UNIT-11
The p-Block Elements

SECTION-A: *NCERT-Intext Questions with Answers*

11.1. Discuss the pattern of variation in the oxidation states of

(i) B to Tl and **(ii) C to Pb**

Ans. (i) In group 13 (Boron family), the group oxidation state is +3 which is obtained by using two electrons from ns and one electron from np subshell. But as we move down the group. The stability of +3 oxidation state decreases and +1 oxidation state increases. This is due to **inert pair effect**. Thallium compounds are stable in +1 oxidation state. Due to the presence of $4f^{14}$ which has a poorest shielding effect, the $6s^2$ electrons are more tightly held by the nucleus than $6p^1$ electron. As a result, only 6p electron take part in bond formation and not 6s electrons.

B	**Al**	**Ga**	**In**	**Tl**
	$\longrightarrow$	decreasing	+3	oxidation state
	$\longrightarrow$	increasing	+1	oxidation state

(ii) In group 14, the valence shell electronic configuration is ns^2np^2 and the group oxidation state is +4 which is obtained by using all four valence electrons. As we move down the group, stability of +4 oxidation state decreases and +2 oxidation state increases Pb compound exist in +2 oxidation state. This is due to **inert pair effect**.

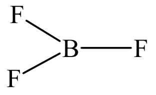
C	**Si**	**Ga**	**Sn**	**Pb**
	$\longrightarrow$	decreasing	+4	oxidation state
	$\longrightarrow$	increasing	+2	oxidation state

11.2. How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

Ans. $TlCl_3$ is less stable than BCl_3, $TlCl_3$ does not exist. Tl form only $TlCl$. This is due to inert pair effect. In Tl, only 6p electron is used in bonding and 6s electron pair remain inert. In BCl_3, B uses all three valence electron in the bond formation and hence BCl_3 is stable.

11.3. Why does boron triflouride behave as a Lewis acid?

Ans. In BF_3, B has form only three covalent bonds and B has only six electrons in the valence shell. In BF_3, B has an incomplete octet and B has a tendency to accept electron pair. Hence, BF_3 is a Lewis acid



11.4. Consider the compounds, BCl_3 and CCl_4. How will they behave with water? Justify.

Ans. In BCl_3, B has an incomplete octet and it can accept electron pair from H_2O. BCl_3 gets hydrolysed by water to form boric acid.

$$BCl_3 + 3H_2O \longrightarrow H_2BO_3 + 3HCl$$

Lewis Lewis boric acid
acid base

In CCl_4, C has a compete octet and also there is no d atomic orbitals available. So, CCl_4 does not react with H_2O, CCl_4 is inert towards water

$$CCl_4 + H_2O \longrightarrow \text{No reaction.}$$

11.5. Is boric acid a protic acid? Explain

Ans. Boric acid is NOT a protic acid. It does not ionize in water to give H^+ and $H_2BO_3^-$. Boric acid is a Lewis acid, it accepts lone pair of electron from H_2O and release H^+ ion. This H^+ ion comes from H_2O.

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_2O^+$$

(from water)

11.6. Explain what happened when boric acid is heated.

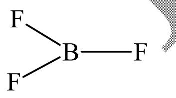
Ans. Effect of heat on boric acid

$$\underset{\text{boric acid}}{H_3BO_3} \xrightarrow{100°C} \underset{\text{metaboric acid}}{HBO_2} + H_2O$$

$$\underset{\text{metaboric acid}}{2HBO_2} \xrightarrow{T > 100°C} \underset{\text{boron oxide}}{B_2O_3} + H_2O$$

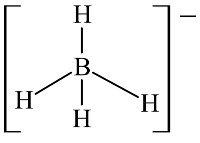
11.7. Describe the shapes of BF_3 and BH_4^-. Assign the hybridization of boron in these species.

Ans. (i) BF_3 $B \longrightarrow sp^2$ hybridized



Trigonal planar in shape, AX_3 type molecule.

(ii) BH_4^- $B \longrightarrow sp^3$ hybridized



Shape is tetrahedral, AX_4 type ion.

11.8 Write reactions to justify amphoteric nature of aluminium.

Ans. Al reacts with both acid and base

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$2Al + 2NaOH + 6H_2O \longrightarrow 2Na[Al(OH)_4] + 3H_2$$

Sodium aluminate

11.9. What are electron deficient compounds? Are BCl_3 and $SiCl_4$ electron deficient species? Explain?

Ans. Electron deficient compound are those compounds in which the central atom has an incomplete octet (having less than eight electrons in the valence shell)

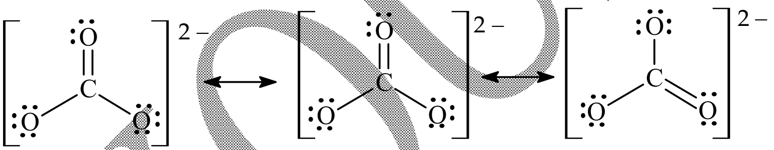
BCl_3 is an electron deficient species as B has only six electrons in the valence shell. It is an electron pair acceptor. It is a Lewis acid.

$$H_3N: + BCl_3 \longrightarrow [H_3N \longrightarrow BCl_3]$$

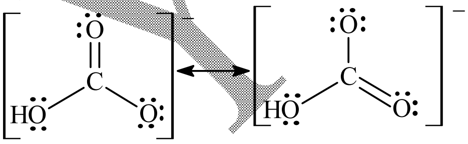
In $SiCl_4$, Si has a complete octet. Due to the presence of empty d-atomic orbitals. Si can accommodate more than eight electrons by accepting 2Cl⁻ ions. But $SiCl_6^{2-}$ does not exist due to large size of Cl, silicon cannot accommodate six chlorine atoms in its coordination shape. Hence, $SiCl_4$ is not an electron deficient species.

11.10. Write the resonance structures of CO_3^{2-} and HCO_3^-.

Ans. **CO_3^{2-}**



HCO_3^-



11.11. What is the state of hybridization of carbon in (a) CO_3^{2-} (b) diamond (c) graphite?

Ans. (a) CO_3^{2-} $C \longrightarrow sp^2$

(b) diamond $C \longrightarrow sp^3$

(c) graphite $C \longrightarrow sp^2$

11.12. Explain the difference in properties of diamond and graphite on the basis of their structures.

Ans.

	Diamond		Graphite
(i)	Each carbon atom is bonded to four other carbon atoms in a tetrahedral fashion.	(i)	Each carbon atom is bonded to three other carbon atoms in a hexagonal layer structure.
(ii)	Each carbon atom is sp^3 hybridised	(ii)	Each carbon atom is sp^2 hybridised
(iii)	Extremely hard with high melting point	(iii)	Soft with high melting point, slippery in touch
(iv)	Insulator since all four electrons have been used in bond formation.	(iv)	Good conductor due to the presence of free electrons.

11.13. Rotationlise the given statements and give chemical reactions.

- **Lead (II) chloride reacts with Cl_2 to give $PbCl_4$.**
- **Lead (IV) chloride is highly unstable towards heat.**
- **Lead is known not to form an iodide. PbI_4.**

Ans. (i) Cl_2 being a strong oxidizing agent oxidizes $PbCl_2$ to $PbCl_4$.

$$PbCl_2 + Cl_2 \longrightarrow PbCl_4$$

(ii) Due to inert pair effect. Pb^{4+} is unstable and will try to attain +2 oxidation state.

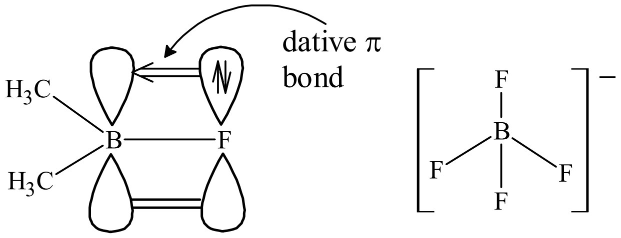
$$PbCl_4 \xrightarrow{\text{Heat}} PbCl_2 + Cl_2$$

(iii) Pb^{4+} being a strong oxidizing agent and I– is a strong reducing agent undergo intramolecular redox reaction to form PbI_2.

$$\overset{4+}{Pb}\ \overset{-1}{I_4} \longrightarrow PbI_2 + I_2$$

11.14. Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

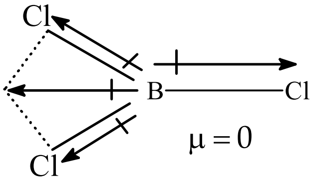
Ans. B–F bond in BF_3 is shorter than B – F bond in BF_4^-. This is due to the presence of dative π bond involving empty 2p atomic orbital of boron and fully filled 2p atomic orbital of fluorine in BF_3. Therefore, B–F bond in BF_3 has a double bond character



B → sp^2 B → sp^3 (complete octet)

11.15. If B – Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

Ans. Due to high electronegativity of Cl, B – Cl bond is polar and has a dipole moment. Each B – Cl bond in BCl_3 has a dipole moment. But BCl_3 is a planar molecule in which the B – Cl bonds are present at an angle of 120°. The resultant of two B – Cl bonds is cancelled by equal and opposite dipole moment of the third B – Cl bond. Hence, BCl_3 molecule has a net dipole moment of zero.



11.16. Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

Ans. Anhydrous H–F is covalent and associated via intermolecular hydrogen bonding. So, AlF_3 is insoluble in anhydrous HF. AlF_3 dissolved in on addition of NaF due to Lewis acid-base reaction and formation of a complex

$$3NaF + AlF_3 \longrightarrow \underset{\text{Soluble}}{Na_3[AlF_6]}$$

When gaseous BF_3 is bubbled through it, then BF_3 being a stronger Lewis acid form a fluoro complex and AlF_3 then get precipitated.

$$Na_3[AlF_6] + 3BF_3 \longrightarrow 3Na^+[BF_4]^- + \underset{\text{precipitate}}{AlF_3}$$

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

Ans. CO molecule is a donor and donates electron pair to the iron present in the haemoglobin and form a complex carboxy-haemoglobin. This complex is about 300 times more stable than oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death. That's why CO is highly poisonous.

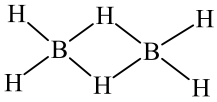
11.18. How is excessive content of CO_2 responsible for global warming?

Ans. Unlike CO, CO_2 is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture increase the content of CO_2 in the atmosphere. This has lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which has serious consequences (like melting of glaciers)

11.19. Explain structures of diborane and boric acid.

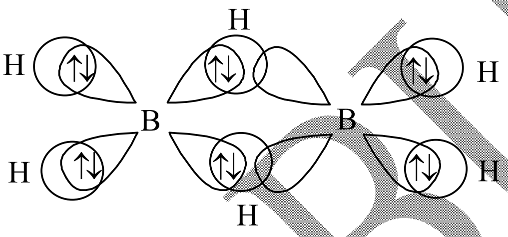
Ans. Structure of diborane

The structure of diborane is



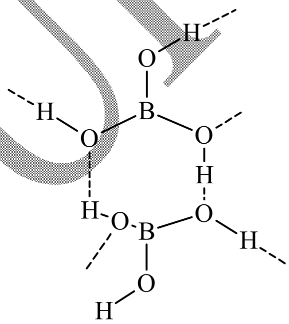
each B atom is sp^3 hybridised.

Four terminal B – H bonds are normal $2e^-$ – 2c covalent bonds and bridged part of the molecule contains $2e^-$ – 3c multicentre covalent bonds. These are also called banana bonds. These bonds are delocalized and gives stability to molecule.



Structure of boric acid

Boric acid has a layer structure in which planar BO_3 units are joined by hydrogen bonds. Boron atom is sp^2 hybridised.



11.20. What happens when

(a) Borax is heated strongly

(b) Boric acid is added to water.

(c) Aluminium is treated with dilute NaOH

(d) BF_3 is reacted with ammonia?

Ans. (a) Borax on strong heating gives sodium meta borate and boron oxide as a transparent glassy bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\text{Strong heat}} 2NaBO_2 + B_2O_3$$

Sodium meta borate

(b) Boric acid when added to water form $[B(OH)_4]^-$ and act as a Lewis acid

$$B(OH)_3 + 2H_2O \rightleftharpoons [B(OH)_4]^- + H_3O^+$$

Boric acid (Lewis acid)

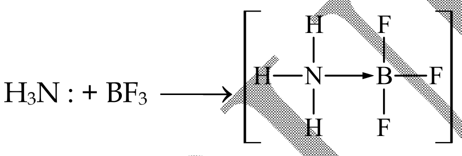
(c) Aluminium when treated with dilute NaOH form sodium aluminate

$$2Al + 2NaOH + 6H_2O \longrightarrow 2Na\,[Al(OH)_4] + 3H_2$$

Sodium aluminate

(d) BF_3 forms an adduct with NH_3.

BF_3 is a Lewis acid and accept lone pair of electron from NH_3.



$$H_3N: + BF_3 \longrightarrow \left[\begin{array}{c} \ \ H\ \ \ \ \ \ \ F \\ H-N\rightarrow B-F \\ \ \ H\ \ \ \ \ \ \ F \end{array}\right]$$

adduct

11.21. 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

(d) Hydrated alumina is treated with aqueous NaOH solution.

Ans. (a) Dimethyl dichloro silane is formed.

$$2CH_3Cl + Si \xrightarrow[300°C]{Cu} (CH_3)_2SiCl_2$$

(b) First SiO_2 reacts with HF to form SiF_4 and with excess of HF, SiF_4 dissolves to give fluoro complex $H_2[SiF_6]$

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

$2HF + SiF_4 \longrightarrow \underset{\text{soluble}}{H_2[SiF_6]}$

(c) CO is a reducing agent and reduces ZnO to Zn in metallurgy

$CO + ZnO \longrightarrow Zn + CO_2$

(d) Hydrated alumina forms sodium aluminate with NaOH

$Al_2O_3.2H_2O + 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4]$

11.22. Give reasons:

(i) Conc. HNO_3 can be transported in aluminium container.

(ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.

(iii) Grahite is used as lubricant.

(iv) Diamond is used as an abrasive

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

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

(vii) Aluminium wire is used to make transmission cables.

Ans. (i) Conc. HNO_3 oxidises Al to Al_2O_3. This Al_2O_3 forms a protective layer on Al and prevent further reaction of Al with HNO_3. Al becomes passive and hence used in the transportation of HNO_3.

$2Al + 6HNO_3 \longrightarrow Al_2O_3 + 6NO_2 + 3H_2O$

(ii) Al reacts with NaOH to liberate H_2 gas with high pressure and is used to open clogged drain

$2Al + 2NaOH + 6H_2O \longrightarrow 2Na[Al(OH)_4] + 3H_2$

(iii) Graphite has a layer structure and there exist weak van der Waal forces between the layers. As a result layers can slip over each other. Hence graphite used as a lubricant.

(iv) Diamond is used as an abrasive due to its hardness. This hardness arises due to its three dimensional network structure with carbon sp^3 hybridised.

(v) Aluminium alloys (like duralumin, magnalium) are hard, light in weight and corrosion resistant.

(vi) Aluminium dissolves in aerated water to form aluminium oxide which may dissolve to give Al^{3+}. This Al^{3+} is poisonous.

$$2Al + H_2O + O_2 \longrightarrow Al_2O_3 + H_2$$

(vii) This is because aluminium is a good conductor of electricity.

11.23. Explain why is there a phenomenal decrease in ionization enthalpy form carbon to silicon?

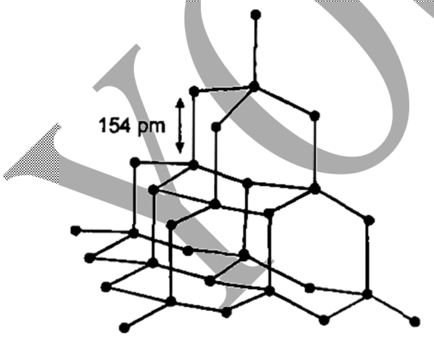
Ans. This is due to considerable increase in atomic size and screening effect that the valence electrons are less tightly held by the nucleus in silicon than in carbon. Hence, there is phenomenal decrease in inionization enthalpy from C to Si.

11.24. How would you explain the lower atomic radius of Ga as compared to Al?

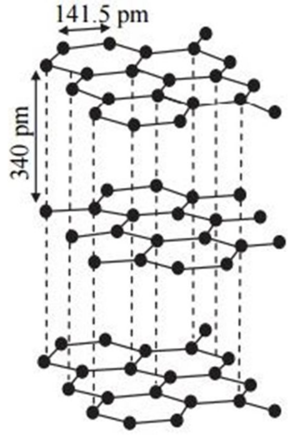
Ans. Ga has a fully filled $3d^{10}$ subshell. These 3d electron have a poor shielding effect and protect the valence electrons from the nucleus less effectively. As a result, nucleus exerts a strong force on the valence electrons. The valence electrons are attracted strongly towards the nucleus. Hence, atomic radius of Ga is lower as compared to Al.

11.25. What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

Ans. Allotropy is a phenomenon in which an element exist in two or more forms which have different physical properties but same chemical properties. The different forms are called **allotropes.**



Structure of Diamond



Structure of graphite

(i) Diamond is extremely hard while graphite is soft.

(ii) Diamond is an insulator while graphite is a good conductor of electricity.

(iii) Diamond has sp^3 carbon while graphite has sp^2 carbonation.

11.26. (a) Classify following oxides as neutral, acidic, basic or amphoteric.

CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

(b) Write suitable chemical equations to show their nature.

Ans. (a) Neutral oxides: CO

(b) Acidic oxides: SiO_2, CO_2, B_2O_3

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O$$

(c) Basic oxide, Ti_2O_3

$$Ti_2O_3 + 6HCl \longrightarrow 2TiCl_3 + 3H_2O$$

(d) Amphoteric oxides: Al_2O_3, PbO_2

$$\left[\begin{array}{l} Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O \\ Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4] \end{array}\right.$$

$$\left[\begin{array}{l} 2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2 \\ PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O \end{array}\right.$$

11.27. In some of the reactions thallium resembles aluminium, whereas in others it resembles with group 1 metals. Support this statement by giving some evidences.

Ans. Aluminium shows only +3 oxidation state. Tl being in the same group also shows +3 oxidation state in $TlCl_3$, Tl_2O_3 and like $[AlF_6]^{3-}$, Tl also form $[TlF_6]^{3-}$. But due to inert pair effect, Tl also shows +1 oxidation state and resembles group 1 metals.

Like NaOH, TlOH is also a strong base and is water soluble.

Like Na_2O, Tl_2O is also strongly basic.

11.28. When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

Ans. X $\longrightarrow$ Al C $\longrightarrow$ $AlCl_3$

A $\longrightarrow$ $Al(OH)_3$ D $\longrightarrow$ Al_2O_3

B $\longrightarrow$ $Na[Al(OH)_4]$

The reactions involved are:

$$\underset{(X)}{2Al} + 2NaOH + 6H_2O \longrightarrow \underset{\substack{(A)\\ \text{White gelatinous ppt}}}{2Al(OH)_3} + 2NaOH + 3H_2$$

$$\underset{(A)}{Al(OH)_3} + \underset{\text{excess}}{NaOH} \longrightarrow \underset{\substack{\text{soluble}\\ (B)}}{Na[Al(OH)_4]}$$

$$\underset{(A)}{Al(OH)_3} + 3HCl \longrightarrow \underset{(C)}{AlCl_3} + 3H_2O$$

$$\underset{(A)}{2Al(OH)_3} \xrightarrow{\text{Heat}} \underset{(D)}{Al_2O_3} + 3H_2O$$

Electrolytic reduction of molten Al_2O_3 gives Al metal at cathode.

11.29. What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

Ans. (a) **Inert pair effect**

As we move down the group in p-block (especially in groups 13, 14, 15), the tendency of the ns electron pair in the valence shell to remain inert or not to take part in the chemical reaction increases. This is known as **inert pair effect**. This is due to ineffective shielding of the valence electrons by the intervening d and f electrons. As a result the last element in a given group shows an oxidation state two units less than the group oxidation state.

(b) **Allotropy**

It is a phenomenon in which the element exists in two or more different physical forms with same chemical properties, the different physical forms are called the allotropes.

(c) **Catenation**

It is defined as the ability of an atom to form a bond with itself. This self-linking property is known as catenation

11.30. 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, white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

Ans. (i) Salt (X) is a salt of a strong base and weak acid as its aqueous solution is alkaline to litmus.

(ii) Salt (X) must be borax as it swells up to a glassy material (Y) on strong heat. (Y) is a mixture of sodium metaborate and boron oxide.

(iii) When conc. H_2SO_4 is added to hot solution of X, while crystal of an acid (Z) separate and (Z) is a boric acid.

The chemical equations involved are:

$$\underset{\text{Borax (X)}}{Na_2B_4O_7.10H_2O} \xrightarrow{H_2O} \underset{\text{(strong base)}}{2NaOH} + \underset{\text{(weak acid)}}{H_2B_4O_7} + 8H_2O$$

$$\underset{\text{(X)}}{Na_2B_4O_7.10H_2O} \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\text{Strong heat}} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy material (Y)}}$$

$$\underset{\text{(X)}}{Na_2B_4O_7.10H_2O} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\substack{\text{Boric acid}\\ \text{(Z)}}}{4H_3BO_3} + 5H_2O$$

11.31. Write balanced equations for:

(i) $BF_3 + LiH \longrightarrow$

(ii) $B_2H_6 + H_2O \longrightarrow$

(iii) $NaH + B_2H_6 \longrightarrow$

(iv) $H_3BO_3 \xrightarrow{\Delta}$

(v) $Al + NaOH \longrightarrow$

(vi) $B_2H_6 + NH_3 \longrightarrow$

Ans. (i) $2BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiF$

(ii) $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

(iii) $2NaH + B_2H_6 \longrightarrow 2Na[BH_4]$

(iv) $H_3BO_3 \xrightarrow{\Delta} HBO_2 + H_2O$

$2HBO_2 \xrightarrow{\Delta} H_2O + B_2O_3$

(v) $2Al + 2NaOH + 6H_2O \longrightarrow 2Na[Al(OH)_4] + 3H_2$

(vi) $B_2H_6 + 2NH_3 \longrightarrow 2BH_3.NH_3$

11.32. Give one method for industrial preparation and one for laboratory preparation of CO and CO₂ each.

Ans.

	Industrial preparation	**Laboratory preparation**
Carbon monoxide, CO	$\underset{(s)}{C} + \underset{(g)}{\frac{1}{2}O_2} \xrightarrow[\text{supply}]{\text{limited}} CO_{(g)}$	$\underset{\text{formic acid}}{HCOOH} \xrightarrow{H_2SO_4} H_2O + CO$
Carbon dioxide, CO₂	$C(s) + O_2(g) \xrightarrow{\text{excess}} CO_2(g)$	$CaCO_3(s) + 2HCl(aq) \longrightarrow$ $CaCl_2(aq) + H_2O(l) + CO_2(g)$

11.33. An aqueous solution of borax is

(a) neutral **(b) amphoteric** **(c) basic** **(d) acidic**

Ans. (c)

Borax is a salt of strong base NaOH nad weak acid $H_2B_4O_7$.

11.34. Boric acid is polymeric due to

(a) its acidic nature **(b) the presence of hydrogen bonds**

(c) it monobasic nature **(d) its geometry**

Ans. (b)

Boric acid is polymeric due to its layer structure in which planar BO_3 units are joined by hydrogen bonds.

11.35. The type of hybridization of boron in diborane is

(a) sp **(b) sp²** **(c) sp³** **(d) dsp²**

Ans. (c)

In B_2H_6, each boron atom is sp^3 hybridised.

11.36. Thermodynamically the most stable form of carbon is

(a) diamond (b) graphite (c) fullerenes (d) coal

Ans. (b)

Thermodynamically, the most stable form of carbon is graphite.

11.37. Elements of group 14

(a) exhibit oxidation state of +4 only

(b) exhibit oxidation state of +2 and +4

(c) form M^{2-} and M^{4+} ions

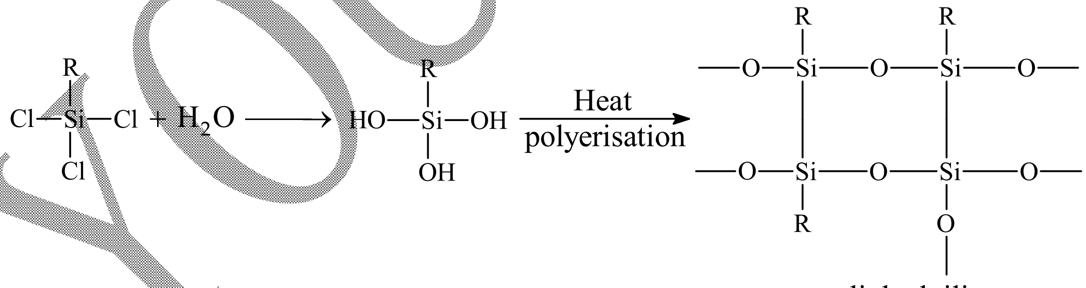
(d) form M^{2+} and M^{4+} ions

Ans. (b)

Elements of group 14 exhibit oxidation state of +2 and +4 due to inert pair effect.

11.38. If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

Ans. Hydrolysis of $RSiCl_3$ gives cross-linked silicones



cross linked silicone

* * *