CHAPTER 11

The p-block elements

Elements in which the last electron enters in the any one of the three p- orbital of their outermost shells – p-block elements

- Gen. electronic configuration of outer shell is ns^2np^{1-6}

The inner core of e-config.may differ which greatly influences their physical & to some extent chemical properties.

- The 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)

(1) Members at the top and on the right of the *p*-block are nonmetals (C, N, P, O, F, S, Cl, Br, I, At).

(2) Those on the left and at the bottom are metals (Al, Ga, In,Tl, Sn, Pb, Sb Bi, Po).

(3) Between the two, from the top left to bottom right, lie an ill-defined group of metalloid elements (B, Si, Ge, As, Te)

GROUP 13 : The boron group

- Outer Electronic Configuration:-ns^2np^1
- group members: boron (B), aluminum (Al), gallium (Ga), indium (In)& thallium (Tl) . All, except boron, are metals.
- Boron show diagonal relationship with Silicon; both are semiconductors metalloids & forms covalent compounds.
- Boron compounds are electron deficient, they are lack of an octet of electrons about the B atom .
- diborane B_2H_6, is simplest boron hydride

- Structure: three-center two-electron: the H atoms are simultaneously bonded to two B atoms the B-H bridging bond lengths are greater than B-H terminal.
- - Boron oxide is acidic (it reacts readily with water to form boric acid)
- aluminium compounds:aluminium oxide is amphoteric
- aluminum halides, e.g., $AlCl_3$ is dimer, an important catalyst in organic chemistry have anincomplete octet, acts as Lewic acid by accepting lone pairs from Lewic bases, forming adduct
- aluminum hydride, e.g., $LiAlH_4$, a reducing agent
- Atomic Properties - 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

. Atomic and ionic radii

- The atomic and ionic radii of group 13 elements are compared to corresponding elements of group 2. From left to right in the period, the magnitude of nuclear charge increases but the electrons are added to, the same shell. These electrons do not screen each other, therefore, the electrons experience greater nuclear charge.
- In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of this group have smaller size than the corresponding elements of second group.
- On moving down the group both atomic and ionic radii are expected to increase due to the addition of new shells. However, the observed atomic radius of Al (143 pm) is slightly more than that of Ga (l35 pm).

Ionization energies

The first ionization energies of group 13 elements are less than the corresponding members of the alkaline earths.

The sharp decrease in I.E. from B to Al is due to increase in size. In case of Ga, there are ten d-electrons in its inner electronic configuration.

The very high value of 3rd I. E. of thallium indicates that +3 O.N. state is not stable, rather +1 is more stable for thallium .

Electropositive (or metallic) character

the elements of group 13 are less electropositive as compared to elements of group 2. On moving down the group the electropositive (metallic) character increases because ionization energy decreases. For e.g., Boron is a non-metal white the other elements are typical metals.

Oxidation states

The common oxidation states of group 13 elements are +3 and + l .The stability of the + 1 oxidation state increases in the sequence Al <Ga< In <Tl, Due to Inert pair effect.

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

Chemical reactivity of Gr.13 Elements

All elements in their compounds exhibit the oxidation state of + 3 and +1.

Hydrides

- None of the group 13 elements reacts directly with hydrogen. However, a no. of hydrides of these elements have been prepared by indirect methods. The boron hydrides are called boranes& classified in two series: (a) B_nH_{n+4} called nidoboranes (b) B_nH_{n+6} called arachnoboranes

- INUDUSTRIAL PREPERATION :-

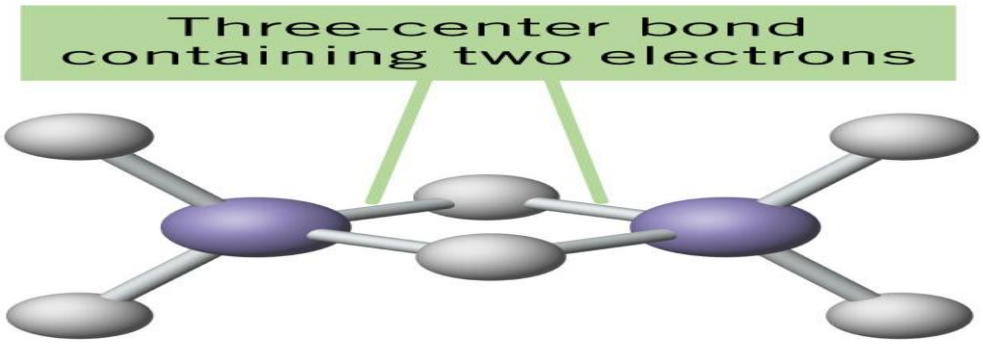
  $2BF_3(g) + 6LiH(s) \rightarrow B_2H_6(g) + 6LiF(s)$

- Laboratory method:

  (i) By the reaction of iodine with sodium borohydride in a high boiling solvent.
  $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

  (ii) By reduction of BCl_3 with $LiAlH_4$
  $4BCl_3 + 3LiAlH_4 \rightarrow 2\ B_2H_6 + 3AlCl_3 + 3\ LiCl$

Structure of Diborane, B_2H_6



Some important characteristics of boranes:

i) Lower boranes are colourless 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 react with alkali metal hydrides in diethyl ether to form borohydride complexes.

$B_2H_6 + 2MH \rightarrow 2M^+[BH_4]^-$ (M= Li or Na)

Metal borohydride

- (iv) Diborane reacts with ammonia to give borazine at 450 K.

  $B_2H_6 + 6NH_3 \rightarrow 3B_3N_3H_6 + 12H_2$

- Borazine has a cyclic structure similar to benzene and thus is called inorganic benzene

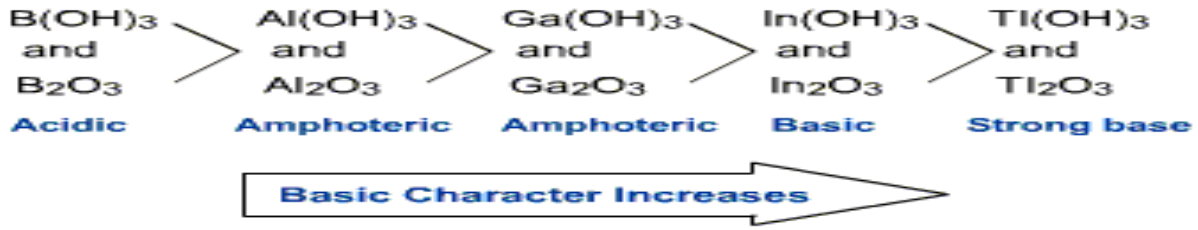
- The other elements of this group form only a few stable hydrides. The thermal stability decreases as we move down the group.

- AlH_3 is a colourless solid polymerized via Al - H - Al bridging units. These hydrides are weak Lewis acids and readily form adducts with strong Lewis base (B:) to give compounds of the type MH_3 (M = Al or Ga). They also form complex-tetrahydrido anions, [MH4]-. The most important tetrahydrido compound is $Li[AlH_4]$

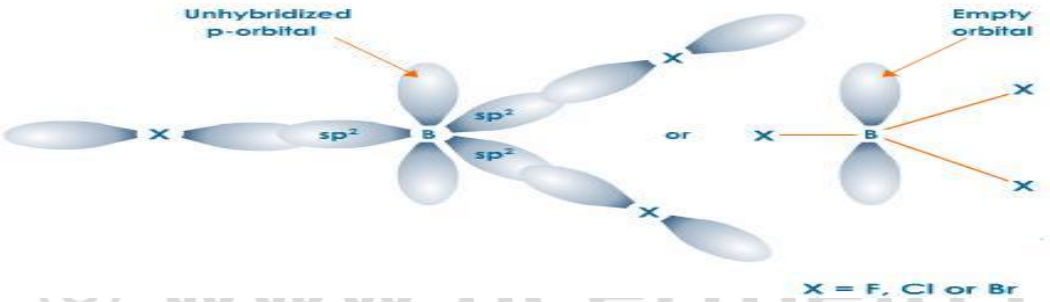
$$4LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$

OXIDES & HYDROXIDES

- M_2O_3& $M(OH)_3$

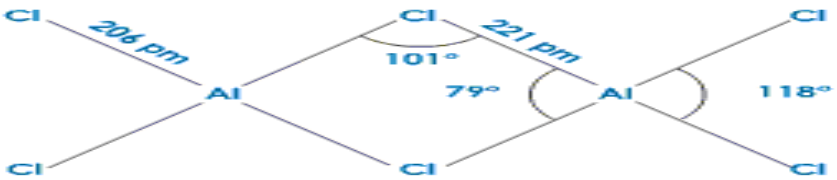


HALIDES: Structure of boron trihalides



Dimeric structure of aluminium chloride

– Boron halides do not form dimers because the size of boron is so small that it is unable to coordinate four large-sized halide ions.



- Anomalous properties of boron

1. Boron is a non-metal & bad conductor of electricity whereas aluminium is a metal & good conductor. B is hard but Al is a soft metal.
2. Boron exists in two forms-crystalline and amorphous. But Al does not exist in different forms.

3. The melting and boiling point of boron are much higher than that of Al .
4. Boron forms only covalent compounds whereas Al forms even some ionic compounds.
5. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.
6. The trihalides of boron exist as monomers. On the other hand, aluminium halides exist as dimers .
7. The hydrides of boron are quite stable while those of aluminium are unstable

- Boron and silicon exhibit the typical properties of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.
- Boron oxide (B_2O_3) and silica (SiO_2) both are acidic and dissolve in alkali solutions to form borates and silicates respectively.

  $B_2O_3 + 6NaOH \rightarrow 2Na_2BO_3 + 3H_2O$

  $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
- The chlorides of both B and Si get hydrolyzed by water to boric acid and silicic acid respectively.

  $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$ $SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$
- The hydrides of Boron and Silicon are quite stable. Numerous volatile hydrides are also known which catch fire on exposure to air and are easily hydrolyzed.
- Both elements are semiconductors.

Behavior in Aqueous Solutions

1 Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their tripositive states. Species like [M(OH)4]-, [M(H2O)2(OH)4]-, [M(OH2)6]3+ for M = Al, Ga, In, exist in aqueous solution.

2. Al, Ga. In and T1 ions exist as octahedral aqua ions, [M(OH2)6]3+ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates.

3. Aluminiumsulphate forms double salts - called alum, having the general formula

$M_2SO_4.Al_2(SO_4)_3.12H_2O$, where M=Na+ or K+.

USES OF BORON & ALUMINIUM

- Aluminium is used extensively in industry and everyday life. It forms many useful alloys with Cu. Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries. It is used as a conductor for transmission of electricity. Aluminium is alsoused in the alumino-thermite process for production of chromium and manganese from their ores.

Group 14 Elements:-The Carbon Family

Group 14 includes carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

General electronic configuration of carbon family is ns^2np^2.

Covalent radius:-Covalent radius expected to increase from Cto Si,

From Si to Pb small increase is found.

Ionization Enthalpy:-The first ionization enthalpies of group 14 elements are higher than those of the corresponding group 13 elements.

Electronegativity:-Group 14 elements are smaller in size as compared to group 13 elements that's why this group elements are slightly more electronegative than group 13

Chemical properties:-

Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state.

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 cannot expand its coordination number beyond 4

$CCl_4 + H_2O$ No Reaction

$SiCl_4 + 4H_2O$ $Si(OH)_4 + 4HCl$

Silicic acid

Allotropes of Carbon:-The three types of allotropes are –

1-Diamond 2-Graphite 3-Fullerence

Diamond:-In diamond each carbon atom undergas SP^3hybridisation.

Each carbon is tetrahedrally linked to four other carbon atoms.

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

FullerenceFullerence was discovered collectively by three scientists namely R.E Smalley,R.F Curl and H.W Kroto

SOME Important Compounds Of Carbon and Silicon

Carbon monoxide:-It I prepared by direct oxdisation of C in limited supply of oxygen.

$$2C+O_2(g) \rightarrow 2CO(g)$$

Commercially it is prepared by the passage of steam over hot coke

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

$$C(s) +O_2(g) \rightarrow CO_2(g)$$

Laboratory method:-

In laboratory it is prepared by the treatment of dilHCl on $CaCO_3$

$$CaCO_3(s) +2HCl(aq) \rightarrow CaCl_2(aq) +CO_2(g)+H_2O(l)$$

Silicon dioxide:-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-siliconpolymers having general formulae $(R_2SiO)_n$ in which R = alkyl (methyl,ethyl or phenyl)

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-}

Zeolites:-Zeolites is aalumino-silicate of metal. Metal cations participating in formationof Zeolite are use usually Na^+,K^+,or Ca^{2+}.

Zeolites are used to remove permanent hardness of water.

ONE MARK QUESTIONS

1. Why is boron used in nuclear reactions?

Ans:-Because Boron can absorb neutrons.

2. By giving a balanced equation show how $B(OH)_3$ behaves as an acid in water.

Ans:-$B(OH)_3 + 2H\overline{OH} \longrightarrow [B(OH)_4]^- + H_3O^+$

3.Name the element of group 14 which exhibits maximum tendency for catenation?

Ans:-Carbon

4. What is the basic building unit of all silicates?

Ans:-$SiO_4^{4-}$is the basic unit of all silicates.

5. What happens when $NaBH_4$ reacts with iodine?

Ans:-$2NaBH_4 + \overline{I_2} \longrightarrow B_2H_6 + 2NaI + H_2$.

6. What happens when boric acid is heated

Ans:-$4H_3BO_3 \longrightarrow 4HBO_{\overline{2}} \longrightarrow H_2B_4O_7$.

7. What is producer gas?

Ans:-Producer gas is a mixture of CO and N_2 in the ratio of 2:1.

8.Write the state of hybridization of 'B' in BF_3.

ANS:-Hybridisation of 'B' in BF_3 is Sp^2.

9.Mention the state of hybridization in B in BH_4^-.

Ans:-Sp^3.

10. Which oxide of carbon is regarded as anhydride of carbonic acid.

Ans:-CO_2 is regarded as a hydride of carbonic acid .

Because $H_2CO_3 \rightarrow H_2O + CO_2$

TWO MARKS QUESTIONS

1. Give the chemical reaction as an evidence for each of the following observations.
   (i) Tin (II) is a reducing agent where as lead (II) is not.

   (ii)Gallium (I) undergoes disproportionation reaction.

Ans:- (i) Due to inert pair effect pb^{2+} is more stable than Pb^{4+}. Whereas Sn^{4+} is more stable than Sn^{2+}.

(ii) $3Ga^{+} \rightarrow \quad 2Ga + Ga^{3+}$

This is because Ga^{3+} is more stable than Ga^{+}.

2. What happens when
   (i) Quick lime is heated with coke?
   (ii) Carbon monoxide reacts with Cl_2

Ans:- (i) $Cao + 3C \rightarrow CaC_2 + CO$

(iii) $CO + Cl_2 \rightarrow COCl_2$

3.Give reason

(i) C and Si are always tetravalent but Ge,Sn,Pb show divalency.

(ii) Gallium has higher ionization enthalpy than Al. Explain.

Ans:-(i) Ge, Sn, Pb show divalency due to inert pair effect, Pb^{2+} is more stable than Pb^{4+}.

(ii) Due to poor shielding effect of d-electrons in Ga effective nuclear charge increases as compared to Al thus the I.E is higher than Al.

4.Give reason why boron and aluminium tend to form covalent compounds.

Ans:-Sumof three ionization of both the element are very high. Thus they have no tendency to lose electrons to form ionic compound.Instead they form covalent compounds.

5.If B-Cl bond has a dipole moment, Explain why BCl_3 molecule has zero dipole moment.

Ans:- B-Cl bond has dipole moment because of polarity.In BCl_3 since the molecule is symmetrical thus the polarities cancel out.

6.Suggest a reason as to why CO is poisonous.

Ans:-CO reacts with haemoglobin to form carboxy-haemoglobin which can destroy the oxygen carrying capacity of haemoglobin and the man dies of suffocation.

7.What do you understand by-

(a) Inert pair effect:-The pair of electron in the valence shell does not take part in bond formation it is called inert pair effect.

(b) 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.

8.How is excessive content of CO_2 responsible for global warming?

Ans:-Excess of CO_2 absorbs heat radiated by the earth.Some of it dissipated into the atmosphere while the remaining part is radiated back to the earth.Temperature of the earth increases.

9.Describe two similarities and two dissimilarities between B and Al.

Ans:-Similarities:-

(i) Both have same number of valence electrons.
(ii) Both have similar electronic configuration.

Dissimilarities:-

(i) Bis a non- metal where Al is a metal
(ii) B forms acidic oxide whereas Al forms atmospheric oxides.

10.What are fullerene? How they were prepared?

Ans:- Fullerene are the allotropes of carbon.Its structure is like a soccer ball.

They are prepared by heating graphite in electric arc in presence of inert gases such as helium or argon.

THREE MARKS QUESTIONS

1.What happens when

(a)Borax is heated strongly

(b)Boric acid is added to water

(c)Aluminium is treated with dilute NaOH

Ans:-(a) $Na_2B_4O_7 . 10H_20 \rightarrow Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$

(b) $B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$

(C) $2Al + 2NaOH + H_2O \rightarrow 2NaAlO_2 + 3H_2$

2.Explain the following reactions.

(a)Silicon is heated with methyl chloride at high temperature in the presence of copper.

(b)Silicon dioxide is treated with hydrogen fluoride.

(c) CO is heated with ZnO.

Ans:- (a) A mixture of mono-,di- and trimethylchlorosilianes along with a small amount of tetramethylsilane is formed.

$CH_3Cl + Si \rightarrow CH_3SiCl_3 + (CH_3)_2 SiCl_2 + (CH_3)_3SiCl + (CH_3)_4 Si$

(b) The initially formed silicon tetrafluroide dissolves in HF to form hydrofluorosilicic acid

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

$SiF_4 + 2HF \rightarrow H_2SiF_6$

(c) ZnO is reduced to zinc metal

$ZnO + CO \rightarrow Zn + CO_2$

3.Give reasons:-

(a)Diamond is used as an abrasive.

(b) Aluminium alloys are used to make aircraft body.

(c) Aluminium utensils should not be kept in water overnight.

Ans:- (a) Diamond is used as an abrasive because it is an extremely hard substance.
(b)Alloys of alumimium likeduralium is used to make aircraft body due to
Someof its property .

(c)Generally aluminium metal does not react with water quickly but when it is kept overnight.It reacts slowly with water in presence of air.

$$2Al(s) + O_2(g) + H_2O(l) \rightarrow Al_2O_3(s) + H_2(g)$$

4.A certain salt X,gives the following results.

(i)Its aqueous solution is alkaline to litmus.

(ii)It swells up to a glassy material Y on strong heating.

(iii)when conc.H_2SO_4 is added to a hot solution of X,whitecrystalof an acid Z separates out.

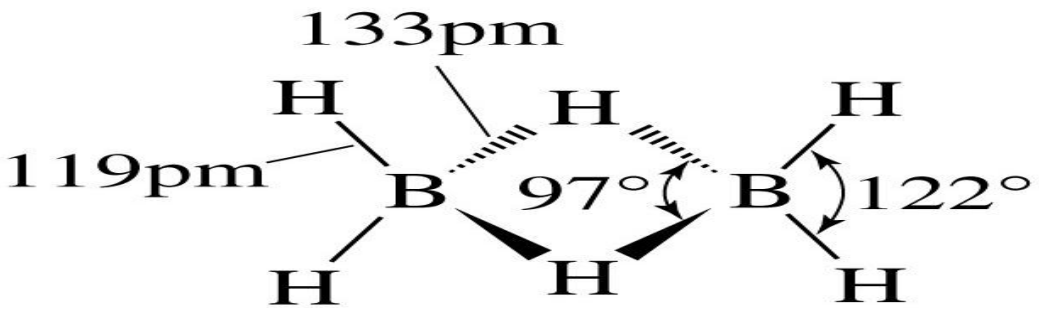
Ans:- (i) $Na_2B_4O_7 + 10H_2O \rightarrow 2NaOH + H_2B_4O_7 + 8H_2O$

(ii) $Na_2B_4O_7 \rightarrow 2NaBO_2 + B_20_3$

(iii)$Na_2B_4O_7.10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$

5. draw structure of diborane .

Ans.



FIVE MARKS QUESTIONS

1 Explain the formation of (i) Water gas (ii) Producer gas. Give their uses. What happens when CO_2 is passed through lime water (i) for short duration (ii) folong duration.

Ans:-(i)$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
(Water gas)

(ii) $2C(s) + O_2 + 4N_2(g) \rightarrow 2CO(g) + 4N_2(g)$
(Producer gas)

Water gas and Producer gas are used as fuel.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

(White ppt.)

(i) $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
(Soluble)

2 (a) Why do Boron halides from addition compound with NH_3 ?
(b) Assign appropriate reason for each of the following observations :-

(i) Anhydrous $AlCl_3$ is used as a catalyst in many organic reactions.
(ii) No form of elemental silicon is comparable to graphite.

Ans:- (a) It is because BX_3 is electron deficient whereas NH_3 is electron rich.

(b) (i) It is Lewis acid.

(ii) It cannot form $p\pi - p\pi$ bond due to large size.

3. (i) Give reason for the following observations:-
(a) The tendency for catenation decreases down the group in Group 14.
(b) The decreasing stability of +3 oxidations state with increasing atomic number in group 13.
(c) PbO_2 is a stronger oxidizing agent than SnO_2.
(d) Molten aluminium bromide is a poor conductor of electricity.

Ans:- (i)(a) 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.

(b) It is due to inert pair effect.

(c) PbO_2 is stronger oxidizing agent than SnO_2 because Pb^{2+} is more stable than Pb^{4+} whereas Sn^{4+} is more stable than Sn^{2+}.

(d) Molten $AlBr_3$ is poor conductor of electricity because it is covalent compound.