11

The p-Block Elements

Multiple Choice Questions (MCQs)

Q. 1 The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is

(a) B (b) Al (c) Ga (d) In

Ans. *(c)* In gallium, the crystal structure is different, suggesting that Ga consists of almost discrete Ga_2 molecule, that's why its melting point is lowest. Ga exists as liquid from 30°C upto 2000°C and hence, it is used in high temperature thermometry.

Q. 2 Which of the following is a Lewis acid?

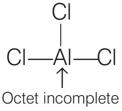
(a) $AlCl_3$ (b) $MgCl_2$ (c) $CaCl_2$ (d) $BaCl_2$

Thinking Process

Lewis acid represent those substances in which octet remains incomplete act as electron acceptors.

Ans. *(a)* Alkaline earth metals form ionic chloride whereas aluminium chloride is covalent. Despite of sharing electrons with chlorine, the octet of aluminium is incomplete. To complete the octet, it needs electrons and thus, acts as a Lewis acid.

$${}_{13}Al = 2, 8, 3 \text{ and } {}_{17}Cl = 2, 8, 7$$



$$\underset{\overset{\uparrow}{\text{Octet incomplete}}}{Cl - \overset{\overset{Cl}{|}}{Al} - Cl}$$

Q. 3 The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[B(OH_4)]^-$ and the geometry of the complex are respectively

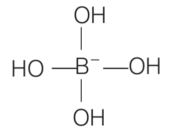
(a) sp^3, tetrahedral (b) sp^3, square planar

(c) sp^3d^2, octahedral (d) dsp^2, square planar

Thinking Process

Hybridisation and geometry of a complex can be found by counting number of bond pairs and lone pairs present in a central atom.

Ans. *(a)* Structure of $B(OH)_4^-$ is



$$\begin{array}{c} OH \\ | \\ HO-B^- -OH \\ | \\ OH \end{array}$$

4 bond pair + 0 lone pair

Hybridisation — sp^3

Geometry — Tetrahedral

Q. 4 Which of the following oxides is acidic in nature?

(a) B_2O_3 (b) Al_2O_3 (c) Ga_2O_3 (d) In_2O_3

Ans. *(a)* The acidic nature of oxides changes from acidic to basic through amphoteric on moving down the group.

$$\underbrace{B_2O_3}_{\substack{\text{More acidic}\\\text{less basic}}},\ \underbrace{Al_2O_3 \text{ and } Ga_2O_3}_{\text{Amphoteric}},\ \underbrace{In_2O_3 \text{ and } Tl_2O_3}_{\text{Basic}}$$

Q. 5 The exhibition of highest coordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-}?

(a) B (b) Al (c) Ga (d) In

Ans. *(a)* The lowest atomic number among the given is boron. Boron has atomic number 5 and do not have vacant *d*-orbital. The element *M* in the complex ion MF_6^{3-} has a coordination number of six. Boron can show maximum coordination number of 4. Thus, B can not form complex of the type MF_6^{3-}.

Q. 6 Boric acid is an acid because its molecule

(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

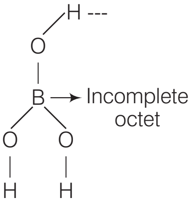
Ans. *(c)* Lewis acids are substances whose octet is incomplete and accepts electrons.

Boric acid is a monobasic weak acid. It does not liberate H^+ ion but accepts electrons from OH^- ion *i.e.,* behaves as Lewis acid.

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

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

The structure of H_3BO_3 is as shown below, where the octet of boron in H_3BO_3 is incomplete.



Q. 7 Catenation *i.e.,* linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in group 14 elements follows the order

(a) C > Si > Ge > Sn
(b) C > > Si > Ge ≈ Sn
(c) Si > C > Sn > Ge
(d) Ge > Sn > Si > C

Ans. *(b)* The tendency to form long open or closed atom chains by combination of some atoms in themselves is known as catenation. The catenation is maximum in carbon and decreases down the group.

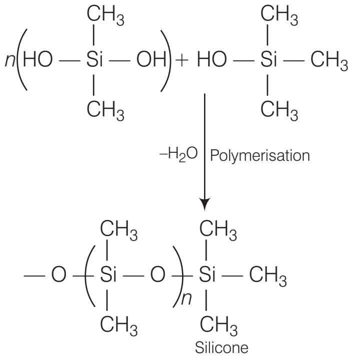
$$C >> Si > Ge \approx Sn > Pb$$

This is due to high bond energy of C — C bonds. Down the group, size increases and electronegativity decreases, thereby, tendency to show catenation decreases.

Q. 8 Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding

(a) $MeSiCl_3$
(b) Me_2SiCl_2
(c) Me_3SiCl
(d) Me_4Si

Ans. *(c)* Silicon has a strong tendency to form polymers like silicones. The chain length of silicon polymer can be controlled by adding Me_3SiCl which block the ends as shown below



Q. 9 Ionisation enthalpy ($\Delta_i H$ kJ mol^{-1}) for the elements of group 13 follows the order

(a) B > Al > Ga > In > Tl
(b) B < Al < Ga < In < Tl
(c) B < Al > Ga < In > Tl
(d) B > Al < Ga > In < Tl

Thinking Process

Ionisation enthalpy ($\Delta_i H$) is the energy required to remove a valence electron. On moving down the group 13, there is decrease in first ionisation enthalpy due to an increase in atomic size and screening effect.

Ans. *(d)* On moving from B to Al, all the ionisation enthalpies decreases as expected and this decrease is due to an increase in atomic size and shielding effect.

On moving from Al to Ga, the ionisation enthalpy increases slightly, because on moving from Al to Ga, both nuclear charge and shielding effect increase but due to poor shielding by *d*-electron in Ga, effective nuclear charge on valence electron increases resulting in *d*-block contraction, that's why ionisation enthalpies increase.

On moving from Ga to In, again there is slight decrease in ionisation enthalpies due to increased shielding effect by additional ten 4*d* electrons, which outweighs the effect of increased nuclear charge.

On moving from In to Tl, ionisation enthalpies show the increase again because fourteen 4*f* electrons shield valence electron poorly (order of shielding effect $s > p > d > f$) and so effective nuclear charge increases, consequently ionisation enthalpies increase.

Q. 10 In the structure of diborane,

(a) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane

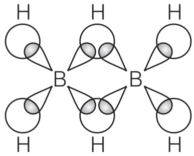
(b) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane

(c) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane

(d) All the atoms are in the same plane

Ans. *(b)* Boron is trivalent, we would expect a simple hydride BH_3. However BH_3 is not stable. The boron possess incomplete octet and BH_3 dimerises to form B_2H_6 molecule with covalent and three centre 2-electron bond. The simplest boron hydride is diborane B_2H_6.

As seen from the structure drawn, 6 electrons are required for the formation of conventional covalent bond structure by B-atom, whereas in diborane, there are 12 valence electrons, three from each boron atoms and six from the six hydrogen atoms. The geometry of B_2H_6 can be represented as



Bonding in diborane

The four terminal hydrogen atoms and two boron atoms lie one plane. Above and below the plane, there are two bridging hydrogen atoms. Each boron atom forms four bonds even though it has only three electrons. The terminal B—H bonds are regular bonds but the bridge B—H bonds are different.

Each bridge hydrogen is bonded to the two boron atoms only by sharing of two electrons. Such covalent bond is called t`hree centre electron pair bond or a multi centre bond or banana bond.

Q. 11 A compound *X*, of boron reacts with NH_3 on heating to give another compound *Y* which is called inorganic benzene. The compound *X* can be prepared by treating BF_3 with lithium aluminium hydride. The compounds *X* and *Y* are represented by the formulas.

(a) B_2H_6, $B_3N_3H_6$ (b) B_2O_3, $B_3N_3H_6$ (c) BF_3, $B_3N_3H_6$ (d) $B_3N_3H_6$, B_2H_6

Ans. *(a)* **(i)** Reaction of ammonia with diborane gives initially $B_2H_6 \cdot 2NH_3$ which is fermulated as $[BH_2(NH_3)_2]^+ [BH_4]$ further heating gives borazine, $B_3N_3H_6$ also called borazole.

$$\underset{\substack{\text{Diborane}\\(X)}}{3B_2H_6} + 6NH_3 \xrightarrow{473\text{ K}} \underset{\substack{\text{Borazole}\\(Y)}}{2B_3N_3H_6} + 12H_2$$

Borazole has cyclic structure and is isoelectronic and isosteric with benzene and thus called inorganic benzene or triborine triammine or borazine.

(ii) Diborane can be prepared by the reduction of BF_3 with lithium aluminium hydride in diethyl ether.

$$4BF_3 + 3LiAlH_4 \longrightarrow \underset{(X)}{2B_2H_6} + 3AlF_3 + 3LiF$$

Q. 12 Quartz is extensively used as a piezoelectric material, it contains ....
.

(a) Pb (b) Si (c) Ti (d) Sn

Ans. *(b)* Quartz, cristobalite and tridymite are some of the crystalline forms of silica and they are interconvertable at suitable temperature. Quartz is extensively used as a piezoelectric material.

Q. 13 The most commonly used reducing agent is

(a) $AlCl_3$ (b) $PbCl_2$ (c) $SnCl_4$ (d) $SnCl_2$

Ans. *(d)* Reducing agents are those substances which reduces other substances and it self oxidises.

In $SnCl_2$, Sn exists in +2 oxidation state, thus, acts as a strong reducing agent. *i.e.,*

$$SnCl_2 + 2FeCl_3 \longrightarrow 2FeCl_2 + SnCl_4$$
$$SnCl_2 + 2CuCl_2 \longrightarrow 2CuCl + SnCl_4$$

Q. 14 Dry ice is

(a) solid NH_3 (b) solid SO_2 (c) solid CO_2 (d) solid N_2

Ans. *(c)* Carbon dioxide can be obtained as a solid in the form of dry ice allowing the liquified CO_2 to expand rapidly.

Note *Dry ice is also called cardice. It is obtained when CO_2 is cooled under pressure (50-60 atm). Dry ice is used for making cold baths in the laboratory by mixing it with volatile organic solvents. It is also used as a coolant for preserving perishable articles in food industry, curing local burns and in hospitals for surgical operation of sores.*

Q. 15 Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group (*s*) are present in the mixture?

(a) Group 2
(b) Groups 2, 13 and 14
(c) Groups 2 and 13
(d) Groups 2 and 14

Ans. *(b)* Cement is a product obtained by combining a material rich in lime. CaO with other material like clay which contains silica SiO_2 alongwith the oxides of aluminium, iron and magnesium. The average composition of Portland cement is

CaO (50 – 60%)
SiO_2 (20 – 25%)
Al_2O_3 (5 – 10%)
Fe_2O_3 (1 – 2%)
SO_2 (1 – 2%)
MgO (2 – 3%).

Thus, it contains elements of group 2 (Ca), group 13 (Al) and group 14 (Si).

Multiple Choice Questions (More Than One Options)

Q. 16 The reason for small radius of Ga compared to Al is ....

(a) poor screening effect of *d* and *f*-orbitals
(b) increase in nuclear charge
(c) presence of higher orbitals
(d) higher atomic number

Ans. ***(a, b)***

On moving down the group from Al to Ga, atomic radius decrease (exception) due to poor shielding by *d*-electrons. On moving from Al to Ga, shielding effect in *d*-electrons is unable to compensate increased nuclear charge.

Hence, successive increase of atomic radius as expected is not observed.

Q. 17 The linear shape of CO_2 is due to ....

(a) sp^3 hybridisation of carbon
(b) *sp* hybridisation of carbon
(c) $p\pi - p\pi$ bonding between carbon and oxygen
(d) sp^2 hybridisation of carbon

Ans. ***(b, c)***

Sigma bond formed by $s—s$ overlap, $s—p$ overlap and $p—p$ overlapping. pi (π) bond formed by $p—p$ overlapping.

The structure of CO_2 is

$$\underset{sp-p\ (\sigma)}{\overset{p-p\ (\pi)}{O{=}C}}\ \underset{sp-p(\sigma)}{\overset{p-p\ (\pi)}{{=}O}}$$ is2 sigma bonds and 2 pi bonds.

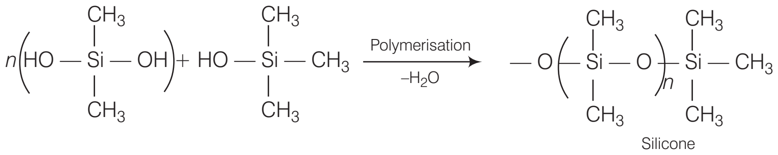
Hybridisation of CO_2 is *sp* and the shape is linear. Due to pi bond, it has $p\pi—p\pi$ bonding between carbon and oxygen.

Q. 18 Me_3SiCl is used during polymerisation of organo silicones because

(a) chain length of organo silicone polymers can be controlled by adding Me_3SiCl
(b) Me_3SiCl blocks the end terminal of silicone polymer
(c) Me_3SiCl improves the quality and yield of the polymer
(d) Me_3SiCl acts as a catalyst during polymerisation

Ans. ***(a, b)***

The chain length of the polymer can be controlled by adding $(CH_3)_3$ SiCl which blocks the ends as shown below



$$n\left(HO—\underset{CH_3}{\overset{CH_3}{Si}}—OH\right) + HO—\underset{CH_3}{\overset{CH_3}{Si}}—CH_3 \xrightarrow[-H_2O]{\text{Polymerisation}} —O\left(—\underset{CH_3}{\overset{CH_3}{Si}}—O\right)_n\!—\underset{CH_3}{\overset{CH_3}{Si}}—CH_3$$

Q. 19 Which of the following statements are correct ?

(a) Fullerenes have dangling bonds

(b) Fullerenes are cage-like molecules

(c) Graphite is thermodynamically most stable allotrope of carbon

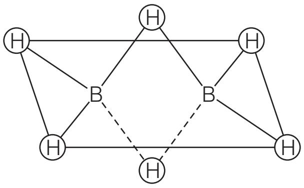
(d) Graphite is slippery and hard and therefore used as a dry lubricant in machines.

Ans. *(b, c)*

Fullerene an allotrope of carbon with finite number of carbon atoms with closed cage structure has been identified. The C_{60} isotope is more dominants. The structure is nearly spherical, like football.

Sphere is formed by the combination of 20 hexagons and 12 pentagons. Graphite is thermodynamically more stable than all allotropes of carbon.

Q. 20 Which of the following statements are correct? Answer on the basis of given figure.



(a) The two bridged hydrogen atoms and the two boron atoms lie in one plane

(b) Out of six B—H bonds two bonds can be described in terms of 3 centre 2 electron bonds

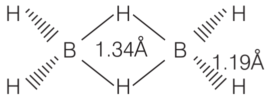
(c) Out of six B— H bonds four B— H bonds can be described in terms of 3 centre 2 electron bonds

(d) The four terminal B— H bonds are two centre-two electron regular bonds

Ans. *(a, b, d)*

The bonding and structure of the boranes are of great interest. They are different from all other hydrides as they are electron deficient.

In diborane, there are 12 valene electrons, three from each B-atom and six from H-atoms. Electron structure shown in figure.



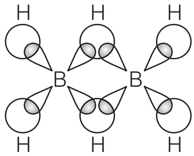
The two bridging H-atoms are in a plane perpendicular to the rest of the molecule and prevent rotation between the two B-atoms.

The terminal B—H distances are the same as the bond lengths measured in non-electron deficient compounds. These are assumed to be normal covalent bonds, with two electrons shared between two atoms. We can describe these bonds are two centre two electron bond (*2c*—*2e*).

Obviously, they are abnormal bonds as the two bridges involve only one electron each from one of the boron atoms and hydrogen atoms, making a total of four electrons.

According to molecular orbital theory, each B-atom uses sp^3-hybrid orbitals for bonding. Out of the four sp^3-hybrid orbitals on each B-atom, one is with out an electron shown in broken lines.

The terminal B—H bonds are normal 2 centre—2 electron bonds but the two bridge bonds are 3 centre—2 electron bonds. The 3 - centre—2 electron bridge bonds are also called banana bonds.



Bonding in diborane

Q. 21 Identify the correct resonance structures of carbon dioxide from the ones given below

(a) $O—C\equiv O$
(b) $O=C=O$
(c) $^{-}O\equiv C—O^{+}$
(d) $^{-}O—C\equiv O^{+}$

Thinking Process

Resonance is a way of describing delocalised electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by one single Lewis formula.

Ans. ***(d)***

The resonating structure of CO_2 are

$O=C=O \leftrightarrow {}^{+}O\equiv C—O^{-} \leftrightarrow {}^{-}O—C\equiv O^{+}$

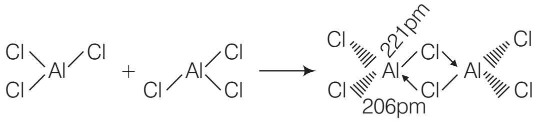
Short Answer Type Questions

Q. 22 Draw the structures of $BCl_3 \cdot NH_3$ and $AlCl_3$ (dimer).

Ans. In the BCl_3, due to small size of B^{3+}, BCl_3 is covalent. Still, the octet of B remains incomplete. In NH_3, N has a lone pair of electrons. Hence, N shares lone pair of electron with B to complete the octet. Hence, BCl_3 acts as Lewis acid and NH_3 as Lewis bases.

$$H_3N: + BCl_3 \longrightarrow H_3N \longrightarrow BCl_3 \text{ or } BCl_3 \cdot NH_3$$

$AlCl_3$ forms dimer by completing octet of Al involving *p*-orbitals to accept electron pair from chlorine.

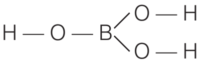


Q. 23 Explain the nature of boric acid as a Lewis acid in water.

Ans. Orthoboric acid is less soluble in cold water but highly soluble in hot water. It is a monobasic acid. It does not liberate H^{+} ion but accepts OH^{-} from water, behaving as a Lewis acid.

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^{-} + H^{+}$$

The structure of H_3BO_3 is



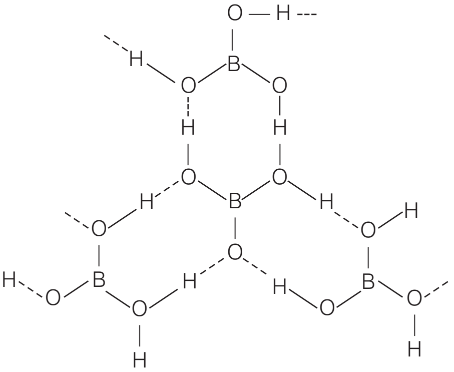
$$H—O—B\begin{matrix} \diagup O—H \\ \diagdown O—H \end{matrix}$$

Octet of boron remains incomplete. Oxygen atom contains lone pair of electrons in water molecule. Hence, instead of donating proton (H^+), boric acid accepts OH^- from water forming $B(OH)_4^-$ to complete octet.

Since, electron acceptor substance behaves as Lewis acid, therefore, boric acid acts as a Lewis acid in water.

Q. 24 Draw the structure of boric acid showing hydrogen bonding. Which species is present in water ? What is the hybridisation of boron in this species ?

Ans. Orthoboric acid H_3BO_3, in solid state possesses a layer structure made up of $B(OH)_3$ units forming hexagonal rings of H-bonding as given below



Each H-atom acts as a bridge between two oxygen atoms of different BO_3^{3-} units.

Boric acid when dissolved in water, acts as Lewis acid forming $B(OH)_4^-$

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

The hybridisation of boron in $B(OH)_4^-$ is sp^3.

Q. 25 Explain why the following compounds behave as Lewis acids ?

(a) BCl_3 (b) $AlCl_3$

Ans. In trivalent state, the number of electrons around the central atom in a molecule of compounds BCl_3 and $AlCl_3$ will be only six.

Such electron deficient molecules have tendency to accept a pair of electron to achieve stable electronic configuration and thus, act as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group.

Q. 26 Give reasons for the following

(a) CCl_4 is immiscible in water, whereas $SiCl_4$ is easily hydrolysed.

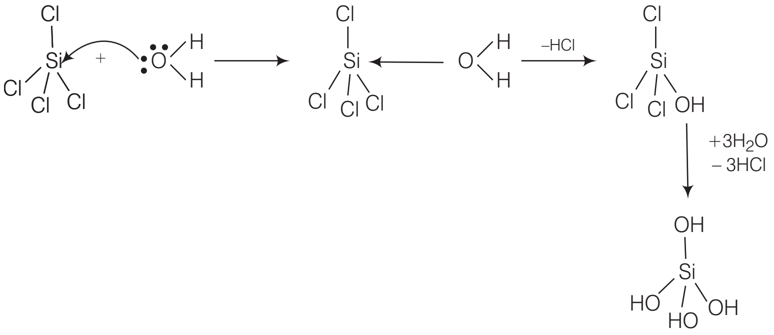
(b) Carbon has a strong tendency for catenation compared to silicon.

Ans. (a) Carbon tetrachloride (CCl_4) is a covalent compound while H_2O is a polar compound. CCl_4 does not form H-bond with water molecule. Hence, it is immiscible in water.

Further more, CCl_4 is not hydrolysed by water because of the absence of *d*-orbitals in carbon while $SiCl_4$ is readily hydrolysed by water.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

The hydrolysis of $SiCl_4$ occurs due to coordination of OH^- with empty 3*d* orbitals in silicon atom of $SiCl_4$ molecule.



(b) Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong.

Down the group, the size increases and electronegativity decreases and thereby, tendency to show catenation decreases. Thus, carbon has a strong tendency for catenation as compared to silicon.

Q. 27 Explain the following.

(a) CO_2 is a gas whereas SiO_2 is a solid.

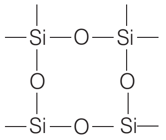
(b) Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known.

Ans. **(a)** CO_2 has a linear structure. Its dipole moment is zero. It is believed that CO_2 molecule is a resonance hybrid has the following structures.

$$O{=}C{=}O \leftrightarrow {}^{-}O-C\equiv O^{+} \leftrightarrow O^{+}\equiv C-O^{-}$$

The CO_2 molecules are held together by weak van der Waals' forces and thus, it exists as gas. In SiO_2, due to large electronegative difference between Si and O, the Si—O bonds have considerable ionic nature.

Therefore, silica has three dimensional network like structure in which Si-atom is tetrahedrally bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms by covalent bonds.



There is no discrete SiO_2 molecule. It is a network solid with octahedral coordination.

(b) In silicon, vacant 3*d* orbitals are available due to which it can accomodate electrons from 6 fluorine atoms, thereby forming Si F_6^{2-} ion. However, in case of C only $2p^2$ filled orbitals are available thus, it cannot expand their covalency more than 4. Thus, CCl_6^{2} is not known.

Q. 28 The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

Ans. The term inert pair effect is often used in relation to the increasing stability of oxidation states that are 2 less than the group valency for the heavier elements of groups 13, 14, 15 and 16.

In group 13 all the elements show +3 oxidation state whereas Ga, In and Tl show +1 oxidation state also.

Boron, being small in size can lose its valence electrons to form B^{3+} ion and shows +3 oxidation state.

+1 oxidation state of Tl, Ga is due to inert pair effect. The outer shell *s*-electrons (ns^2) penetrate to $(n-1)\,d$-electrons and thus becomes closer to nucleus and are more effectively pulled towards the nucleus.

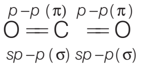
This results in less availability of ns^2 electrons pair for bonding or ns^2 electron pair becomes inert. This reluctance in the participation of ns^2 eletrons in bonding is termed as inert pair effect. The inert pair is more effective after $n \geq 4$ and increases with increasing value of n.

For groups 14, in spite of four valence electrons, they do not form M^{4+} or M^{4-} ionic compounds. They form covalent compounds with four bonds.

Ge, Sn and Pb also exhibit +2 oxidation state due to inert pair effect. Sn^{2+} and Pb^{2+} show ionic nature. The tendency to form + 2 ionic state increases on moving down the group due to inert pair effect.

Q. 29 Carbon and silicon both belong to the group 14, but inspite of the stoichiometric similarity, the dioxides, (*i.e.,* carbon dioxide and silicon dioxide), differ in their structures . Comment.

Ans. All members of group 14 form dioxides of formula MO_2 *i.e.*, for carbon CO_2 and silica SiO_2. CO_2 has a linear structure since, its dipole moment is zero. Both the oxygen atoms are linked by double bonds. The C-atom is *sp* hybridised.



$$O \underset{sp-p\,(\sigma)}{\overset{p-p\,(\pi)}{=}} C \underset{sp-p(\sigma)}{\overset{p-p(\pi)}{=}} O$$

However, C—O bond length is 1.15 Å, which is less than calculated value of C$=$O bond. Hence, it shows resonance hybrid of following structures.

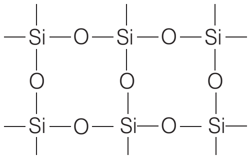
$$O = C = O \longleftrightarrow O^- {-} C \equiv O^+ \longleftrightarrow O \equiv C {-} O^-$$

But, the structure of silica is entirely different from that of CO_2 . Si — O bonds have a considerable ionic character due to large electronegative difference between Si and O. As a result, silica has a three dimensional structure in which silica atom is tetrahedrally bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms by covalent bonds.

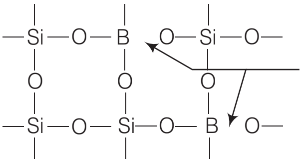
There is no discrete SiO_2 molecule but entire crystal as a giant molecule. Si—O bonds are strongly making it solid having high melting point.

Q. 30 If a trivalent atom replaces a few silicon atoms in three dimensional network of silicon dioxide, what would be the type of charge on overall structure?

Ans. The structure of SiO_2 crystal is as



When some Si-atoms are replaced by trivalent impurity, holes are created, which are equivalent to positive charge. These holes make the crystal structure as conductor of electricity.



Holes take electron from the nearby atom and makes is conductor

Since, the crystals on the whole are always electrically neutral, the obtained crystal is also electrically neutral.

An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it.

Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semiconductors are called *p*-type semiconductors.

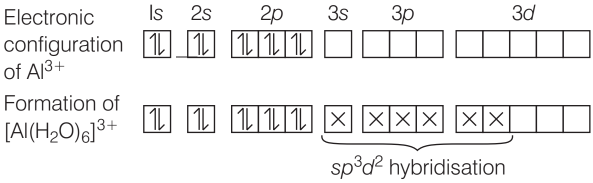
Q. 31 **When BCl_3 is treated with water, it hydrolyses and forms $[B[OH]_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al[H_2O]_6]^{3+}$ ion. Explain what is the hybridisation of boron and aluminium in these species?**

Ans. In trivalent state, most of the compounds being covalent are hydrolysed in water, *e.g.*, BCl_3 on hydrolysis in water form $[B(OH)_4]^-$ species, the hybridisation state of B is sp^3.

$$BCl + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$
$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

$AlCl_3$ in acidified aqueous solution form octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex, the 3*d* orbitals of Al are involved and the hybridisation state of Al is sp^3d^2

$$AlCl_3 + H_2O \xrightarrow{HCl} [Al(H_2O)_6]^{3+} + 3Cl^- (aq)$$



Q. 32 **Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. A piece of aluminium foil is treated with dilute hydrochloric acid or dilute sodium hydroxide solution in a test tube and on bringing a burning matchstick near the mouth of the test tube, a pop sound indicates the evolution of hydrogen gas.**

The same activity when performed with concentrated nitric acid, reaction doesn't proceed. Explain the reason.

Ans. Aluminium being amphoteric in nature dissolves both in acids and alkalies evolving H_2 gas which burns with a pop sound.

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

$$2Al + NaOH + 2H_2O \longrightarrow \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + 3H_2$$

But when Al is treated with conc. HNO_3, a thin protective layer of Al_2O_3 is formed on its surface which prevents further action.

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

Q. 33 Explain the following.

(a) Gallium has higher ionisation enthalpy than aluminium.

(b) Boron does not exist as B^{3+} ion.

(c) Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion.

(d) PbX_2 is more stable than PbX_4.

(e) Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.

(f) Electron gain enthalpy of chlorine is more negative as compared to fluorine.

(g) $Tl(NO_3)_3$ acts as an oxidising agent.

(h) Carbon shows catenation property but lead does not.

(i) BF_3 does not hydrolyse.

(j) Why does the element silicon, not form a graphite like structure whereas carbon does?

Ans. (a) In gallium, due to poor shielding of valence electrons by the intervening 3*d* electrons. The nuclear charge becomes effective, thus, atomic radius decreases and hence, the ionisation enthalpy of gallium is higher than that of aluminium.

(b) Due to small size of boron, the sum of its first three ionisation enthalpies is very high. This prevent it to form +3 ions and force it to form only covalent compound. That's why boron does not exist as B^{3+} ion.

(c) Aluminium forms $[AlF_6]^{3-}$ ion because of the presence of vacant *d*-orbitals so it can expand its coordination number from 4 to 6. In this complex, Al undergoes sp^3d^2 hybridisation.

On the other hand, boron does not form $[BF_6]^{3-}$ ion, because of the unavailability of *d*-orbitals as it cannot expand its coordination number beyond four. Hence, it can form $[BF_4]^-$ ion (sp^3 hybridisation).

(d) Due to inert pair effect, Pb in +2 oxidation state is more stable than in +4 oxidation state hence PbX_2 is more stable than PbX_4.

(e) Due to inert pair effect, tendency to form +2 ions increases down the group, hence Pb^{2+} is more stable than Pb^{4+}. That's why Pb^{4+} acts as an oxidising agent while Sn^{2+} is less stable than Sn^{4+} and hence Sn^{2+} acts as a reducing agent.

$$\underset{\text{Reducing agent}}{Sn^{2+}} \longrightarrow Sn^{4+} + 2e^-$$

$$\underset{\text{Oxidising agent}}{Pb^{4+}} + 2e^- \longrightarrow Pb^{2+}$$

(f) Electron gain enthalpy of Cl is more negative than electron gain enthalpy of fluorine because when an electron is added to F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from other electrons present in this level.

For $n = 3$ quantum level (in Cl) the added electron occupies a larger region of space and the electron-electron repulsion is much less.

(g) Due to inert pair effect, Tl in +1 oxidation state is more stable than that of +3 oxidation state. Therefore, $Tl(NO_3)_3$ acts as an oxidising agent.

(h) Property of catenation depends upon the atomic size of the element. Down the group, size increases and electronegativity decreases, thus the tendency to show catenation decreases. As the size of C is much smaller than Pb, therefore, carbon show property of catenation but lead does not show catenation.

(i) Unlike other boron halides, BF_3 does not hydrolyse completely. However, it form boric acid and fluoroboric acid. This is because the HF first formed reacts with H_3BO_3.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF] \times 4$$

$$H_2BO_3 + 4HF \longrightarrow H^+[BF_4]^- + 3H_2O] \times 3$$

$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3[BF_4]^- + 3H^+$$

(j) In graphite, C is sp^2 hybridised. Carbon due to its smallest size and highest electronegativity among group 14 elements has strong tendency to form $p\pi - p\pi$ multiple bonds while silicon due to its larger size and less electronegativity has poor ability to form $p\pi - p\pi$ multiple bonds. That's why the element silicon does not form a graphite like structure.

Q. 34 Identify the compounds *A*, *X* and *Z* in the following reactions.

$$A + 2HCl + 5H_2O \longrightarrow 2NaCl + X$$

$$X \xrightarrow[370\ K]{\Delta} HBO_2 \xrightarrow[>370\ K]{\Delta} Z$$

Ans. (i) $\underset{\text{Borax }(A)}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\text{Orthoboric acid }(X)}{4H_3BO_3}$

(ii) $H_3BO_3 \xrightarrow{\Delta,\ 370\ K} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

(iii) $4\,HBO_2 \xrightarrow[-H_2O]{\Delta > 370\ K} \underset{\text{Tetraboric acid}}{[H_2B_4O_7]} \xrightarrow[\text{Heat}]{\text{Red}} \underset{\text{Boron trioxide (Z)}}{2B_2O_3} + H_2O$

Q. 35 Complete the following chemical equations.

$$Z + 3LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3$$

$$X + 6H_2O \longrightarrow Y + 6H_2$$

$$3X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

Ans. (i) $4BF_3 + 3LiAlH_4 \longrightarrow \underset{\text{Diborane }(X)}{2B_2H_6} + 3LiF + 3AlF_3$

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

(iii) $\underset{(X)}{B_2H_6} + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

Matching The Columns

Q. 36 Match the species given in Column I with the properties mentioned in Column II.

	Column I		Column II
A.	BF_4^-	1.	Oxidation state of central atom is +4
B.	$AlCl_3$	2.	Strong oxidising agent
C.	SnO	3.	Lewis acid
D.	PbO_2	4.	Can be further oxidised
		5.	Tetrahedral shape

Ans. **A.** → (5) **B.** → (3) **C.** → (4) **D.** → (1, 2)

A. BF_4^- Tetrahedral shape sp^3 hybridisation regular geometry.

B. $AlCl_{3-}$ Octet not complete of Al, act as Lewis acid.

C. SnO Sn^{2+} can show + 4 oxidation state.

D. PbO_2 Oxidation state of Pb in PbO_2 is $+4$. Due to inert pair effect Pb^{4+} is less stable than Pb^{2+}, acts as strong oxidising agent.

Q. 37 Match the species given in Column I with properties given in Column II.

	Column I		Column II
A.	Diborane	1.	Used as a flux for soldering metals
B.	Gallium	2.	Crystalline form of silica
C.	Borax	3.	Banana bonds
D.	Aluminosilicate	4.	Low melting, high boiling, useful for measuring high temperatures
E.	Quartz	5.	Used as catalyst in petrochemical industries

Ans. **A.** → (3) **B.** → (4) **C.** → (1) **D.** → (5) **E.** → (2)

A. BH_3 is unstable forms diborane B_2H_6 by 3 centre—2 electron bond show banana bond.

B. Gallium with low melting point and high boiling point makes it useful to measure high temperatures.

C. Borax is used as a flux for soldering metals for heat, scratch resistant coating in earthernwares.

D. Alumino silicate used as catalyst in petrochemical industries.

E. Quartz, is a crystalline form of silica.

Q. 38 Match the species given in Column I with the hybridisation given in Column II.

	Column I		Column II
A.	Boron in $[B(OH_4)]^-$	1.	sp^2
B.	Aluminium in $[Al(H_2O)_6]^{3+}$	2.	sp^3
C.	Boron in B_2H_6	3.	sp^3d^2
D.	Carbon in buckminster fullerene		
E.	Silicon in SiO_4^{4-}		

F. Germanium in $[GeCl_6]^{2-}$	

Ans. **A.** → (2) **B.** → (3) **C.** → (2) **D.** → (1) **E.** → (2) **F.** → (3)

A. Boron in $[B(OH)_4]^-$ sp^3 hybridised.

B. Aluminium in $[Al(H_2O)_6]^{3+}$ sp^3d^2 hybridised.

C. Boron in B_2H_6 sp^3 hybridised.

D. Carbon in Buckminsterfullerene sp^2 hybridised.

E. Silicon in SiO_4^{4-} sp^3 hybridised.

F. Germanium in $[GeCl_6]^{2-}$ sp^3d^2 hybridised.

Assertion and Reason

In the following questions a statement of Assertion (A) *followed by a statement of Reason* (R) *is given. Choose the correct option out of the choices given below in each question.*

Q. 39 Assertion (A) If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

Reason (R) Aluminium is trivalent while silicon is tetravalent.

(a) Both A and R are correct and R is the correct explanation of A

(b) Both A and R are correct but R is not the correct explanation of A

(c) Both A and R are not correct

(d) A is not correct but R is correct

Ans. *(d)* Assertion is not correct but reason is correct. Aluminium is trivalent whereas silicon is tetravalent. If aluminium atom replaces a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires neutrality. (*Also, refer to Q.* 30)

Q. 40 Assertion (A) Silicones are water repelling in nature.

Reason (R) Silicones are organosilicon polymers, which have $(—R_2SiO—)$ as repeating unit.

(a) A and R both are correct and R is the correct explanation of A

(b) Both A and R are correct but R is not the correct explanation of A

(c) A and R both are correct

(d) A is not true but R is true

Ans. *(b)* Silicones are a group of organo silicon polymers which have (R_2SiO) as a repeating unit. This suggests that silicones are surrounded by non-polar alkyl groups that are water repelling in nature. They have wide applications. It is used for water proofing of fabrics.

Long Answer Type Questions

Q. 41 Describe the general trends in the following properties of the elements in groups 13 and 14.

(a) Atomic size
(b) Ionisation enthalpy
(c) Metallic character
(d) Oxidation states
(e) Nature of halides

Ans. **For Group 13**

(a) **Atomic Size** On moving down the group for each successive member, one extra shell of electrons is added and therefore, atomic radius is expected to increase. However, a deviation can be seen.

Atomic radius of Ga is less than that of Al due to presence of additional 10*d* - electrons, which offer poor screening effect to the outer electron.

(b) **Ionisation Enthalpy** The ionisation enthalpy values as expected from general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size.

The observed discontinued between Al and Ga and between In and Tl due to low screening effect of *d* and *f*-electrons which compensates increased nuclear charge.

(c) **Metallic or Electropositive Character** Boron is a semi-metal (metalloid) due to very high ionisation enthalpy. All others are metals and metallic character first increases from B to Al as size increases. From Al to Tl decrease due to poor shielding of *d*- and *f*-electrons.

(d) **Oxidation States** As we move down the group, the stability of $+3$ oxidation state decreases while that of $+1$ oxidation state progressively increases. In other words, the order of stability of $+1$ oxidation state increase in the order. $Al < Ga < In < Tl$. Infact, in Ga, In and Tl, both $+1$ and $+3$ oxidation states are observed.

(e) **Nature of Halides** These elements react with halogens to form trihalids (except TlI_3)

$$2E(s) + 3X_2(g) \longrightarrow 2EX_3(s) \qquad [X = F, Cl, Br, I]$$

Boron in halides are electron deficient molecules and behave as Lewis acids. The Lewis character decreases in the order : $BI_3 > BBr_3 > BCl_3 > BF_3$

For Group 14

(a) **Atomic Size** There is considerable increase in covalent radius from C to Si thereafter from Si to Pb as small increase in radius is observed.This is due to the presence of completely filled *d* and *f*- orbitals in heavier member.

(b) **Ionisation Enthalpy** The first ionisation enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here. In general the ionisation enthalpy decreases down the group. Small decrease in Δ; H from Si to Ge to Sn and slight increase in Δ; H from Sn to Pb is the consequence of poor shielding effect of intervening *d* and *f*-orbitals and increase in size of the atom.

(c) **Metallic Character** Metallic character increases down the group C (non-metal) Si, Ge (metalloid) Sn,Pb (metals).

(d) **Oxidation States** The group 14 elements have four electrons in the outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since, the sum of the first four ionisation enthalpies is very high, compounds in +4 oxidation states are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the $Ge < Sn < Pd$ due to inert pair effect.

(e) **Nature of Halides** These elements can form halides of formula MX_2 and MX_4 (where, X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides.

Most of MX_4 are covalent with sp^3 hybridisation and tetrahedral in structure. Exceptions are SnF_4 and PbF_4 which are ionic in nature. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of halides increases down the group.

Q. 42 Account for the following observations.

(a) $AlCl_3$ is a Lewis acid.

(b) Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than CI_3.

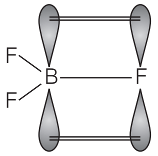
(c) PbO_2 is a stronger oxidising agent than SnO_2.

(d) The +1 oxidation state of thallium is more stable than its+3 state.

Ans. (a) In $AlCl_3$, Al has only six electrons in its valence shell. It is an electron deficient species. Therefore, it acts as a Lewis acid (electron acceptor).

(b) In BF_3 boron has a vacant $2p$-orbital and fluorine has one $2p$-completely filled unutilised orbital. Both of these orbitals belong to same energy level therefore, they can overlap effectively and form $p\pi—p\pi$ bond. This type of bond formation is known as back bonding.

While back bonding is not possible in BCl_3, because there is no effective overlapping between the $2p$-orbital of boron and $3p$-orbital of chlorine. Therefore, electron deficiency of B is higher in BCl_3 than that of BF_3. That's why BF_3 is a weaker Lewis acid than BCl_3.



2p orbital (Vacant) 2p orbital (Completely filled)

(c) In PbO_2 and SnO_2, both lead and tin are present in + 4 oxidation state. But due to stronger inert pair effect, Pb^{2+} ion is more stable than Sn^{2+} ion. In other words, Pb^{4+} ions *i.e.,* PbO_4 is more easily reduced to Pb^{2+} ions than Sn^{4+} ions reduced to Sn^{2+} ions. Thus, PbO_2 acts as a stronger oxidising agent than SnO_2.

(d) Tl^+ is more stable than Tl^{3+} because of inert pair effect.

Q. 43 When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. Is this solid acidic or basic in nature ? Explain.

Ans. When an aqueous solution of borax is acidified with HCl boric acid is formed.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\text{Boric acid}}{4H_3BO_3}$$

Boric acid is a white crystalline solid. It is soapy to touch because of its planar layered structure. Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion.

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

Q. 44 Three pairs of compounds are given below. Identify that compound in each of the pairs which has group 13 element in more stable oxidation state. Given reason for your choice. State the nature of bonding also.

(a) $TlCl_3$, TlCl (b) $AlCl_3$, AlCl

(c) $InCl_3$, InCl

Ans. (a) TlCl more stable than $TlCl_3$ due to inert pair effect. $TlCl_3$ is less stable and covalent in nature but TlCl is more stable and ionic in nature.

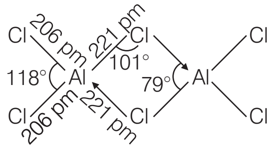
(b) Due to absence of *d*-orbitals, Al does not show inert pair effect. Hence, its most stable oxidation state is + 3. Thus, $AlCl_3$ is much more stable than AlCl. Further, in the solid or the vapour state, $AlCl_3$ covalent in nature but in aqueous solutions, it ionises to form *A* Al^{3+} (*aq*) and Cl^- (*aq*) ions.

(c) Due to inert pair effect, indium exists in both +1 and +3 oxidation states out of which + 3 oxidation state is more stable than +1 oxidation state. In other words, $InCl_3$ is more stable than InCl. Being unstable, In Cl undergoes disproportionation reaction.

$$3\,InCl\,(aq) \longrightarrow 2In(s) + In^{3+}(aq) + 3Cl^-(aq)$$

Q. 45 BCl_3 exists as monomer whereas $AlCl_3$ is dimerised through halogen bridging. Give reason. Explain the structure of the dimer of $AlCl_3$ also.

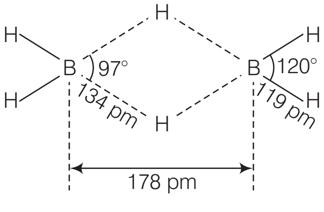
Ans. Boron halides do not exist as dimer due to small size of boron atom which makes it unable to accommodate four large sized halide ions. $AlCl_3$ exists as dimer. Al makes use of vacant 3*p*—orbital by coordinate bond *i.e.,* Al atoms complete their octet by forming dimers.



Dimer structure of $AlCl_3$ (Al_2Cl_6)

Q. 46 Boron fluoride exists as BF_3 but boron hydride doesn't exist as BH_3. Give reason. In which form does it exist ? Explain its structure.

Ans. Due to $p\pi - p\pi$ back bonding, the lone pair of electrons of F is donated to the B-atom. This delocalisation reduces the deficiency of electrons on B thereby increasing the stability of BF_3 molecule.



Structure of diborane

Due to absence of lone pair of electrons on H-atom, this compensation does not occur in BH_3. In other words, electron deficiency of B stays and hence to reduce its electron deficiency, BH_3 dimerises to form B_2H_6.

In B_2H_6, four terminal hydrogen atoms and two boron atoms lie in one plane. Above and below this plane there are two bridging H–atoms. The four terminal B—H bonds are regular while the two bridge (B—H—B) bonds are three centre- two electron bonds.

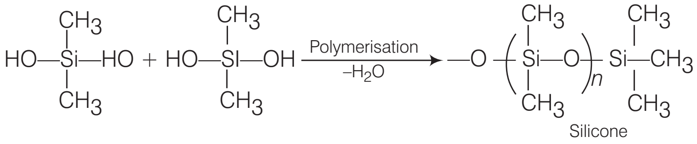
Q. 47 **(a) What are silicones? State the uses of silicones.**

(b) What are boranes ? Give chemical equation for the preparation of diborane.

Ans. (a) Silicones are a group of organosilicon polymers, which have (R_2SiO) as a repeating unit. These may be linear silicones, cyclic silicones and cross-linked silicones.

These are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$, like $RSiCl_3$, R_2SiCl_2, and R_3SiCl and polymerisation of alkyl or aryl hydroxy derivatives obtained by hydrolysis.

$$2CH_3Cl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} (CH_3)_2SiCl_2 \xrightarrow[+2H_2O,-2HCl]{\text{Hydrolysis}} (CH_3)_2Si(OH)_2$$



$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-HO + HO-\underset{CH_3}{\overset{CH_3}{SI}}-OH \xrightarrow[-H_2O]{\text{Polymerisation}} -O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n\underset{\text{Silicone}}{\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

Uses

These are used as sealant, greases, electrical insulators and for water proofing of fabrics. These are also used in surgical and cosmetic plants.

(b) Boron forms a number of covalent hydrides with general formulae $B_n\ H_{n+4}$ and $B_n\ H_{n+6}$. These are called boranes. B_2H_6 and B_4H_{10} are the representative compounds of the two series respectively.

Preparation of Diborane

It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

On industrial scale it is prepared by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$$

Q. 48 **A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid. Identify the compounds A, B, and C. Give the reactions involved.**

Ans. Since, compound (*A*) of boron reacts with NMe_3 to form an adduct (*B*) thus, compound (*A*) is a Lewis acid. Since, adduct (*B*) on hydrolysis gives an acid (*C*) and hydrogen gas, therefore, (*A*) must be B_2H_6 and (*C*) must be boric acid.

$$\underset{\text{Diborane }(A)}{B_2H_6} + \underset{\text{Adduct }(B)}{2NMe_3} \longrightarrow \underset{\text{Adduct }(B)}{2BH_3NMe_3}$$

$$\underset{(B)}{BH_3 \cdot NMe_3} + 3H_2O \longrightarrow \underset{\text{Boric acid }(C)}{H_3BO_3} + NMe_3 + 6H_2$$

Q. 49 A non-metallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as Lewis acid towards ammonia.

The element exihibits maximum covalency of four. Identify the element and write the reaction of its trifluoride with ammonia. Explain why does the trifluoride act as a Lewis acid?

Ans. The only non-metallic element of group 13 is boron. It is an extremely hard substance and is used in making bullet proof vests. It exists in many allotropy forms and usually high melting point. Since *B* has only *s* and *p*-orbitals but no *d*-orbitals. The maximum covalency of boron is 4.

In trivalent state, the number of electrons around the central atom in a molecule will be six as in case of BF_3. Such electron deficient molecules have tendency to accept a pair of electron to achieve stable electronic configuration and behave as Lewis acid. BF_3 easily accepts lone pair of electron from NH_3.

$$BF_3 + \overset{\bullet\bullet}{N}H_3 \longrightarrow F_3B \longleftarrow NH_3$$

Q. 50 A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron.

Identify the element and write formulae of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

Ans. Producer gas is a mixture of CO and N_2, therefore, the tetravalent element is carbon and its monoxide and dioxide are CO and CO_2 respectively.

$$2C(s) + \underbrace{O_2(s) + 4N_2(g)}_{\text{Air}} \xrightarrow{1273\text{ K}} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

The carbon monoxide is a strong reducing agent and reduces ferric oxide to iron.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$