Chapter 20

p-Block Elements

BORON FAMILY (GROUP-13 ELEMENTS)

Atomic and Physical Properties

Electropositive Nature : Less electropositive as compared to alkali metals and alkaline earth metals.

The electropositive character increases from B to Al and then decreases upto Tl. It is due to ineffective shielding caused by *d* and *f* electrons which results in the stronger nuclear pull on the electrons of outermost shell.

Compounds of Boron

1. **Orthoboric Acid : H_3BO_3**

Preparation :

(a) From Borax

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$$

(b) By hydrolysis of boron compounds

$$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$$

Properties :

(a) Boric acid has layer type structure in which planar BO_3^3 units are linked to one another through Hydrogen bonds.

(b) Boric acid is a weak monobasic acid. It does not act as proton donor but acts as a lewis acid by accepting electrons from hydroxyl ion.

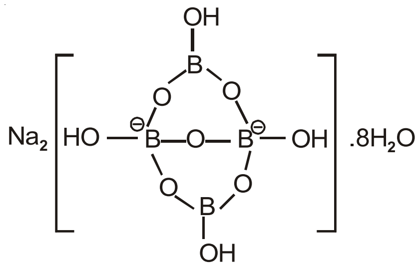
$$H_2O + H_3BO_3 \rightarrow H^+ + [B(OH_4)]^-$$

(c) $H_3BO_3 + NaOH \rightarrow NaBO_2 + 2H_2O$

(d) **Effect of heat**

$$H_3BO_3 \xrightarrow{100\ C} \underset{\text{metaboric acid}}{HBO_2} + H_2O \xrightarrow{160\ C} \underset{\text{tetraboric acid}}{H_2B_4O_7} + H_2O \xrightarrow{\text{Red heat}} 2B_2O_3 + H_2O$$

2. **Borax :** $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$



Preparation

$4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$

Properties

(a) It hydrolyses in water to form alkaline solution.

(b) **Borax bead Test** (Test for Transition Elements)

Glassy bead + metal oxide → metal metaborate (coloured)

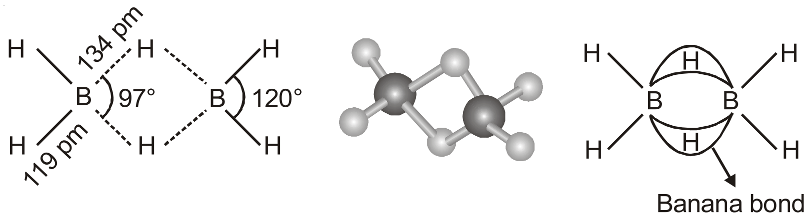
3. **Diborane: B_2H_6**

Structure of B_2H_6 (Diborane)

Boron in B_2H_6 is *sp*^{3} hybridised.

Two bridging B – H > Terminal B – H bond

Boron is dimerised by Banana bond known as **3-centred-2electron** (3c – 2e) **bond**.



Diborane

Preparation :

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

(b) $2BCl_3 + 6H_2 \xrightarrow[\text{Discharge}]{\text{Silent Electric}} B_2H_6 + 6HCl$

Properties :

(a) Stable at low temperature only, colourless and highly toxic.

(b) $B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$

(c) $B_2H_6 + 6Cl_2 \xrightarrow{25\ C} 2BCl_3 + 6HCl$

(d) $B_2H_6 + 2NH_3 \rightarrow B_2H_6 .2NH_3$ (white solid)

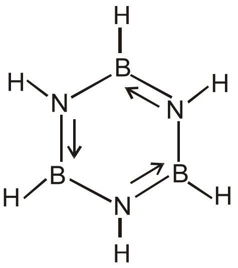
(e) $2B_2H_6 + 6NH_3 \xrightarrow{450\ K} 2B_3N_3H_6 + 12H_2$

(f) $B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$

4. **$B_3N_3H_6$: Borazole** also known as **Borazine** or Inorganic Benzene.

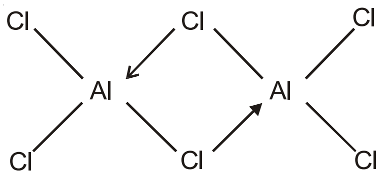
Preparation

$$B_2H_6 \xrightarrow[\text{1000 temp}]{\text{Excess of } NH_3} B_2H_6.2NH_3 \text{ or } [BH_2(NH_3)_2]^+ [BH_4]^- \xrightarrow{450\,K} B_3N_3H_6 + H_2$$



5. **Alums** : General formula, M_2SO_4 . $M'_2(SO_4)_3$ $24H_2O$ where M is a monovalent ion like Na^+, K^+, NH_4^+ while M' is a trivalent ion like Fe^{3+}, Cr^{3+}, Al^{3+}, K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$-Potash alum; $(NH_4)_2SO_4$. $Fe_2(SO_4)_3$. $24H_2O$-Ferric alum; K_2SO_4.$Cr_2(SO_4)_3$. $24H_2O$-Chrome alum. Out of all these potash alum is very common. When the crystals of potash alum are heated it swells and loses water. Anhydrous alum thus obtained is called burnt alum.

$AlCl_3$ Aluminium chloride exists as a dimer where two $AlCl_3$ units are joined together with the formation of two dative bonds (co-ordinate bonds) because $AlCl_3$ is electron-deficient (Lewis acid).



In $AlCl_3$ dimer, four bond length are larger while bond length of four bonds are small.

$AlCl_3$ is used as catalyst in Friedel Craft's reaction, where it is a Lewis acid.

CARBON FAMILY (GROUP-14 ELEMENTS)

Element	Symbol	Atomic No.
Carbon	C	6
Silicon	Si	14
Germanium	Ge	32
Tin	Sn	50
Lead	Pb	82

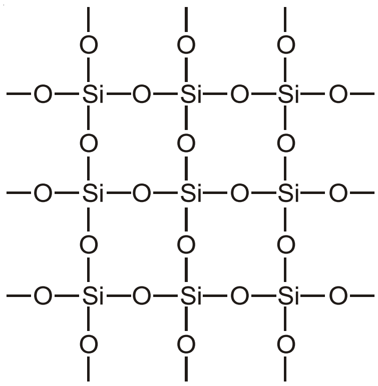
Compounds of Silicon

1. **Silicon dioxide (SiO_2):**

   SiO_2 is solid at room temperature and has a three dimensional network structure as shown below

   (a) In this structure, silicon atom is bonded to four oxygen atom which are tetrahedrally arranged around it.

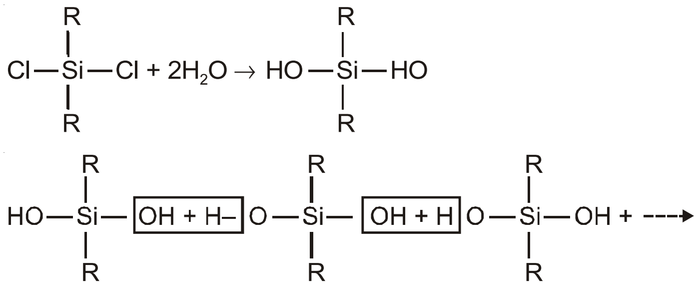
   (b) Since Si—O bonds are very strong, silica is relatively inert and has a very high melting point.



2. Silicones :

Silicones are synthetic organosilicon compounds containing repeated unit of R_2SiO held by Si–O–Si linkages.

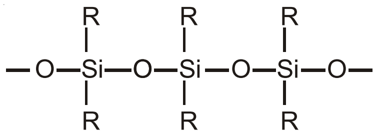
Preparation : The silicones are prepared by the hydrolysis of dialkyl dichloro silane (R_2SiCl_2)



$$Cl-\overset{R}{\underset{R}{Si}}-Cl + 2H_2O \rightarrow HO-\overset{R}{\underset{R}{Si}}-HO$$

$$HO-\overset{R}{\underset{R}{Si}}-\boxed{OH + H-}O-\overset{R}{\underset{R}{Si}}-\boxed{OH + H}O-\overset{R}{\underset{R}{Si}}-OH + \dashrightarrow$$

Polymerisation :



$$-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-$$

The hydrolysis of $RSiCl_3$, gives cross linked silicones.

Properties :

(a) Silicones are chemically inert towards oxidation, thermal decomposition or attack by organic reagents.

(b) They are water repellant and heat resistant.

3. Silicates : Silicates are the compounds in which the anions present are either discrete SiO_4^{4-} tetrahedra or a number of such units joined together through corners.

Types of Silicates : Silicates are classified into different types depending upon the number of corners of SiO_4^{4-} tetrahedron shared with other tetrahedron.

		Formula
1.	**Orthosilicate** Ex. Zircon. ($ZrSiO_4$)	SiO_4^{4-}
2.	**Pyrosilicates** Ex. Thortveitite $Sc_2(Si_2O_7)$	$Si_2O_7^{6-}$
3.	**Cyclic silicates** Ex. Beryl : $Be_3Al_2Si_6O_{18}$	$(SiO_3)_n^{2n-}$
4.	**Chain Silicates** Ex. Spodumene; $LiAl(SiO_3)_2$	$(SiO_3^{2-})_n$ (Pyroxene)
5.	**Sheet silicates** Ex. Clay	$(Si_2O_5)_n^{2-}$
6.	**Three dimensional silicates** Ex. Quartz	All the four corners are shared with other tetrahedra (SiO_2)

Note : *Chain silicates are of two types*

(i) Pyroxene

(ii) Amphibole

NITROGEN FAMILY (GROUP-15 ELEMENTS)

Element	Symbol	Atomic No.
Nitrogen	N	7
Phosphorous	P	15
Arsenic	As	33
Antimony	Sb	51
Bismuth	Bi	83

Characteristics of Hydrides

(a) Basic Strength : All these hydrides act as Lewis bases. They can donate an electron pair to electron deficient species. (Lewis acids). **As we go down the group, the basic character of these hydrides decreases.**

(b) Thermal Stability : Thermal stability of the hydrides of group 15 elements decreases as we go down the group.

$NH_3 \quad PH_3 \quad AsH_3 \quad SbH_3 \quad BiH_3$

(c) Reducing Character : The reducing character of the hydrides of group 15 elements increases from NH_3 to BiH_3. Thus, increasing order of reducing character is as follows :

$NH_3 \quad PH_3 \quad AsH_3 \quad SbH_3 \quad BiH_3$

(d) Boiling Points : Ammonia (240 K) has a higher boiling point than phosphine (190 K) and then the boiling point increases down the group because of increase in size.

Thus boiling point order is $\underbrace{BiH_3 > SbH_3}_{\textbf{Mol. Mass}} > \underbrace{NH_3}_{\textbf{H–bonding}} > \underbrace{AsH_3 > PH_3}_{\textbf{Mol. Mass}}$

Nitric Acid (HNO_3) :

Preparation : Nitric acid is mostly prepared by

(a) Birkeland - Eyde Process

$N_2 + O_2 \xrightarrow[\text{3000 C}]{\text{Electric arc}} 2NO$

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

(b) Ostwald's Process

$4NH_3 + 5O_2 \xrightarrow[\text{800 C}]{\text{Pt}} 4NO + 6H_2O$

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

The important reaction of Nitric acid are given below :

Properties :

(a) Reaction with Metals

(i) $Mg + 2HNO_3$ (dil) $\rightarrow Mg(NO_3)_2 + H_2$

(ii) $Mn + 2HNO_3$ (dil) $\rightarrow Mn(NO_3)_2 + H_2$

(iii) $3Cu + 8HNO_3$ (hot and dilute) $\rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

(iv) $Cu + 4HNO_3$ (hot and Conc.) $\rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

[Ag, Pb and Bi also react as Cu]

(b) Reaction with non-metals and compounds

(i) $C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$

(ii) $6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

OXYGEN FAMILY-(GROUP-16 ELEMENTS)

Element	Symbol	Atomic No.
Oxygen	O	8
Sulphur	S	16
Selenium	Se	34
Tellurium	Te	52
Polonium	Po	84

OXYGEN

Preparation : Oxygen is mostly prepared by the following methods :

1. In laboratory it is prepared by heating $KMnO_4$ or $KClO_3$ in presence of MnO_2.

   $2KClO_3\ (s) \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$

2. It can also be prepared by reaction of H_2O on Na_2O_2

   $2Na_2O_2 + 2H_2O\ (l) \rightarrow 4NaOH + O_2$

Chemical properties : Oxygen reacts with metals and non-metals to form different oxides

Ozone (O_3)

Preparation : Ozone is prepared by subjecting pure oxygen to silent electric discharge

$3O_2 \rightarrow 2O_3$; H = + 284.5 kJ mole^{-1}.

Properties :

It is pale blue gas having a strong characteristic smell. It is neutral to litmus. It condenses to blue liquid (b. pt 161. 2K). It condenses to a violet- black solid (melting point 80.6 K).

The important reactions are given below:

1. $O_3 \xrightarrow{250\ C} O_2 + O$
2. $H_2S + O \rightarrow H_2O + S$
3. $2Ag + O \rightarrow Ag_2O$
4. $2Hg + [O] \rightarrow Hg_2O$ (Tailing of Mercury)
5. $I_2 + H_2O + 5[O] \rightarrow 2HIO_3$
6. It is better oxidising agent as compared to H_2O_2.

   $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$

Sulphuric Acid : (H_2SO_4)

Preparation :

It is manufactured by **Contact process**. Reaction of the process is as under :

(a) $S + O_2 \longrightarrow SO_2$ or $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(b) $2SO_2 + O_2 \xrightleftharpoons[V_2O_5 \text{ or Pt Catalyst}]{723K - 823K\ 2\text{-}3 \text{ atmosphere}} 2SO_3$

(c) $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ (oleum)

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

Properties : The important properties are

1. It is a strong dibasic acid

   $H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$

2. On heating it liberates oxygen and thus it acts as a strong oxidising agent

   $\underset{\text{(Conc.)}}{Cu + 2H_2SO_4} \rightarrow CuSO_4 + SO_2 + 2H_2O$

   Oxidation of non-metals

   $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$

   It liberates iodine from KI

   $2KI + 2H_2SO_4 \rightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$

3. H_2SO_4 is a powerful dehydrating agent

HALOGEN FAMILY-(GROUP-17 ELEMENTS)

Element	Symbol	Atomic No.
Fluorine	F	9
Chlorine	Cl	17
Bromine	Br	35
Iodine	I	53
Astatine	At	85

Atomic and Physical Properties:

1. **Atomic and Ionic Radii:** The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.
2. **Ionization Energies:** The ionization energies of halogens are very high. It decreases from fluorine to iodine
3. **Melting and Boiling Points :** The melting and boiling points of halogens increases with increase in atomic number as we go down the group.
4. **Electron Affinity**
   (a) All these have maximum electron affinities in their respective periods.
   (b) In general, electron affinity decreases from top to bottom in a group.
   (c) Fluorine has unexpectedly low electron affinity than chlorine. Therefore, **chlorine has the highest electron affinity in this group.**

   Thus, **electron affinity** among halogens varies as : **F < Cl > Br > I**
5. **Colour :** All the halogens are coloured.

   Fluorine – Pale yellow, Chlorine – Greenish yellow, Bromine – Reddish brown liquid, Iodine – Greyish black solid (Deep violet in vapour state).
6. **Oxidation States**
   (a) They all show an oxidation state of –1.
   (b) Since fluorine is the most electronegative element, it always show an oxidation state of –1. It does not show any positive oxidation state.
   (c) The other elements also show positive oxidation state of +1, +3, +5 and +7. The higher oxidation state of chlorine, bromine and iodine are due to the presence of vacant d–orbitals in their valency shells.

7. **Low Dissociation Energies**

All the halogen have very low dissociation energies. As a result, they can readily dissociate into atoms and react with other substance.

Molecule	**F_2**	**Cl_2**	**Br_2**	**I_2**
Dissociation energies	159	243	193	151

$X_2 \rightleftharpoons 2X$ (kJ mol^{-1})

8. **Oxidising Power**

(a) Halogens have high electron affinity values and therefore they have strong tendency to take up the electron :

$$\frac{1}{2}X_2 + e^- \rightarrow X^-$$

(b) As a result, they **act as powerful oxidising agents.**

(c) The decreasing oxidising power of the halogen as we go down the group is shown by their decreasing reduction potentials.

X_2	F_2	Cl_2	Br_2	I_2
E_{RP} (volts)	2.87	1.40	1.09	0.62

OXYACIDS OF CHLORINE

Different oxyacids of chlorine are

Formula	Name	Corresponding salt
HOCl	Hypochlorous acid	Hypochlorites
$HClO_2$	Chlorous acid	Chlorites
$HClO_3$	Chloric acid	Chlorates
$HClO_4$	Perchloric acid	Perchlorates

Acidic Character : Acidic Character of the same halogen increases with the increase in oxidation number of the halogen.

$HClO_4 > HClO_3 > HClO_2 > HOCl$

Reason : It is because the release of H^+ ion in each case would result in the formation of ClO_4^-, ClO_3^-, ClO_2^-, ClO^- ions. More is the stability of resulting ion, greater will be the ease with which the ion is formed. Therefore, the ease of formation of ions would be.

$ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

Interhalogen Compounds

The halogens on account of the difference in their electronegativities combine with each other and form binary covalent compounds of AB_n type which are called interhalogen compounds. A is always bigger atom and B is a smaller atom. n may have value 1, 3, 5 and 7 corresponding to oxidation state of halogens.

AB type	ClF, BrF, BrCl, ICl, IBr	→ sp^3 hybridization, Linear shape
AB_3 type	ClF_3, BrF_3, ICl_3	→ sp^3d hybridization, T-shape
AB_5 type	BrF_5, IF_5	→ sp^3d^2 hybridization, distorted square pyramidal shape
AB_7 type	IF_7	→ sp^3d^3 hybridization, pentagonal bipyramidal shape

NOBLE GASES - (GROUP-18 ELEMENTS)

Element	Symbol	Atomic Number
Helium	He	2
Neon	Ne	10
Argon	Ar	18
Krypton	Kr	36
Xenon	Xe	54
Radon	Rn	86

Atomic & Physical Properties :

In general, noble gases are not very reactive. Their inertness to chemical reactivity is due to

1. The noble gases have completely filled ns^2np^6 electronic configurations in their valence shells.
2. The noble gases have very high ionisation energies.

Chemical Properties :

Among group 18 members only Xenon and Krypton show chemical reactivity. The important compounds of Xe are given below :

1. **Fluorides :** The common fluorides of xenon such as XeF_2, XeF_4 and XeF_6 can be prepared by the direct combination of xenon and fluorine under different conditions :

$$\underset{(2:1)}{Xe+F_2} \xrightarrow[673\ K]{Ni\ vessel} XeF_2$$

$$\underset{(1:5)}{Xe+2F_2} \xrightarrow[673\ K,\ 5\ \ 6\ atm]{Ni\ vessel} XeF_4$$

$$\underset{(1:20)}{Xe+3F_2} \xrightarrow[573\ K,\ 50\ \ 60\ atm]{Ni\ vessel} XeF_6$$

2. **Oxides :** XeO_3 is the most common oxide and it is prepared by the hydrolysis of XeF_4 or XeF_6.

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

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

3. **Oxyfluorides:** The oxyfluorides of xenon are prepared by the partial hydrolysis of XeF_4 or XeF_6.

$$XeF_4 + H_2O \xrightarrow{800\ C} \underset{\text{Xenon oxydifluoride}}{XeOF_2} + 2HF$$

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

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