11 The p-Block Elements

LESSON AT A GLANCE

- **P-Block elements:** Contains, metals, non-metals and metalloids.
- **General configuration:** ns^2np^{1-6}
- Boron is a typical non-metal and the other members are metals.
- Boron halides are considered to be have like Lewis acids.
- Boric acid is a Lewis acid.
- Borax is a white crystalline solid. Formula is $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$
- Aluminium exhibits +3 oxidation state.
- **Catenation:** Ability of carbon to form chains or rings not only with *C-C* single bonds but also with multiple bonds (*C* ° *C* or *C* ° *C*). The tendency of catenation decreases as C >> Si > Ge » Sn > Pb
- **Allotropy:** The important allotropes of carbon are diamond and graphite.
- The members of carbon family exhibit +4 and +2 oxidation state. The tendency to show +2 oxidation state increases among heavier elements.
- Lead in +2 state is stable whereas in +4 oxidation state it is a strong oxidising agent.
- Carbon monoxide is neutral whereas CO_2 is acidic in nature.
- Carbon monoxide having lone pair of electrons on *C* forms metal carbonyls.
- Carbon monoxide forms a haemoglobin complex which is deadly poisonous due to its higher stability.
- Zeolites are complex aluminium silicates.

TEXTBOOK QUESTIONS SOLVED

Q1. *Discuss the pattern of variation in the oxidation states of (i) B to Tl and (ii) C to Pb.*

Ans. (*i*) *B* to *Tl*

Common oxidation states are +1 and +3. The stability of +3 oxidation state decreases from *B* to *Tl*.

+1 oxidation state increase from *B* to *Tl*.

(*ii*) From ***C* to *Pb***

The common oxidation states are +4 and +2. Stability of +4 oxidation state decreases from *C* to *Pb*.

Q2. *How can you explain higher stability of BCl_3 as compared to $TlCl_3$?*

Ans. Higher oxidation state in BCl_3, is more stable while in $TlCl_3$, it is the lower oxidation state. Also in BCl_3, the molecule attains extra stability via back bonding ($p\pi$-$p\pi$) and the octet of boron atom is satisfied.

Q3. *Why does boron trifluoride behave as a Lewis acid?*

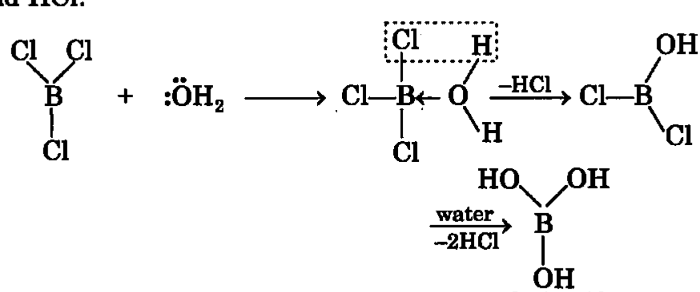
Ans. In BF_3, boron atom is electron deficient. Its octet is not complete where a 2*p*-orbital in B atom is empty. It has the tendency to accept a pair of electrons and so acts as a Lewis acid, *e.g.*,

$$F_3B \longleftarrow :NH_3 \quad \text{or} \quad F_3B \longleftarrow :F^-$$

Lewis acid Lewis base

Q4. *Consider the compounds, BCl_3 and CCl_4. How will they behave with water? Justify.*

Ans. BCl_3 is an electron deficient molecule whereas B atom has an empty 2*p*-orbital. A water molecule acts as a ligand and donates a pair of electrons to B atom. In this process, BCl_3 undergoes hydrolysis to form boric acid $B(OH)_3$ or H_3BO_3 and HCl:



Boric acid

CCl_4 does not get hydrolysed because octet in C atom is complete and also it does not have any vacant *d*-orbital in the valence shell.

Q5. *Is boric acid a protic acid? Explain.*

Ans. Boric acid is a Lewis acid, it is not a protic acid.

Boric accepts electrons from hydroxyl ion of H_2O molecule.

$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

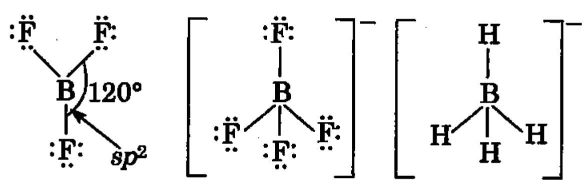
Q6. *Explain what happens when boric acid is heated.*

Ans. On heating boric acid above 370 K it forms metaboric acid, HBO_2 which on further heating yields boric oxide B_2O_3.

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

Q7. *Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.*

Ans.



B is sp^3 in both.

Q8. *Write reactions to justify amphoteric nature of aluminium.*

Ans. Amphoteric nature of Al is shown by the following reactions:

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

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

Q9. *What are electron deficient compounds? Are BCl_3 and $SiCl_4$ electron deficient species? Explain.*

Ans. Electron deficient species are those in which the central atom in their molecule has the tendency to accept one or more electron pairs. They are also known as Lewis acid. BCl_3 and $SiCl_4$ both are electron different species.

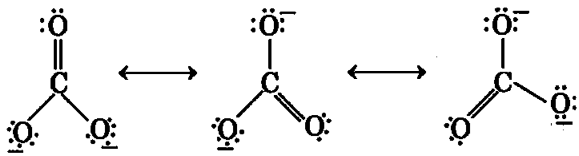
In BCl_3 *B* atom has only six electrons. Therefore, it is an electron deficient compound.

In $SiCl_4$ the central atom has 8 electrons but it can expand its covalency beyond 4 due to the presence of *d*-orbitals.

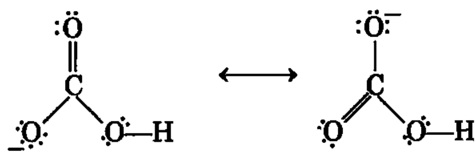
Thus $SiCl_4$ should also be considered as electron deficient species.

Q10. *Write the resonance structures of CO_3^{2-} and HCO_3^-.*

Ans. Resonating structures of CO_3^{2-} ion are



Resonating structures of HCO_3^- ion



Q11. *What is the state of hybridisation of carbon in (a) CO_3^{2-} (b) diamond (c) graphite?*

Ans. (*a*) sp^2; (*b*) sp^3; (*c*) sp^2

Q12. *Explain the difference in properties of diamond and graphite on the basis of their structures.*

Ans. (*i*) Since diamond exists as a three dimensional network solid, it is the hardest substance known with high density and high melting point.

Whereas in graphite any two successive layers are held together by weak forces of attraction. This makes graphite soft.

(*ii*) In graphite carbon atom is sp^2 hybridized whereas in diamond carbon atom is sp^3 hybridized.

Q13. *Rationalise 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*) Lead shows two oxidation states +2 and +4 due to the inert-pair effect. The lower oxidation state is more stable and thus the compound $PbCl_2$ is more ionic than $PbCl_4$:

$$PbCl_2(s) + Cl_2(g) \longrightarrow PbCl_4(l)$$

(*ii*) $PbCl_4$ is more covalent than ionic because of inert-pair effect. The covalent character can also be explained on the basis of the very high polarizing power of Pb^{4+}

ion for Cl^- ions (Fajans' Rules). Covalent $PbCl_4$ gets easily decomposed on heating:

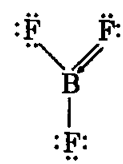
$$PbCl_4(l) \xrightarrow{\Delta} PbCl_2(s) + Cl_2(g)$$

(*iii*) Pb^{4+} is highly oxidising in nature because of its tendency to change to Pb^{2+} (inert-pair effect). Iodide ions, I^-, on the other hand, have strong reducing power hence PbI_4 does not exist. High oxidising power of Pb^{4+} and high reducing power of I^- ions always result in the formation of PbI_2 and not PbI_4.

Q14. *Suggest reasons why the B—F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.*

Ans. BF_3 molecule is planar trigonal with B atom assuming sp^2 hybridisation.

BF_3 gets stabilised via $p\pi$-$p\pi$ back-bonding as:



When $[BF_4]^-$ is formed as:

$$BF_3 + F^- \longrightarrow [BF_4]^-$$

the hybridisation of B atom changes to sp^3 with four single σ-bonds. In BF_3, the sp^2 bonds have double bond character and so are shorter in length.

Q15. *If B—Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.*

Ans. Bond moment depends on the difference in the electronegativity values as in B—Cl bond in BCl_3 molecule. However, the overall dipole moment of the molecule depends on the geometry of the molecule. Since BCl_3 is symmetrical molecule, trigonal planar and the resultant moments cancel the effect of bond moments and the net result is that the dipole moment of BCl_3 molecule is zero.

Q16. *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. (*i*) HF is extensively hydrogen bonded and furnishes little F^+ ions. In the absence of an excess F^- ions, AlF_3 does not dissolve in HF. However, NaF in HF furnishes excess F^- ions for AlF_3 which dissolves forming the complex $Na_3[AlF_3]$:

$$3NaF + AlF_3 \longrightarrow Na_3[AlF_6]$$

Sod. hexafluoridoaluminate (III)

(*ii*) When BF_3 is bubbled through $Na_3[AlF_6]$, a stronger Boron complex is formed and AlF_3 is precipitated.

$$Na_3[AlF_6] + 3BF_3 \longrightarrow 3Na[BF_4] + AlF_3(s)$$

Sod. tetrafluoridoborate (III)

Q17. *Suggest a reason as to why CO is poisonous.*

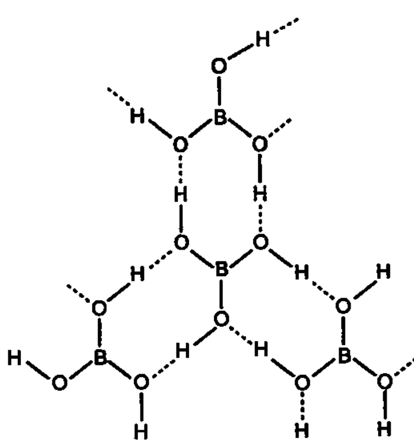
Ans. CO reacts with haemoglobin to form carboxyhaemoglobin which can destroy the oxygen carrying capacity of haemoglobin and the man dies of suffocation.

Q18. *How is excessive content of CO_2 responsible for global warming?*

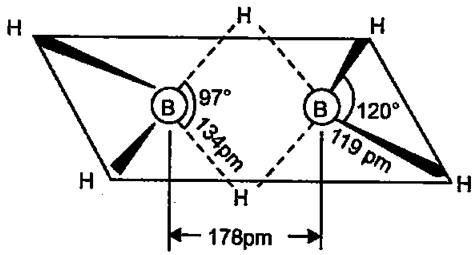
Ans. Excess of CO_2 absorbs heat radiated by the earth. Some of it is dissipated into the atmosphere while the remaining part is radiated back to the earth. As a result, temperature of the earth increases. This is the cause of global warning.

Q19. *Explain structures of diborane and boric acid.*

Ans. Boric acid contains planar BO_3^{3-} ions which are linked together through hydrogen bonding shown in the fig.



Structure of boric acid



Structure of Diborane (B_2H_6) molecule

Q20. *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*) When borax is heated strongly, a transparent glassy substance is formed which consists of sodium metaborate ($NaBO_2$) and boron (III) oxide, B_2O_3:

$$\underset{\text{Borax}}{Na_2B_4O_7 \cdot 10H_2O(s)} \xrightarrow{\text{heat}} \underbrace{2NaBO_2(s) + B_2O_3(s)}_{\text{Transparent glassy substance}} + 10H_2O(g)$$

(*b*) Boric acid is a very weak monobasic acid and acts as an electron acceptor (Lewis acid) rather than a proton donor:

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

(*c*) Hydrogen gas is evolved when Al is treated with dil. NaOH :

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

(*d*) When BF_3 and NH_3 are interacted, a complex compound is formed where BF_3 acts as a Lewis acid while NH_3 as a Lewis base:

$$BF_3 + :NH_3 \longrightarrow \underset{\text{Complex}}{[F_3B \leftarrow NH_3]}$$

Q21. *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*) A mixture of mono-, di- and trimethylchlorosilanes are formed along with a small amount of tetramethylsilane:

$$\underset{\text{Methyl chloride}}{CH_3Cl} + Si \xrightarrow[573\text{ K}]{\text{Cu catalyst}} CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl + (CH_3)_4Si$$

(*b*) Silicon tetrafluoride is formed which dissolves in excess of HF to give hexafluorosilicic acid (H_2SiF_6):

$$SiO_2(s) + 4HF(l) \longrightarrow SiF_4(g) + 2H_2O(l)$$

$$SiF_4(g) + 2HF(l) \longrightarrow H_2SiF_6(l)$$

(*c*) ZnO is reduced to Zn metal:

$$ZnO(s) + CO(g) \xrightarrow{\text{heat}} Zn(l) + CO_2(g)$$

(*d*) $$Al_2O_3 \cdot 2H_2O(s) + 2NaOH(aq) + H_2O(l) \xrightarrow{\text{heat}} 2Na[Al(OH)_4](aq).$$

Q22. *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*) *Graphite 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*) Al, initially, reacts with conc. HNO_3 but soon it is covered with a very tough thin layer of aluminium oxide. This thin film protects aluminium surface from further attack. In this way, Al becomes passive and thus, conc. HNO_3 can be transported in aluminium container.

$$2Al(s) + 6HNO_3(aq) \longrightarrow Al_2O_3(s) + 6NO_2(g) + 3H_2O(l)$$

(*ii*) NaOH reacts with Al to evolve H_2 gas. Thus the pressure of the gas produced can be used for clogged drains.

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

(*iii*) Graphite has layered structure where the layers are held by means of weak van der Waals' forces. These layers slide over each other which accounts for the lubricating properties and also the softness of graphite.

(*iv*) Because of the extreme hardness of diamond, it is used as an abrasive.

(*v*) It is due to the fact that Al alloys are light, tough and resistant to corrosion, thus are used to make aircraft body.

(*vi*) If kept in water, aluminium utensil reacts slowly with water containing impurities (disoslved salts):

$$2Al(s) + 6H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3H_2(g)$$

(*vii*) Since Al is a very good conductor of electricity, it is used to make transmission wires. Weight by weight Al is a better conductor than copper.

Q23. *Explain why is there a phenomenal decrease in ionisation enthalpy from carbon to silicon?*

Ans. Ionisation enthalpy decreases from C to Si as a group trend but the decrease is more than what is expected. It is basically due to the much larger size of Si(118 pm) as compared to C(77 pm). For the large Si atom, the force of attraction between the valence electrons and nucleus is much less and so the ionisation enthalpy decreases much sharply.

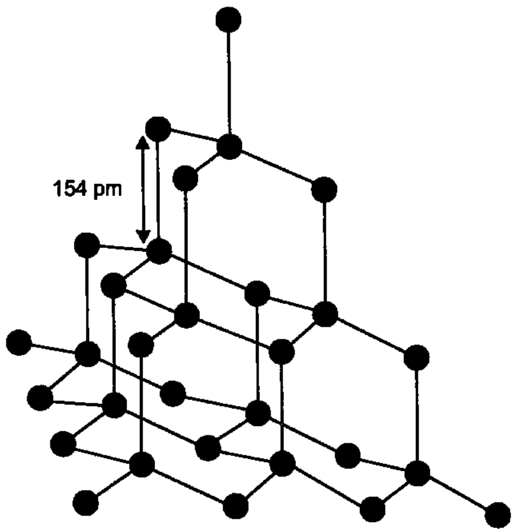
Q24. *How would you explain the lower atomic radius of Ga as compared to Al?*

Ans. Due to poor shielding effect of *d*-electrons in Ga.

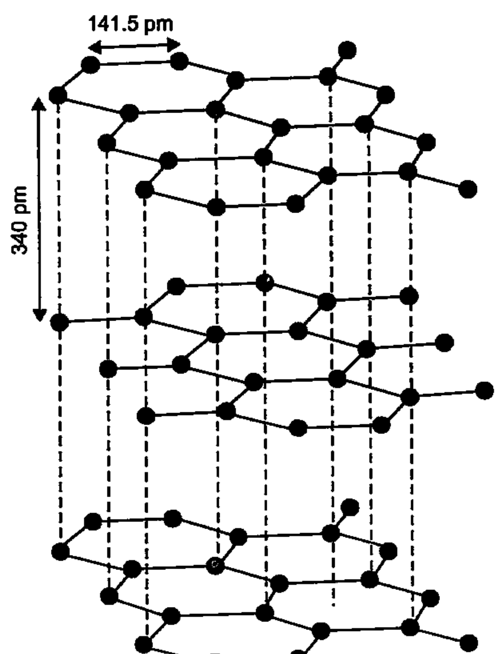
The electrons in gallium experience great force of attraction by nucleus as compared to Al.

Q25. *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. **Allotropes:** Allotropes are the different forms of an element which are having same chemical properties but different physical properties due to their structures.



Structure of diamond



Graphite

Q26. (*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. Neutral oxides: CO

Acidic oxides: B_2O_3, SiO_2 and CO_2

Amphoteric oxides: Al_2O_3 and PbO_2

Basic oxide: Tl_2O_3.

Q27. *In some of the reactions thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.*

Ans. (*i*) Like Al, thallium shows +3 oxidation state in some of its compounds such as $TlCl_3$, Tl_2O_3. Both form similar octahedral complexes, *e.g.*, $[AlF_6]^{3-}$ and $[TlF_6]^{3-}$.

(*ii*) Because of inert-pair effect, Tl shows +1 oxidation state in some of its compounds like Group 1 elements, *e.g.*, TlCl, $TlClO_4$ and Tl_2O. Tl_2O is a basic oxide like Group 1 oxides, Na_2O.

Q28. *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. From the information, the metal X is aluminium. The reactions are:

$$\underset{(X)}{Al(s)} + 3NaOH(aq) \longrightarrow \underset{\text{White (A)}}{Al(OH)_3(s)} + 3Na^+(aq)$$

$$\underset{(A)}{Al(OH)_3(s)} + NaOH(aq) \longrightarrow \underset{\text{Soluble complex (B)}}{Na[Al(OH)_4](aq)}$$

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

$$2Al(OH)_3(s) \xrightarrow{\text{heat}} Al_2O_3(s) + 3H_2O(g)$$

Al_2O_3 (alumina) is used to extract Al.

Q29. *What do you understand by (a) inert-pair effect (b) allotropy and (c) catenation?*

Ans. (*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 or forms which have same chemical properties but different physical properties due to their structures.

(*c*) **Catenation:** The property to form chains or rings not only with single bonds but also with multiple bonds with it self is called catenation.

For ex carbon forms chains with ($C - C$) single bonds and also with multiple bonds ($C = C$ or $C \equiv C$).

Q30. *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. From the information provided:

X is borax $Na_2B_4O_7.10H_2O$.

Y is a mixture of $NaBO_2$ and B_2O_3.

Z is boric acid, H_3BO_3.

Reactions occurring are:

(*i*) $$\underset{\text{Borax(X)}}{Na_2B_4O_7.10H_2O(s)} \xrightarrow{\text{water}} \underset{\text{(Strong base)}}{2NaOH(aq)} + \underset{\text{(Weak acid)}}{H_2B_4O_7(aq)} + 8H_2O(l)$$

(*ii*) $$\underset{\text{(X)}}{Na_2B_4O_7.10H_2O(s)} \xrightarrow{\text{heat}} Na_2B_4O_7(s) + 10H_2O(g)$$

(X swells and loses water)

$$Na_2B_4O_7(s) \xrightarrow{\text{heat}} \underbrace{\underset{\text{Sod. metaborate}}{2NaBO_2(s)} + B_2O_3(s)}_{\text{glassy material(Y)}}$$

(*iii*) $$Na_2B_4O_7.10H_2O(aq) + \text{conc.}H_2SO_4 \longrightarrow \underset{\text{Boric acid (Z)}}{4H_3BO_3(s)} + Na_2SO_4(aq) + 5H_2O(l)$$

Q31. *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*) $2BF_3 + 6LiH \longrightarrow \underset{\text{Diborane}}{B_2H_6} + 6LiF$

(*ii*) $B_2H_6 + 6H_2O \longrightarrow \underset{\text{Boric acid}}{2H_3BO_3} + 6H_2$

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

Sod. tetrahydridoborate (III) or sod. borohydride

(*iv*) $H_3BO_3 \xrightarrow{\Delta} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

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

(*vi*) $B_2H_6 + 2NH_3 \longrightarrow 2[BH_3 \cdot NH_3]$

Q32. *Give one method for industrial preparation and one for laboratory preparation of CO and* CO_2 *each.*

Ans. Carbon monoxide

Industrial: $2C(s) + O_2(g) \xrightarrow[\text{air}]{\text{Limited}} 2CO(g)$

Laboratory: $HCOOH \xrightarrow{H_2SO_4} CO + H_2O$

Carbon dioxide $C(s) + O_2(g) \xrightarrow[\text{air}]{\text{Excess}} CO_2(g)$

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

Q33. *An aqueous solution of borax is*

(*a*) *neutral* (*b*) *amphoteric*

(*c*) *basic* (*d*) *acidic*

Ans. (*c*) basic

Q34. *Boric acid is polymeric due to*

(*a*) *its acidic nature*

(*b*) *the presence of hydrogen bonds*

(*c*) *its monobasic nature*

(*d*) *its geometry*

Ans. (*b*) the presence of hydrogen bonds

Q35. *The type of hybridisation of boron in diborane is*

(*a*) sp (*b*) sp^2

(*c*) sp^3 (*d*) dsp^2

Ans. (*c*) sp^3

Q36. *Thermodynamically the most stable form of carbon is*

(*a*) *diamond* (*b*) *graphite*

(*c*) *fullerenes* (*d*) *coal*

Ans. (*b*) graphite

Q37. *Elements of Group 14*

(*a*) *exhibit oxidation state of +4 only*

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

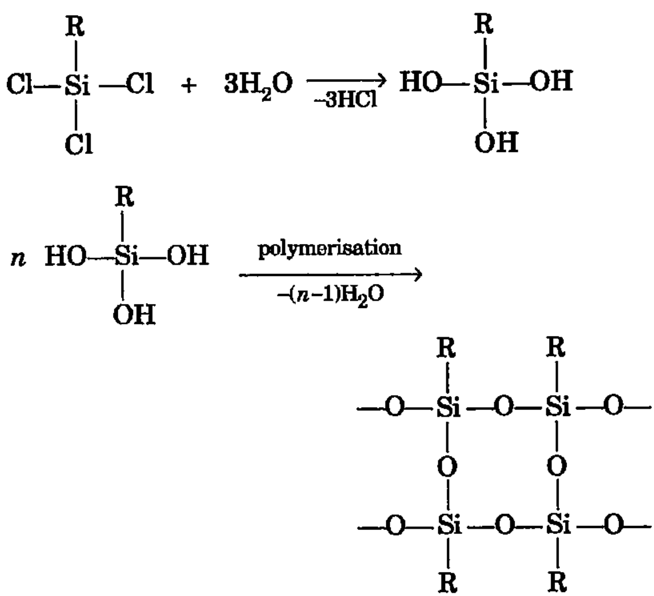
(*c*) *form M^{2-} and M^{4+} ion*

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

Ans. (*b*) exhibit oxidation state of +2 and +4

Q38. *If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.*

Ans. Hydrolysis of trichlorosilane, ($RSiCl_3$) gives a very complex cross-linked polymer:



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