Chapter- 11: The p-Block Elements

Introduction:

- Elements in which the last electron enters in the any one of the three p- orbital of their outermost shells.
- Gen. electronic configuration of outer shell is ns^2np^{1-6}
- The inner core of electronic configuration may differ which greatly influences their physical & to some extent chemical properties.
- The p block of elements in the periodic table consisting of the main groups:
  - Group 13 (B to Tl)
  - Group14 (C to Pb)
  - Group15 (N to Bi)
  - Group 16 (O to Po)
  - Group17 (F to At)
  - Group18 (He to Rn)
- Members at the top and on the right of the *p*-block are non metals (C, N, P, O, F, S, Cl, Br, I, At).
- Those on the left and at the bottom are metals (Al, Ga, In, Tl, Sn, Pb, Sb, Bi, Po).
- Between the two, from the top left to bottom right, defined group of metalloid elements (B, Si, Ge, As, Te)

GROUP 13: The Boron Family

- Outer Electronic Configuration: ns^2np^1
- Group members: boron (B), aluminum (Al), gallium (Ga), indium (In) & thallium (Tl).
- Except boron, all are metals.
- Boron show diagonal relationship with Silicon; both are semiconductors metalloids & forms covalent compounds.
- Boron compds are electron deficient; they are lack of an octet of electrons about the B atom.
- Diborane (B_2H_6) is simplest boron hydride.
- Boron oxide is acidic (it reacts readily with water to form boric acid)
- Aluminum compounds, aluminum oxide is amphoteric
- Aluminum hydride, e.g., $LiAlH_4$, is a reducing agent

1. **Electronic Configurations:**

Element	Symbol	Atomic No.	Electronic Configuration	Abundance in Earth's Crest (in ppm)
Boron	B	5	$[He]2s^2\ 2p^1$	8
Aluminium	Al	13	$[Ne]3s^2\ 3p^1$	81,300
Galium	Ga	31	$[Ar]3d^{10}4s^2\ 4p^1$	15
Indium	In	49	$[Kr]\ 4d^{10}5s^2\ 5p^1$	1
Thallium	Tl	81	$[Xe]\ 5d^{10}6s^2\ 6p^1$	0.3

2. Atomic and ionic radii:

- Group 13 elements have smaller size than those of alkaline earth metals due to greater effective nuclear charge.
- Atomic radii increase on going down the group with an anomaly at gallium (Ga).
- Unexpected decrease in the atomic size of Ga is due to the presence of electrons in d-orbitals which do not screen the attraction of nucleus effectively.
- The ionic radius regularly increases from B^{3+} to TI^{3+}.

3. Ionization energies:

- The first ionization enthalpy values of group 13 elements are lower than the corresponding alkaline earth metals, due to the fact that removal of electron is easy. [ns2 npl configuration] .
- On moving down the group, IE decreases from B to Al, but the next element Ga has slightly higher ionization enthalpy than A1 due to the poor shielding of intervening d-electrons. It again decreases in In and then increases in the last element Tl.

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

4. Oxidation states:

- B and Al show an oxidation state of +3 only while Ga, In and Tl exhibit oxidation states of both +1 and +3.

Element	B	Al	Ga	In	Tl
Oxidation state	+3	+3	+3, +1	+3, +1	+3, +1

- As we move down the group, the tendency to exhibit +3 oxidation state decreases and the tendency to attain +1 oxidation state increases due to inert pair effect.
- Inert Pair Effect: It is the tendency of the electrons in the outermost atomic s orbital to remain unionized or unshared in compounds of post- transition metals.
- Stability of +1 oxidation state follows the order Al < Ga < In < Tl.

5. Electropositive (or metallic) character:

- These elements are less electropositive than the alkaline earth metals due to their smaller size and higher ionization enthalpies.
- On moving down the group, the electropositive character first increases from B to Al and then decreases from Ga to TI, due to the presence of d and I-orbitals which causes poor shielding. For example Boron is a non-metal while the other elements are typical metals.

6. Chemical Properties of 13 Group Elements:

(i) Action of air: Crystalline boron is unreactive whereas amorphous boron is reactive. It reacts with air at 700°C as follows

$4B + 3O_2 \rightarrow 2B_2O_3$

$2B + N_2 \rightarrow 2BN$

Al is stable in air due to the formation of protective oxide film.

$4Al + 3O_2 \rightarrow 2Al_2O_3$

Thallium is more reactive than Ga and In due to the formation of unipositive ion, TI^+.

$4Tl + O_2 \rightarrow 2Tl_2O$

(ii) Reaction with acids and alkalies: Boron does not react with acids and alkalies but aluminum dissolve in acids and alkalies and show amphoteric character.

$2Al\ (s) + 6HCl\ (aq) \rightarrow 2Al^{3+}\ (aq) + 6Cl^-\ (aq) + 3H_2$

$2Al\ (s) + 2NaOH\ (aq) + 6H_2O\ (l) \rightarrow 2Na^+[Al(OH)_4]^-\ (aq) + 3H_2$

Sod. tetrahydroxoaluminate

(iii) Reaction with halogens: React with halogens its form trihalides (except $Tl\ I_3$)

$2B(s) + 3X_2\ (g) \rightarrow 2BX_3(s)$ (X = F, Cl, Br, I)

$2Al(s) + 3X_2\ (g) \rightarrow 2AlX_3(s)$

7. Anomalous Behaviour of Boron: Boron shows anomalous behaviour with the other members of the group, due to the following reasons:

(i) Smallest size in the group.

(ii) High ionisation energy.

(iii) Highest electronegativity in the group.

(iv) Absence of vacant d-orbital.

A few points of difference are

(i) It is a non-metal while other members of the group are metallic.

(ii) It shows allotropy while other members do not.

(iii) It has the highest melting point and boiling point in group 13.

(iv) It forms only covalent compounds while other members form both ionic and covalent compounds.

(v) The halides of boron exist as monomers while aluminum halides exist as a dimer.

(vi) The oxides and hydroxides of boron are weakly acidic while those of aluminum are amphoteric and those of other elements are basic.

(vii) It can be oxidised by concentrated HNO_3 while aluminum becomes passive due to the formation of oxide layer on the surface.

$$2B + 6HNO_3 \rightarrow 2H_3BO_3 + 6NO_2$$

8. Diagonal Relationship between Boron and Silicon: Boron exhibit resemblance with its diagonal element silicon of group 14.

1. Both B and Si are non-metals.

2. Both are semi-conductors.

3. Both B and Si form covalent hydrides, i.e.. boranes and silanes respectively.

4. Both form covalent and volatile halides which fume in moist air due to release of HCI gas.

5. Both form solid oxides which get dissolve in alkalies forming borates and silicates respectively. ..

6. Both react with electropositive metals and give binary compounds, which yield mixture of boranes and silanes on hydrolysis.

Boron and Its Compounds

Occurrence: It does not occur in Free State. Its important minerals are

1) Borax or Tineal ($Na_2B_4O_7.10H_2O$)
2) Orthoboric acid (H_3BO_3)
3) Diborane (B_2H_6)

1) Borax or Sodium Tetraborate Decahydrate [$Na_2B_4O_7.10H_2O$]

Preparation:

(i) It occurs naturally as tineal in dried up lakes. It is obtained by boiling of mineral colemanite with a solution of Na_2CO_3.

$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow 2CaCO_3 + 2NaBO_2 + Na_2B_4O_7$

Sodium metaborate ($NaBO_2$) can be removed by passing CO_2 through it.

$4NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_4O_7$

Properties:

(i) Its aqueous solution is basic in nature.

$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$ Orthoboric acid

(ii) Action of heat: Its give borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\text{Heat, Swells}} Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{\underset{\text{Sod. metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{glassy bead}}$$

(iii) Borax bead is used for the detection of colored basic radicals under the name borax bead test e.g., $CoSO_4 \rightarrow CoO + SO_3$

$CoO + B_2O_3 \rightarrow Co(BO_2)_2$ Cobalt metaborate (blue)

Basic radical or salt	Fe	Cr	Ni
Colours of borax bead	Green	Green	Brown

2) Boric Acid or Orthoboric Acid [H_3BO_3 or $B(OH)_3$]

Preparation:

(i) By treating borax with dil. HCl or dil. H_2SO_4.

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

Properties:

(i) It is a weak monobasic acid (Lewis acid). It is not a protonic acid but acts as a Lewis acid by accepting electron from a hydroxyl ion like as

$H_3BO_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$

(ii) On heating above 370k, Orthoboric acid forms metaboric acid (HBO_2) which further heating give boric oxide (B_2O_3).

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

3) Diborane (B_2H_6)

Preparation:

(i) It can be prepared by the reduction of boron trihalide with lithium aluminum-hydride.

$4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiCl + 3AlCl$

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(ii) Laboratory Method: Diborane prepared by oxidation of sodium borohydride ($NaBH_4$) with I_2.

$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$ (98% yield)

(iii) Industrial Method: $4BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$

Properties:

i) Lower boranes are color less gases while higher boranes are volatile liquids or solids.

ii) They undergo spontaneous combustion in air due to strong affinity of boron for oxygen.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$ + Heat

iii) Boranes readily hydrolysed by water and give boric acid.

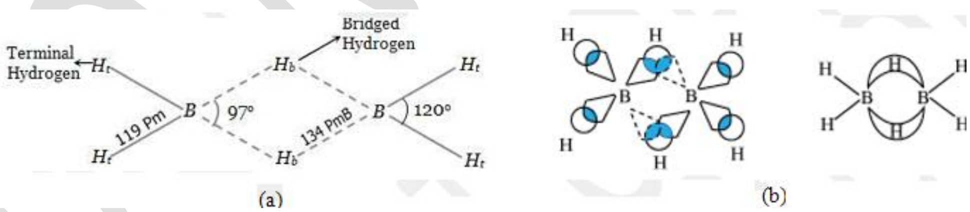
$B_2H_6 + 6\ H_2O\ (l) \rightarrow 2H_3BO_3\ (aq) + 6H_2(g)$

(iv) Diborane reacts with ammonia to give borazine at 450 K. **Borazine** has a cyclic structure similar to benzene and thus is called **inorganic benzene.**

$B_2H_6 + 6NH_3 \rightarrow 3B_3N_3H_3 + 12H_2$

Structure of Diborane: Diborane is an electron deficient molecule. The two boron atoms and the four terminal hydrogen atoms of the molecule are all in the same plane. These four terminal B -H bonds are regular 2-centered- 2 electron bonds.

The bridging hydrogen atoms lie above and below this plane. The two bridges B-H-B bonds are unusual three centered two electron bonds. The boron atoms in diborane undergo sp^3 hybridisation. The overlapping of a vacant sp^3 hybrid orbital of one boron atom and sp^3 hybrid orbital of another boron atom containing one electron with the pure s -orbital of bridging hydrogen containing one electron results in the "banana bond" .Similarly other banana bond is formed on other side .



Uses of Boron and Aluminum:

- As a semi-conductor.
- Boron steel rods are used to control the nuclear reactions because it can absorb neutron.

Uses of Aluminum:

- It forms many useful alloys with Cu, Ag, Mn, Mg, Si and Zn. Those use in packaging, utensil making, construction, aerospace and other transportation industries.
- It is used as a conductor for transmission of electricity.

- Aluminum is also used in the alumino-thermite process for production of chromium and manganese from their ores.

Group 14 Elements: The Carbon Family

General Characteristics:

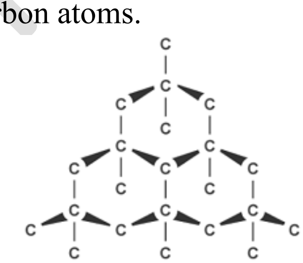
- It includes carbon (C), silicon (Si), germanium (Ge), tin or stannous (Sn) & lead (Pb).
- **General electronic configuration of carbon family:** ns^2np^2.
- **Ionization Enthalpy:** The first ionization enthalpies of group 14 elements are higher than those of the corresponding group 13 elements.
- **Electronegativity:** this group elements are slightly more electronegative than group 13.
- **Catenation tendency:** The tendency for catenation decreases down the group in Group 14. It is due to decrease in bond dissociation energy which is due to increase in atomic size.

  C-C > Si-Si > Ge-Ge > Sn-Sn > Pb-Pb.
- **Chemical properties:** Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 states.
- Tin forms compounds in both oxidation states. Lead compounds in +2 state are stable and in +4 state are strong oxidizing agents.
- Exception: Pb_4 and SnF_4 are ionic in nature.
- Except CCl_4 other tetrachlorides are easily hydrolysed by water.
- Since carbon does not have d-orbitals and hence can't expand its coordination number beyond 4.

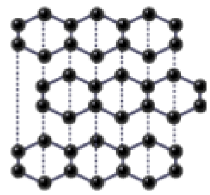
  $CCl_4 + H_2O \rightarrow$ No Reaction

  $SiCl_4 + 4H_2O \rightarrow 4HCl + Si(OH)_4$ Silicic acid
- **Allotropy:** It is the property of the element by which an element can exists in two forms which have same chemical properties but different physical properties due to their structures.
- **Allotropes of Carbon:** The three types of allotropes are –

i) Diamond: In diamond each carbon atom undergoes SP^3 hybridisation. Each carbon is tetrahedrally linked to four other carbon atoms.



ii) Graphite: In graphite, carbon is SP^2 hyberdized. Graphite has a two-dimensional sheet like structure consisting of a number of hexagonal rings fused together. Graphite conducts electricity along the sheet. It is very soft and Slippery.



iii) Fullerence: Its structure is like a soccer ball. It was discovered collectively by three scientists namely R.E Smalley, R.F Curl and H.W Kroto.
They are prepared by heating the graphite in electric arc in presence of inert gases such as helium or argon.

Some Important Compounds of Carbon

Carbon monoxide:
Preparation:
i) It is prepared by direct oxidation of C in limited supply of oxygen.
$2C+O_2\ (g) \rightarrow 2CO\ (g)$
ii) Commercially it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.
$C\ (s) + H_2O\ (g) \rightarrow CO\ (g) + H_2\ (g)$
(Water gas)
(iii) When air is used instead of steam, a mixture of CO and N_2 is produced, which is called Producer gas so Producer gas is a mixture of CO and N_2 in the ratio of 2:1
$C(s) + O_2 + 4N_2\ (g) \rightarrow 2CO\ (g) + 4N_2\ (g)$
(Producer gas)
Water gas and Producer gas are used as fuel.
Properties:
i) It is a powerful reducing agent and reduces all metals oxides. This property is used for extraction of many metals from their oxides ores.
$Fe_2O_3\ (s) + 3CO\ (g) \rightarrow 2Fe\ (s) + 3CO_2\ (g)$
$ZnO\ (s) + CO\ (g) \rightarrow Zn\ (s) + CO_2\ (g)$
ii) CO is poisonous because CO reacts with haemoglobin to form carboxy-haemoglobin which can destroy the oxygen carrying capacity of haemoglobin and the man dies due to suffocation.

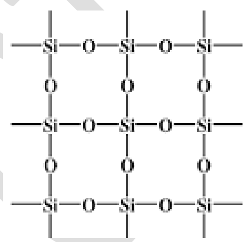
Carbon Dioxide:
Preparation:
i) It is prepared by complete combustion of carbon and carbon fuels in excess of air.

$C(s) + O_2(g) \rightarrow CO_2(g)$
$CH_4 + 2O_2 = CO_2 + 2H_2O$
ii) Laboratory method: In laboratory it is prepared by the treatment of dilute HCl on $CaCO_3$
$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

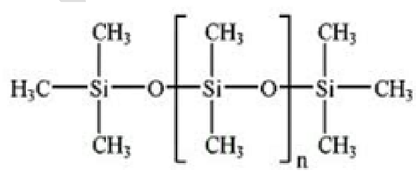
Properties:
i) Photosynthesis: It is the process by which green plants (chlorophyll) convert atmospheric CO_2 in to carbohydrates such as glucose.
$6\,CO_2 + 12\,H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
ii) Excessive content of CO_2 responsible for global warming because excess CO_2 absorbs heat which radiated by the earth. Some of it dissipated into the atmosphere while the remaining part is radiated back to the earth so temperature of the earth increases.
iii) CO_2 also used in solid form as dry ice for refrigerant.
iv) Gaseous CO_2 is extensively used to carbonated soft drinks.

Some Important Compounds of Silicon

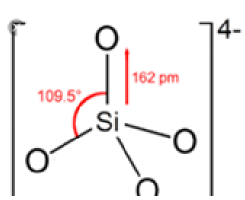
Silicon dioxide (SiO_2): Silicon dioxide is a covalent three dimensional network solid. Each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms.

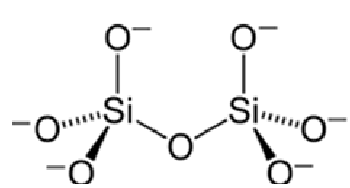


Silicones: Silicones are the synthetic organo-silicon polymers having general formulae $(R_2SiO)n$ in which R = alkyl (methyl,ethyl or phenyl). They are hydrophobic in nature.



Silicates: Silicates are exist in nature in the form of feldspar, zeolites, mica and asbestos etc. The basic structure of silicates is SiO_4^{4-}.Two man-made silicates are glass and cement





Zeolites: Zeolites is an alumino-silicate of metal. Metal cations participating in formation of Zeolite are using usually Na^+, K^+, or Ca^{2+}.

Zeolites are used to remove permanent hardness of water. It widely used as a catalyst in petrochemical industries for cracking of hydrocarbons. ZSM-5 (a type of zeolite) used to convert alcohols in to gasoline.