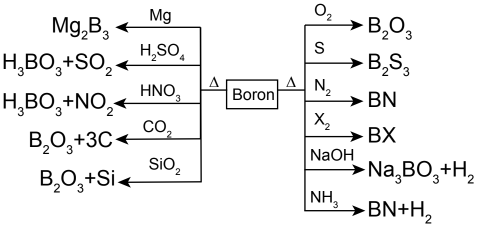
Method of preparation of boron

(a) $\underset{\text{Borax}}{Na_2[B_4O_5(OH)_4]8H_2O} \xrightarrow{\text{Acid}} H_3BO_3 \xrightarrow{\Delta} B_2O_3 \xrightarrow{\text{Mg}} 2B + 3MgO$

(b) $2BCl_3 + 3H_2 \xrightarrow[\text{W fillament}]{\text{Red hot}} 2B + 3l_2$

(c) $2Bl_3 \xrightarrow[\text{van Arkel}]{\text{Red Hot}} 2B + 3l_2$

Chemical properties of boron



Hydroxide: Al and Ga hydroxides are amphoteric, hydroxide of In is more basic than Ga. Tl reacts with steam and form TlOH.

Halides: Boron halides are monomeric and make up the deficiency either by back bonding (in halides) or by dimerization (in hydrides). The shortening of B–X bond, and also their lewis acidic character is because of back bonding. Inability of heavier elements to form multiple bond is due to large size of the central atom, less effective overlapping of more diffused np orbitals and repulsion of inner filled orbitals. Lewis acidic character of boron halides is in the order $BI_3 > BBr_3 > BCl_3 > BF_3$.

Hydrides: Hydrides of boron are known as boranes (B-sp^3 hybridized) which are electron deficient, catch fire in air and get hydrolyzed by water.

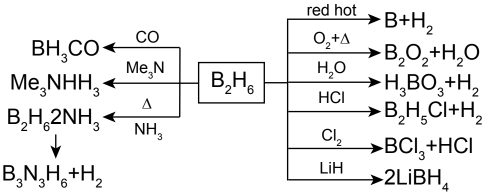
Method of preparation of B_2H_6

(a) $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$

(b) $2BCl_3 + 6H_2 \xrightarrow[\text{discharge}]{\text{Slient electric}} B_2H_6 + 6HCl$

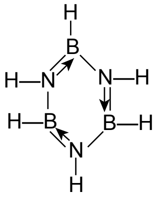
(c) $8BF_3 + 6LiH \rightarrow B_2H_6 + 3LiBF_4$

Chemical properties of B_2H_6

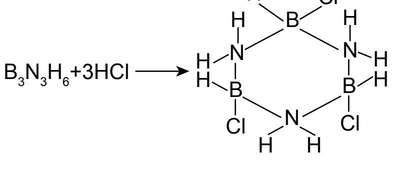


Maximum covalency of boron is four but for other elements is six. Boron shows diagonal relationship with silicon. Boron halides undergo hydrolysis and give orthoboric acid.

Important compounds of boron: **Borazole** also called inorganic benzene is isosteric with benzene. Borazole on heating at 3000°C and 10,000 atm pressure produces BN also called inorganic graphite and is as hard as diamond. It is chemically inert and do not react with mineral acids.


Inorganic benzene

Borazole reacts with HCl to produce an addition product as follows:

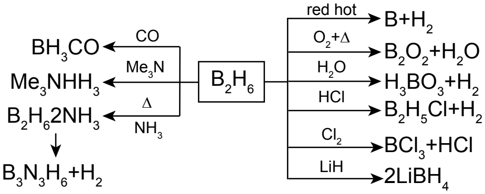


Aluminium: Al, the third most abundant element in earth's crust, occurs as complex aluminosilicates (clay, feldspar).

Ores of aluminium are bauxite and cryolite. If bauxite contains silica as the major impurity it is known as white bauxite and if it contains red oxide as an impurity it is known as red bauxite. Aluminium is soft, light and weak when pure but become hard, strong and resistant to corrosion.

Extraction of aluminium: Bayer's process [Alumina + caustic alkali] and Hall's process [Alumina + Na_2CO_3] are used for the purification of red bauxite and Serpeck's process [Alumina + N_2 + C] is used for the purification of white bauxite. Pure bauxite is mixed with cryolite (to increase conductivity) and fluorspar (to lower the melting point) and subjected to electrolysis by Hall and Heroult process to obtain aluminium. Aluminium is purified by Hoop's process.

Chemical properties of aluminium



Key Points

- Alloy duralumin [Al, Cu, Mg, Mn] is used in the construction of aeroplanes, cable rivets, etc.
- Aluminium bronze [Al, Sn, Cu] is used in making utensile, coins, statues, etc.
- Alnico [Al, Ni, Co, Fe] is used in making permanent magnets.
- Magnalium [Al, Mg] is used for making balances and machine parts.
- **Nickeloy:** Al + Cu + Ni.
- Alcald [duralumin coated with pure Al] is used in making sea planes.
- Y alloy contains Al + Cu + Ni + Mg.
- Due to the corrosion resistant and non-toxic nature aluminium foil is used for wrapping in food industry. Mixed with linseed oil, aluminium powder is used in silver paints and lacquers.
- Due to its low SRP (–1.66 V) it should reduce water but due to the presence of a protective layer of Al_3O_3 on its surface it cannot. Aqueous salts of aluminium are acidic due to cationic hydrolysis.

Alums: Double salt of aluminium and monovalent metals like sodium and potassium with $24H_3O$ are known as alums $[M_2^{I}SO_4M_2^{III}(SO_4)_3\ .\ 24H_2O]$. Alums acts as coagulants, germicides, antiseptic and mordants.

16.2 GROUP 14 (CARBON FAMILY}

C, Si, Ge, Sn and Pb have electronic configuration as $ns^2\ np^3$ and show +2 and +4 oxidation states. Tendency to show +2 oxidation state increases down the group due to inert pair effect. Except lead, all other element of this group show allotropy.

All elements, except carbon, can expand their octet due to the presence of vacant d-orbitals, Silicon, due to its large size, is inable to form pπ–pπ bond and therefore does not exhibit graphite like structure.

Hydrides: Stability of hydrides decreases down the group and reducing power of hydrides increase down the group.

$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$

16.2.1 Oxides

1. **Carbon monoxide:** Neutral, colourless, odourless and poisonous gas.

   Method of preparation:

   (a) $HCOOH \xrightarrow{\text{Conc. } H_2SO_4} CO + H_2O$

   (b) $H_2C_2O_4 \xrightarrow{\text{Conc. } H_2SO_4} CO + CO_2 + H_2O$

   (c) $ZnO + C \xrightarrow{\Delta} Zn + CO$

   Properties:

   CO forms carboxy heamoglobin with blood which is fatal. CO due to the presence of a lone pair of electrons on carbon as well as oxygen form metal carbonyls with transition elements in which carbon is directly attached to the metal. It is a good reducing agent.

   $ZnO + CO \rightarrow Zn + CO_2$

   $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

   $PbO + CO \rightarrow Pb + CO_2$

   $I_2O_5 + CO \rightarrow I_2 + 5CO_2$

2. **Carbon dioxide:** It is an acidic oxide, colourless and odourless gas. Acidic nature of dioxides $CO_2 > SiO_2 > GeO_2 > SnO_2 > PbO_2$

   Method of preparation:

   (a) $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

   (b) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

   (c) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

   It turns lime water milky.

   $$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{Milky}}{CaCO_3} + H_2O \xrightarrow{CO_2} \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

3. **Silica:** It is an acidic oxide. It is widely found as sand and quartz. The main forms of SiO_2 are quartz, tridymite and crystobalite. Coloured quartz are used as gems. Amethyst (violet), rose quartz (pink), etc.

   Application of silica:

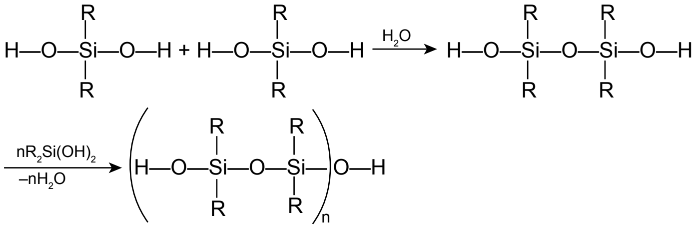
   1. Flint, opal, agate, onyx and jasper are amorphous silica.
   2. Kieselguhr is a siliceous rock composed of remains of minute sea organisms.
   3. SiO_2 is soluble in HF$SiO_2 + 4HF \rightarrow SiF_4 \xrightarrow{2HF} H_2SiF_6$
   4. Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate and is used as a drying agent.
   5. Amongst dioxides, only CO_2 a is gas, and PbO_2 is a strong oxidizing agent due to the greater stability of +2 oxidation state.

4. **Carborundum (SiC):** Carborundum or artificial diamond $SiO_2 + 3C \xrightarrow{\Delta} SiC + 2CO$

   Very hard (Diamond > B_4C > SiC). Chemically inert.

Soluble in alkali in presence of oxygen $SiC + O_2 + 4NaOH \rightarrow Na_2SiO_3 + Na_2CO_3 + H_2O$.
It is used as an abrasive.

5. **Halides:** Form tetrahalities, except carbon, others form dihalide also. $PbBr_4$ and Pbl_4 does not exit due to strong oxidizing power of Fb^{4+} and strong reducing power of Br^- and I^-.
   Stability of dihalides increases down the group. Thermal stability of halides is in the order ($CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$).
   For the common central atom the thermal stability and volatility of tetrahalides is in the order $MF_4 > MCl_4 > MBr_4 > MI_4$.
   Except carbon halides the other tetrahalides act as strong Lewis acids.
   Silicones are Si–O–Si compounds, formed by the hydrolysis ofalkyl substituted chlorosilanes.
   $2RCl + Si \xrightarrow[-2HCl]{Cu;\ 573K} R_2SiCl_2$
   $R_2SiCl_3 + 2H_3O \rightarrow R_2Si(OH)_2$ (dialkylsilandiol| which polymerizes to give linear thermoplastic silicon.



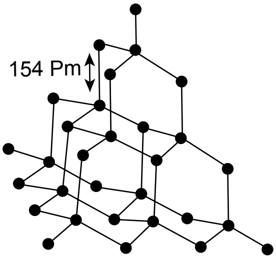
$$SiCl_4 \xrightarrow[-MgCl_2]{RMgCl} RSiCl_3 \xrightarrow[-MgCl_2]{RMgCl} R_2SiCl_2 \xrightarrow[-MgCl_2]{RMgCl} R_3SiCl \xrightarrow[-MgCl_2]{RMgCl} R_4Si$$

6. **Tin and lead:** Tin occurs as cassiterite (SnO_2) from which tin is obtained by carbon reduction and tin is purified by zone refining.
   Lead occurs as galena (PbS), which is concentrated by froath floatation process, roasted and then the oxide is reduced by coke to give lead.
   Pewter [Pb = 80 per cent, Sn = 20 per cent] Solder [Pb 50 per cent; Sn 50 per cent]; Type metal [Pb, Sb, Sn]
   Stannous chloride which is prepared by boiling tin with conc, HC1 in a mild reducing agent and reducing Fe (III) to Fe (II); Hg(II) to Hg(I) and finally to Hg, Mn (VI) to Mn(VI) ; Cr(VI) to Cr(II).
   Lead oxide (PbO, litharge) is yellow when cold and orange when hot.
   Pb_3O_4, red lead, decomposes to PbO and PbO_2 on heating.
   Except nitrate and acetate Pb^{2+} salts are insoluble in water.
   Lead is used in making vessels for radioactive materials and for making cathode (PbO_2) in lead storage batteries. Since Pb_3O_4 is a strong oxidizing agent, it is used to give a coating on steel before painting.
   Tetraethyllead is used as antiknock in petrol but its use has been restricted due to its toxicity as it inhibits the action of certain enzymes.
   $PbSO_4$ is soluble in acetic acid due to the formation of stable acetate complexion.

16.3 ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as fullerenes was discovered by H W Kroto, E Smalley and R F Curl.

16.4 DIAMOND

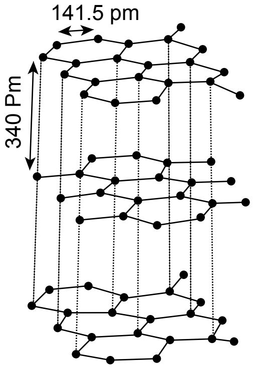


The Structure of Diamond

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridization and linked to four other carbon atoms by using hybridized orbitals in tetrahedral fashion. The C – C bond length is 154 pm. The structure extends in space and produces a rigid 3D network of carbon atoms. In this structure, directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

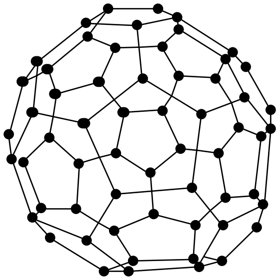
16.5 GRAPHITE



The structure of graphite

Graphite has a layered structure. Layers are held by van der waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C — C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridization and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π-bond. The electrons are delocalized over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

16.5.1 Fullerenes



Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourized C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerences are the only pure form of carbon because they have smooth structure without having 'dangling bonds. Fullerenes are cage-like molecules. C_{60} molecule has a shape like a soccer ball and is called Buckminsterfullerene.

It contains twenty six-membered rings and twelve five-membered rings. A six-membered ring is fused with six or five-membered rings but a five-membered ring can only fuse with six-membered rings. All the carbon atoms are equal and they undergo sp^2 hybridization. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electrons at each carbon is delocalized in molecular orbitals, which in turn give aromatic character to molecule. This ball-shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C — C distance of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.

The structure of C_{60}. Bukminster fullerene: Note that the molecule has the shape of a soccer ball (football).

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\ominus$ of graphite is taken as zero. $\Delta_f H^\ominus$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.

16.6 ZEOLITES

If aluminium atoms replace few silicon atoms in 3D network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites, are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization, e.g., ZSM-5 (a type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of 'hard' water.

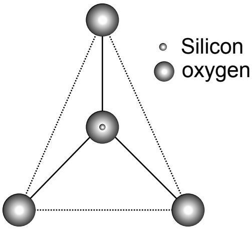
16.7 SILICATES

Silicate minerals together with silica and aluminosilicate clay make 95 per cent of the Earth's crust. They contain different modes of combination of $(SiO_4)^{4-}$ tetrahedral units. The Si–O bond is 50 per cent ionic and 50 per cent covalent.

The radius of Si^{4-} (0.4 A°) and O^{2-} (1.4 A°) makes the radius ratio 0.29 with coordination number 4 around Si.

The $(SO_4)^{4-}$ tetrahedral units may be single or share 1, 2, 3 or 4 O-atoms through corners only giving rise to various types

16.7.1 Type of Silicates



1. **Orthosilicates:** (Neso–silivates). No O–atoms are shared

   Contain discrete SiO_4^{4-} units with the general formula, $M_2^{||}SiO_4$.

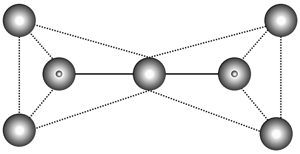
   e.g., Zircon = $ZSiO_4$

   Olivine = $(Mg.\ Fe)_2\ .[SiO_4]$

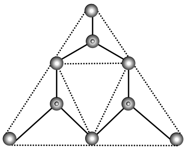
   Fenacite = Be_2SiO_4

   Forsterite = Mg_2SiO_4

   Williemite = $Zn_2\ SiO_4$



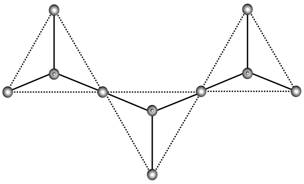
2. **Pyrosilicates (Soro–silicates)**
   One O-atom is shared at one corner.
   Contains discrete $(Si_2O_7)^{6-}$ unit.
   e.g., **Thortveitite:** $Sc_2\ Si_2O_7$
   Hemimorphite: $Zn_4\ Si_2O_7(OH)_2\ .\ H_2O$
   Pyrosilicates are rare.



3. **Ring (cyclic) silicates:**
   Two O-atoms are shared per tetrahedron
   and contain $(SiO_3)_n^{2n-}$ units

   e.g., **Benitoite:** $BaTiSi_3O_9$
   Beryl: $Be_3\ Al_2\ (SiO_3)_6$

4. **Chain silicates:**
   (a) **Single chain (pyroxenes)**
   Two O-atoms are shared per tetrahedron and contain $(SiO_3)_n^{2-}$ units.
   E.g., **Spodumene:** $LiAl(SiO_3)_2$
   Diopsite: $CaMg(SiO_3)_2$
   Enstatite: $Mg_2(SiO_3)_2$
   Wollastonite: $Ca_3(SiO_3)_3$



   (b) **Double chains (amphiboles)**
   Contain $(Si_4O_{11})_n^{6n-}$ units, asbestos minerals. Some tetrahedrons share two and some share three corners $\left(2\frac{1}{2}0-\text{atoms}\right)$.
   E.g., **Tremolite:** $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$
   Crocidolite: $Na_2Fe_3^{ii}Fe_2^{iii}(Si_4O_{11})_2(OH)_2$
5. **Sheet silicates (phyllo-silicates)**
   Three O-atoms are shared at three corners of the tetrahedron. Contains $(Si_2O_5)_n^{2n-}$.
   e.g., **Muscovite:** $KAl_2(OH)_2AlSi_3O_{10}$ Mica
   Talc: $Mg_3(OH)_2Si_4O_{10}$
   Kaolin: $Al_2(OH)_4Si_2O_5$ Clay
6. **3D silicates**
   Four O-atoms are shared from all corners of SiO_4 tetrahedron resulting in 3D lattice of formula SiO_2
   e.g., **Quartz:** $(SiO_2)_n$
   Due to replacement of Si atoms it forms
   (a) **Orthoclase feldspar:** $KalSi_3O_8$
   (b) **Zeolite:** $Na_2Al_2Si_2O_8 . \times H_2O$
   (c) **Ultramarine:** $Na_8[(AlSiO_4)_6]S_2$

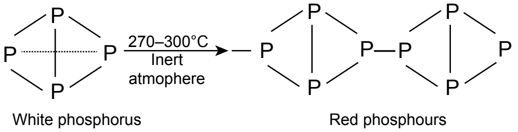
16.8 GROUP 15 ELEMENTS (NITROGEN FAMILY)

- The group 15 elements are collectively called as pnictogens.
- General outer electronic configuration: $ns^2 np^3$ (where, n = 2 to 6)

Element	Electronic configuration	Oxidation number
Nitrogen (N)	$[He]2s^22p^3$	−3, −2, −1, +1, +2, +3, +4, +5
Phosphorus (P)	$[Ne]3s^2 3p^3$	−3, +3, +4, +5
Arsenic (As)	$[Ar]3d^{10} 4s^24p^3$	−3, +3, +5
Antimony (Sb)	$[Kr]4d^{10} 5s^25p^3$	−3, +3, +5
Bismuth (Bi)	$[Xe]4f^{14}5d^{10} 6s^26p^3$	+3, +5

- Non-metals: N, P Metalloids: As, Sb Metal Bi
- **Allotropy:** All elements of group 15 (except N and Bi) show allotropy.
- Atomic radii and density order N < P < As < Sb < Bi.

- I E and E N order N > P > As > Sb > Bi
- N_2(N≡N) is diatomic, white P, As, Sb are tetraatomic (P_4, As_4, Sb_4) and tetrahedral with a bond angle of 60°.



White phosphorus	Red phosphorus	Black phosphorus
Soft, whitish yellow, waxy solid	Red powdery, microcrystalline solid	Black solid
Spontaneously inflames in air above 50°C to give P_4O_{10} and P_4O_6 in limited supply of O_2	Only ignites at temperature greater than 260°C	Does not ignite even above 400°C
Combines violently with all halogens	Combines slowly with halogens	Kinetically inert/stable
Volatile, highly reactive	Non-volatile, less reactive	Non-volatile, chemically inert
Structure consists of discrete P_4 tetrahedra	Structure consist of chain/sheets	Structure is sheet-like similar to graphite
Poisonous, insoluble in H_2O	Non-poisonous, insoluble in H_2O but soluble in CS_2	Non-poisonous, insoluble in both H_2O and CS_2

- Black phosphorus is of two types: α-block and β-block. α-block prosphorus do not conduct electricity, where, as β-block phosphorus can conduct electricity.

  Preperation of N_2: $NH_4Cl + NaNO_3 \rightarrow N_2 + 2H_2O + NaCl$

  $\left(NH_4\right)_2 Cr_2O_7 \xrightarrow{\Delta} N_2 + C_1H_2O + Cr_2O_3$; $2NH_3 + Cuo \xrightarrow{\Delta} 2Cu + 3H_2O + N_2$

  $2NH_3 + CaOCl_2 \rightarrow 3CaCl_2 + 3H_2O + N_2$

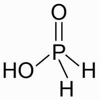
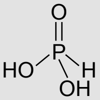
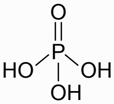
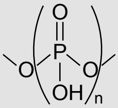
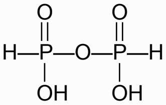
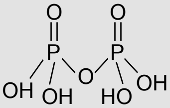
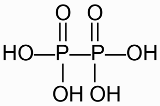
- **Oxides:** All these elements form oxides of the type X_2O_3, X_2O_4 and X_2O_5.

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	BiO_3	
N_2O_4	P_2O_4	As_2O_4	Sb_2O_4	BiO_4	↓ Acidic nature increase
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5	→ Acidic nature decreases

  As the electronegativity increases, acidic character of the oxide also increases. Among the oxides of the same element, higher the oxidation state, greater the acidic character.

- Nitrogen does not form pentahalide due to inability to expand octet and Bi does not form pentahalide due to inert pair effect.
- **Holme's signals:** The spontaneous combustion of phosphine is used in Holme's signals. Containers containing CaC_2 and Ca_3P_2 are pierced and thrown into the sea where on reaction with H_2O, PH_3 and C_2H_2 is produced along with traces of P_2H_4 which are highly inflammable. This ignites acetylene which burns with a luminous flame.

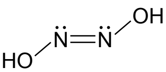
- **Oxo acids of phosphorus:**

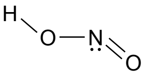
Oxoacid	Structure	Basicity	Preparation
Phosphinic acid (hypo phosphorus acid), H_3PO_2		1	White P_4 + alkali
Phosphonic acid (ortho phosphorus acid or phosphorous acid), H_3PO_3		2	$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$ $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
Orthophosphoric acid H_3PO_4		3	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
Meta phosphoric acid (glacial phosphoric acid), $(HPO_3)_n$		1	$3H_3PO_3 + 3Br_2 \xrightarrow[\text{Soalid tube}]{\Delta} (HPO_3)_3 + 6HBr$
Pyrophosphorous acid (diphosphorus acid), $H_4P_2O_5$		2	$PCl_3 + 5H_3PO_3 \rightarrow 3H_4P_2O_5 + 3HCl$
Pyrophosphoric acid (diphosphoric acid), $H_4P_2O_7$		4	$2H_3PO_4 \xrightarrow{250°C} H_4P_2O_7 + H_2O$
Hypophosphoric acid, $H_4P_2O_6$		4	$2P(red) + 4NaOCl + 2H_2O \rightarrow H_4P_2O_6 + 4NaCl$

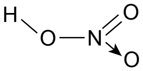
States decrease gradually with decrease in electronegativity of the central atom.

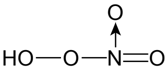
HNO_2	H_3PO_3	H_3AsO_3	H_3SbO_3
HNO_3	H_3PO_4	H_3AsO_4	H_3SbO_4

- Oxoacids of nitrogen

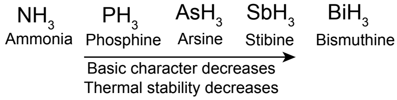

Hyponitrous acid
($H_2N_2O_2$)


Nitrous acid
(HNO_2)


Hyponitrous acid
($H_2N_2O_2$)

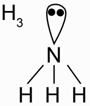
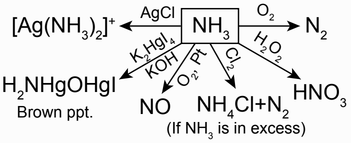
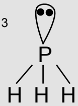
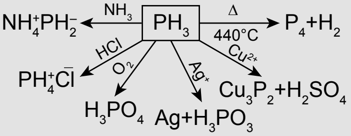
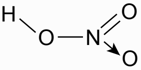
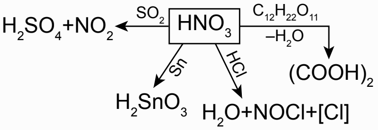
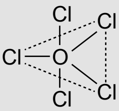
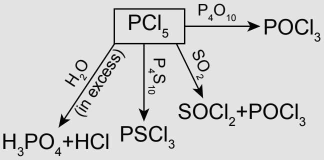

Pernitric acid
(HNO_4)

- **Hydrides:** MH_3 type hydrides



- As the size increases, the electron density gets diffused over a larger region (due to bigger size) and hence the ability to donate the electron pair (basic nature) decreases.

16.8.1 Important compounds of nitrogen family

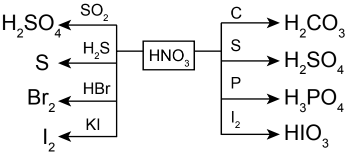
Structure	Preparation	Properties	Uses
NH_3 	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta H_f^\circ = -92.4$ kJ/mol (Haber's process)		Used in refrigerators manufacturing of rayon, HNO_3, $NaHCO_3$, nitrogenous fertilizers
PH_3 	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$		Used as dehydrating agent
HNO_3 	$2KNO_3 + H_2SO_4 \rightarrow 2HNO_3 + K_2SO_4$		Used as fertilizers explosives, perfumes and dyes
PCl_5 	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ (White or red)		Used as chlorinating and dehydrating agent

Properties of HNO_3: HNO_3 is a powerful oxidizing agent; it oxidizes almost all metals, non-metals and many compounds.

It gets reduced as

$$\underset{+5}{HNO_3} \rightarrow \underset{+4}{NO_2} \rightarrow \underset{+2}{NO} \rightarrow \underset{+1}{N_2O} \rightarrow \underset{0}{N_2} \rightarrow \underset{-3}{NH_3}$$

Greater the change in oxidation state, weaker the oxidizing action of HNO_3. Non-metals are oxidized to their higher oxyacids and HNO_3 is reduced to NO_2:



Aqua regia ($HNO_3 + 3HCl$);

$$HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + 2Cl$$

$$Au + 3Cl \rightarrow AuCl_3 \xrightarrow{HCl} HAuCl_4$$

16.8.1.1 *Action of HNO_3 with metal*

HNO_3	Metal	Main Product
Very dilute	Mg, Mn →	$H_2 + MNO_3$
	Fe, Zn, Sn →	$NH_4NO_3 + MNO_3$
Dilute	Pb, Cu, Ag, Hg →	$NO + MNO_3$
	Fe, Zn →	$N_2O + MNO_3$
	Sn →	$NH_4NO_3 + Sn(NO_3)_2$
Concentrated	Zn, Pb, Cu, Ag →	$NO_2 + MNO_3$
	Sn →	$NO_2 + H_2SnO_3$
	Fe, Ni, Co, Cr, Al →	Passive (inert)

Key Points

- **Stability:** $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
- **Boiling point:** $PH_3 > AsH_3 > NH_3 > SbH_3 > BiH_3$.
- **Bond angle:** $NH_3(107.8°) > PH_3(93.6°) > AsH_3(91.8°) \approx SbH_3(91.3°) > BiH_3(90°)$.
- **Basicity:** $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
- **Reducing power:** $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5$.
- **Reducing power:** $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.
- **Stability:** $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$.
- $\underbrace{N_2O < NO}_{\text{Neutral}} < \underbrace{N_2O_3}_{\text{Acidic}} < N_2O_4 < N_2O_5$ (acidity)
- **Nitrous oxide (N_2O):** Diamagnetic, produces hysteria (laughing gas), used as an anaesthetic.
- Conc. HNO_3 appears yellow due to the presence of dissolved NO_2 formed by the photochemical decomposition of HNO_3.

16.9 GROUP 16 ELEMENTS (OXYGEN FAMILY)

- They are collectively called chalcogens.
- General outer electronic configuration is ns^2np^4 (where n = 2 to 6).

Element	Electronic configuration	Oxidation number
Oxygen (O)	$[He]2s^22p^4$	−2, −1, +1, +2
Sulphur (S)	$[Ne]3s^2\,3p^4$	−2, +2, +4, +6
Selenium (Se)	$[Ar]3d^{10}\,4s^24p^4$	−2, +2, +4, +6
Tellurium (Te)	$[Kr]5d^{10}\,5s^25p^4$	−2, +2, +4, +6
Polonium (Po)	$[Xe]4f^{14}5d^{10}\,6s^26p^4$	+2, +4, +6

All element of this group except oxygen are diamagnetic. At room temperature, O_2 gas is paramagnetic.

- **Atomicity:**

O	Multiple bonds (pπ – pπ)	Diatomic
S, Se, Te	single bonds	Octaatomic
	Multiple bonds (pπ – dπ)	

Atomic radii and density order: O < S < Se < Te

Ionization energy and electronegativity order: O > S > Se > Te

O_2(O=O) is diatomic but others are octaatomic (S_8)

- **Catenation:** Sulphur has highest bond strength of S–S bond. Therefore, S > Se > O > Te.
- **Allotropy:** This property is shown by all. Sulphur occurs in a number of allotropic forms such as rhombic (α), monoclinic (β), plastic (γ), colloidal (δ), λ and μ-sulphur. These are all non-metallic in nature.

  Sulphur (R) $\xrightleftharpoons[95.6]{}$ Sulphur (M)
- **Hydrides:** H_2M type (where, M is sp^3 hybridized)

  Melting and boiling points: $H_2O > H_2Te > H_2Se > H_2S$

  Acidic nature of hydrides: $H_2Te > H_2Se > H_2S > H_2O$

  Stability order: $H_2O > H_2S > H_2Se > H_2Te$

  Thermal stability: $H_2O < H_2S < H_2Se < H_2Te$

  Volatility: $H_2O < H_2Te < H_2Se < H_2S$

  Reducing character: $H_2S < H_2Se < H_2Te$

  Bond angle and dipole moment: $H_2Te < H_2Se < H_2S < H_2O$

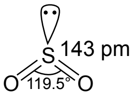
16.9.1.1 Halides

Element	Fluorine	Chlorine	Bromine	Iodine
Oxygen	F_2O	Cl_2O, ClO_2, Cl_2O_7	Br_2O	I_2O_5
Sulphur	SF_6, S_2F_{10}, SF_4, S_2F_2	SCl_4, SCl_2, S_2Cl_2	S_2Br_2	-------
Selenium	SeF_6, SeF_4, Se_2Fe_2	$SeCl_4$, $SeCl_2$, Se_2Cl_2	$SeBr_4$, $SeBr_2$, Se_2Br_2	-------
Tellurium	TeF_6, Te_2F_{10}, TeF_4	$TeCl_2$, $TeCl_4$	$TeBr_4$, $TeBr_2$	TeI_4
Polonium	PoF_6	$PoCl_4$, $PoCl_2$	$PoBr_4$, $PoBr_2$	PoI_4

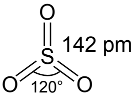
- **Oxides:** The most important oxides are of the MO_2 and MO_3 type.

  SO_2 and SeO_2 → Acidic

  TeO_2 and PoO_2 → Amphoteric

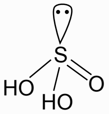
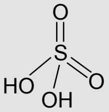
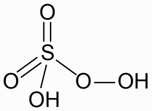
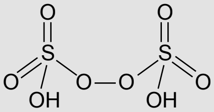
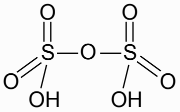
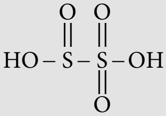
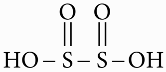
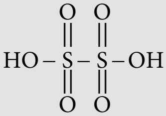
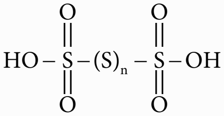


SO_2

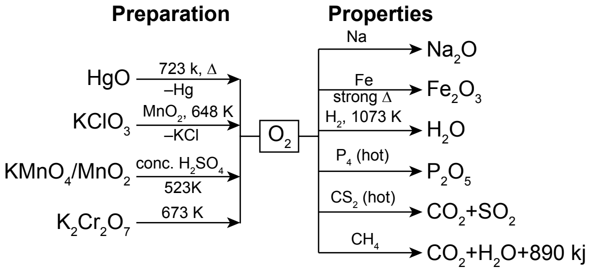


SO_3

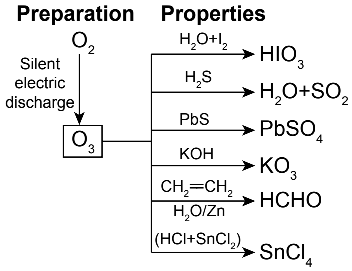
- **Acidity:** SO < SO_2 < SO_3 (acidity increases with increase in oxidation number).
- **Thermal stability:** $SO_2 > TeO_2 > SeO_2 > PoO_2$
- Oxoacids of sulphur

Oxoacid	Oxidation state, basicity and salt type	Structure	Properties
Sulphurous acid (H_2SO_3)	S = +4, dibasic, and forms two series of salts, sulphites (SO_3^{2-}) and bisulphites (HSO_3^-)		Does not exist in free form Acts as reducing as well as oxidizing agents
Sulphuric acid (H_2SO_4) or oil vitriol	S = +6 monobasic and forms two series of salts, sulphates (SO_4^{2-}) and bisulphates (HSO^-_4)		Stable, acts as oxidizing and dehydrating agents
Peroxomonosulphuric acid (H_2SO_5) or Caro's acid	S = +6 monobasic and forms single type of salt, peroxy disulphates		Stable crystalline and hygroscopic solid. Powerful oxidizing agent
Peroxodisulphuric acid ($H_2S_2O_8$) or Marshall's acid	S = +6 and forms single type of salt, peroxydisulphates ($S_2O_8^{2-}$)		Stable crystalline and hygroscopic solid. Strong oxidizing agent
Pyrosulphuric acid, disulphuric acid ($H_2S_2O_7$) or Oleum	S = +6, dibasic		Acts as a strong dehydrating agent
$H_2S_2O_5$ Di or pyrosulphirous acid	S(+5), S(+3) dibasic	 $\mathrm{HO-\overset{\overset{O}{\|}}{S}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$	Corrosive oily, hygroscopic
$H_2S_2O_4$ Dithionous acid	S(+3), 5(+3) dibasic	 $\mathrm{HO-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-OH}$	Unstable in pure form
$H_2S_2O_4$ Dithionic acid	S(+5) dibasic	 $\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$	Water soluble mild oxidizing and reducing agents
$H_2S_nO_6$ Polythionic acid	S(+5), S(0) dibasic n < 80	 $\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-(S)_n-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$	Stable in aqueous solutions, interact with strong reducing agents

16.9.1.2 *Dioxygen (O_2)*



16.9.1.3 *Ozone*



Oxygen is soluble in alkaline pyrogallol, whereas ozone is soluble in turpentine oil also called oil of cinnamon.

Compound	Oxidation state of O	Compound	Oxidation state of O
In oxides	–2	In dioxygen	0
In peroxides	–1	In oxygen difluoride	+2
In superoxides	–1/2	In oxygen monoflouride	+1

16.10 GROUP 17 ELEMENTS (HALOGEN FAMILY)

- General outer electronic configuration is ns^2np^5 (where n = 2 to 6)

Element	Electronic configuration	Oxidation number
Fluorine (F)	$[He]2s^22p^5$	–1
Chlorine (Cl)	$[Ne]3s^2\ 3p^5$	–1, +1, +3, +5, +7
Bromine (Br)	$[Ar]3d^{10}\ 4s^24p^5$	–1, +1, +3, +5, +7
Iodine (I)	$[Kr]4d^{10}\ 5s^25p^5$	–1, +1, +3, +5, +7
Astatine (At)	$[Xe]4f^{14}5d^{10}\ 6s^26p^5$	-----

- **Atomic radii, ionic radii and density increase from F to I.**
- **Electro negativity:** F > Cl > Br > I

  F is the most electronegative element in the periodic table.
- **Electron gain enthalpy:** Cl > F > Br > I
- **Bond energy:** $Cl_2 > Br_2 > F_2 > I_2$.
- **Solubility and oxidizing power:** $F_2 > Cl_2 > Br_2 > I_2$.
- Oxidizing nature order is F > Cl > Br > I.
- Reducing nature order is $Cl^- > Br^- > I^-$.
- The solution of iodine (I_2) in water increases with addition of KI or NaI due to the formation of polyamide (triiodide, I_3^-) ion. $KI_{(aq)} + I_{2(s)} \rightleftharpoons KI_{3(aq)} \rightleftharpoons K^+_{(aq)} + I_{3(aq)}^-$
- **Bond length, melting and boiling point:** $F_2 > Cl_2 > Br_2 > I_2$.
- **Heat of hydration:** $F^- > Cl^- > Br^- > I^-$.

16.10.1 Comparison of Halogens

Property	Fluorine	Chlorine	Bromine	Iodine
Physical state	Gas	Gas	Liquid	Solid
Colour	Pale yellow	Greenish yellow	Reddish brown	Voilet
Oxidizing nature	Very strong oxidizing agent	Strong oxidizing agent	Good oxidizing agent	Mild oxidizing agent
Bleaching action	Destroys the reducible coloured substance	Bleaches vegetable colours easily	Mild bleaching agent	--------
Chemical reactivity	Highly reactive	Quite reactive	Less reactive than chlorine	Least reactive
Reaction with (i) Hydrogen	Combines explosively even in the dark	Explosive in light, slow in dark	Only on heating	On heating and in presence of a catalyst
(ii) Water	Decomposes forming HF, O_2 and O_3	Forms chlorine hydrate with ice cold water. Decomposes slowly forming HCl and HClO or HCl and O_2.	Decomposes slowly in presence of light, forming HBr and HBrO or HBr and O_2	No action
(iii) Metals	Reacts with all metals to form fluorides	Reacts with almost all metals forming chlorides.	Many metals are acted upon and bromides are formed	Reacts only with few metals to form iodides
(iv) Starch	No reaction on starch	No action on starch	Yellow colour with starch	Blue colour with starch

- **Halides:** Halogens combine with all elements except He, Ne and Ar forming a large number of binary halides.

  Ionic character of M–X bond and melting point and boiling point

  M – F > M – Cl < M – Br > M – I

  Melting and boiling point of metal halides

  M – I > M – Br > M – Cl > M – F

  Reducing character

  $I^- > Br^- > Cl^- > F^-$

  Hydrogen halide: Percentage of ionic character, thermal stability and dipole moments

  HF > HCl > HBr > HI

  Acidity and bond length

  HI > HBr > HCl > HF

  Stability order HF > HCl > HBr > HI

  Boiling point order HCl > HBr > HI > HF

- Here, HF is not stored in glass vessels since it reacts with SiO_2 of glasses. It is stored in copper, wax polythene or gutta-percha.
- Here, HF reacts with glass to form sodium and calcium fluorosilicates Na_2SiF_6 and $CaSiF_6$. So, it is used for etching of glass (mixture of sodium and calcium silicates).

  $Na_2SiO_3 + 6HF \rightarrow Na_2SiF_6 + 3H_2O$

  $CaSiO_3 + 6HF \rightarrow CaSiF_6 + 3H_2O$

  or $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$

  $SiF_4 + 3HF \rightarrow H_2SiF_6$

  Reaction of Cl_2: $2HgO + H_2O + 2Cl_2 \rightarrow Hgo.HgCl_2 + 2HOCl$

  $Cl_2 + 2OH^-_{(cold)} \rightarrow OCl^- + Cl^- + H_2O$

  $3Cl_2 + 6OH^-$ (hot and conc) $\rightarrow Cl^- + ClO_3^- + 3H_2O$

  $2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + O_2$

  $2ClO_2 + Na_2O_2 \rightarrow NaClO_2 + NaClO_3 + H_2O$

  $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + O_2$

  $2CaCl_2 \xrightarrow{\Delta} 2CaCl_2 + O_2$

  $CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$ (available chlorine)

- **Oxides:** OF_2, O_2F_2

  Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7

  Br_2O, BrO_2, BrO_3

  I_2O_4, I_2O_5, I_4O_9

  All are covalent and powerful oxidizing agents

- **Oxidizing power:** $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$
- **Stability:** $Cl_2O < ClO_2 < Cl_2O_6 < Cl_2O_7$.
- Solid Cl_2O_6 is ionic and exists as ClO_2^+ and ClO_4^- ions.

- **Oxoacids:** Hypohalous acid: HXO, Halous acid: HXO_2, Halic acid:HXO_3, Perhalic acid:HXO_4.
- **Acidity of hypohalous acids:** HOCl > HOBr > HOI
  Oxygen is more electronegative than halogens. As the electronegativity decreases from Cl to I, electrons density on the oxygen atom increases from Cl to I, therefore tendency to attract electrons of O–H bond decreases from Cl to I, hence acidity decreases.
- **Oxidizing power of hypohalous acids:** HOCl ≈ HOBr > HOI
  Oxidising power decreases as the thermal stability of O–H bond increases with increase in the size of X from Cl to I.
- **Acidity of perhalic acids:** $HOClO_3 > HOBrO_3 > HOIO_3$
  As the electronegativity decreases from Cl to I, tendency to withdraw electrons of O–H bond by XO_3 group decreases and hence the acidity decreases from Cl to I.
- **Oxidizing power of perhalates:** $BrO_4^- > IO_4^- > ClO_4^-$
- **Acidity of oxoacids with same halogen in different oxidation states:** Acidic strength increases with increase in oxidation state of the halogen atom. $HClO < HClO_2 < HClO_3 < HClO_4$
  This is based on the stability of their conjugate bases. Greater the number of oxygen atoms, greater will be the dispersal of the negative charge through pπ–dπ back bonding.
  $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$
- Oxidizing power of oxoacids with same halogen in different oxidation states:
  $HClO > HClO_2 > HClO_3 > HClO_4$
  Oxidizing power decreases, as the stability of their conjugate bases increases.

16.11 INTERHALOGEN COMPOUNDS

Molecules	**Hybridization**	**Shape**	**Examples**
XY	Sp^3	Linear	ClF, BrF, BrCl, ICl, IBr, IF (very unstable)
XY_3	Sp^3d	T-shaped	ClF_3, BrF_3, ICl_3, IF_3
XY_5	Sp^3d^2	Square pyramidal	ClF_5, BrF_5, IF_5
XY_7	Sp^3d^3	Pentagonal bipyramidal	IF_7

- Pseudohalogens and pseudohalides:
- Molecules like cyanogens $(CN)_2$, thiocyanogen $(SCN)_2$ and selecocyanogen $(SeCN)_2$ have properties similar to those of the halogens. Therefore, these are called pseudohalogens.
- They form anions such as CN^-, OCN^-, etc. which are called as pseudohalides. CN^- resembles Cl^-, Br^- and I^-.
- **Polyhalides:** Halide ions often react with molecules of halogens or interhalogen and form polyhalide ions. Iodine is only slightly soluble in water. Its solubility is greatly increased if some iodide ions are present in the solution due to formation of polyhalide ion, I_3^-. $I^- + I_2 \rightarrow I_3^-$
  Polyhalides are formed from interhalogens and metal halides: $K[ICl_2]$, $K[ICl_4]$, Cs[IBrF] and K[IBrCl].

Key Points

- Because of the tendency to form hydrogen bond, metal fluorides are solvated by HF giving species of the type HF_2^-, etc.

  KHF_2 (KF . HF), KH_2F_3(KF.2HF) and KH_3F_4 (KF.3HF) are known examples.
- Concentrated H_2SO_4 (a strong oxidizing agent) cannot be used since it would oxidize HBr to Br_2 and HI to I_2, etc.
- Magnesium perchlorate, $Mg(ClO_4)_2$ is used in dry batteries and is also an effective desiccant called anhydrone. $KClO_4$ is used in fireworks and flares.

16.12 GROUP 18 ELEMENTS (NOBLE GASES)

- General outer electronic configuration is ns^2np^6 (where n = 2 to 6)

Known as	Reason
Rare gases	Occur in very minute quantities
Noble gases	Obtained under specific conditions
Intert gases	Do not react at ordinary temperature
Zero valent element	Show zero valency

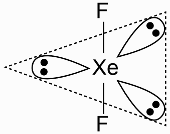
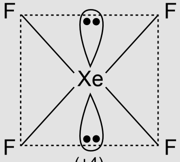
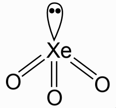
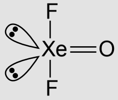
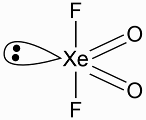
Element	Electronic configuration
Helium (He)	$1s^2$
Neon (Ne)	$1s^2\ 2s^2\ 2p^6$
Argon (Ar)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Krypton (Kr)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
Xenon (Xe)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
Radon (Rn)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5f^{14}\ 5s^6\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6$

Properties:

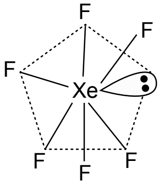
- Because of fully filled electronic configuration, they have very high ionization energies.
- They can be liquefied with great difficulty. It is because of the existence of weak Van der Waal's forces in these gases.
- **Most abundant noble gas:** Argon
- **Melting point, boiling point, polarizability, ease of liquefication and solubility in water:**

  He < Ne < Ar < Kr < Xe < Rn
- **Ionization enthalpy:** He > Ne > Ar < Kr > Xe > Rn
- **Electron gain enthalpy:** Ne > Ar = Kr > Xe > Rn > He
- Noble gases form clathrate compounds except He and Ne. Noble gases compressed with water or quinol gets entrapped between water molecules; such compounds are called clathorates or enclosures.

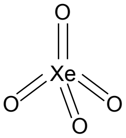
16.13 COMPOUNDS OF XENON

Compound	Structure	Preparation	Properties
XeF_2 (Xenon difluoride)	 (+2) Linear, sp^3d	$\underset{(2:1)}{Xe + F_2} \xrightarrow[400°C]{\text{Ni tube}} XeF_2$ $\underset{(2:1)}{Xe + F_2} \xrightarrow[\text{discharge}]{\text{Electric}} XeF_2$ $Xe + F_2 \xrightarrow[\text{(Hg vapour)}]{h\upsilon} XeF_2$	Acts as fluorinating agent $XeF_2 + H_2O \rightarrow XeOF_2 + 2HF$
XeF_4 (Xenon tetrafluoride)	 (+4) Square planar, sp^3d^2	$\underset{(1:5)}{Xe + F_2} \xrightarrow[600°C]{\text{Ni tube}} XeF_4$ $\underset{(2:1)}{Xe + F_2} \xrightarrow[\text{discharge } -78°C]{\text{Electric}} XeF_4$	Colourless crystalline solid with melting point = 117.1°C $XeF_4 + 2H_2 \rightarrow 4Xe + 4HF$ Undergoes disproportionation in water $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$ Gives adduct $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$ Acts as oxidizing and fluorinating agent Dissolves in anhydrous HF
XeO_3 (Xenon trioxide)	 (+6) Pyramidal, sp^3	Complete hydrolysis of XeF_4 and XeF_6 $6XeF_4 + 12H_2O \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$ $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$	Colourless, highly explosive and powerful oxidizing agent With water forms xenic acid $XeO_3 + H_2O \rightarrow H_2XeO_4$ Undergoes disproportionation when dissolved in alkali $2XeO_3 + 4OH^- \rightarrow Xe + O_2 + XeO_6^{4-} + 2H_2O$
$XeOF_2$ (Xenon oxy-difluoride)	 (+4) T-shaped, sp^3d	Partial hydrolysis of XeF_4 $XeF_4 + H_2O \xrightarrow{-80°C} XeOF_2 + 2HF$	Unstable
XeO_2F_2 (Xenon dioxy difluoride)	 (+6) Distorted trigonal bipyramidal, sp^3d	Partial hydrolysis of $XeOF_4$ or XeF_6 $XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF$ $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$ Action of SiO_2 on $XeOF_4$ $2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$	Colourless solid Undergoes hydrolysis readily $XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$

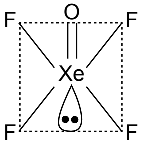
Structure of some other important compounds



XeF_6, sp^3d^3
Distorted octahedral



XeO_4, sp^3
Tetrahedral



$XeOF_4$, sp^3d^3
Square pyramidal

16.13.1 Uses of Noble Gases

	Uses	Reasons
He	Filling of observation balloons	Non flammable; 93 per cent lifting power as compared to flammable H_2
	$He–O_2$ mixture for deep-sea breathing instead of $N_2–O_2$ mixture	Low solubility in blood; prevents nitrogen narcosis and 'bends'
	Diluent for gaseous anaesthetics	Non flammable, non-reactive
	$He–O_2$ mixture for respiratory patients	Low density flows easily through restricted passages
	Heat transfer medium for nuclear reactions	Transfers heat readily, does not become radioactive, chemically inert
	Liquid He to maintain very low temperature in research (cryogenics)	Extremely low boiling point
Ne	Neon is used for filling discharge tubes for optical decorations and advertisements. It is used for filling sodium vapour lamps. It is also used in beacon light as safety signal for air navigators	Even at low pressure, moderate electric current causes bright orange-red glow, can be modified by coloured glass or mixing with Ar or Hg vapour
Ar	Argon is used for filling incandescent metal filament of electric bulbs. It is used in advertising signs, for filling radio-values, rectifiers and fluorescent tubes	Inert; prevents vapourization of tungsten and blackening of bulbs
Kr	Ariport runway and approach lights	Gives longer life to incandescent lights than Ar, but more expensive
Xe	Xe and Kr mixture in high-intensity, short exposure photographic flash tubes	Both have fast response to electric current
Rn	Rn is used in radiotherapy	Its ability to control cell growth