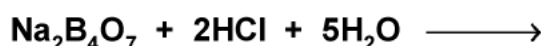
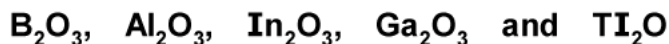


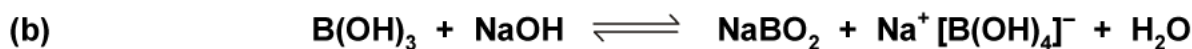
- Q1. The first ionisation energy of carbon atom is greater than that of boron atom, whereas the reverse is true for the second ionisation energy. Why?
- Q2. What happens when
- silicon dioxide is treated with hydrogen fluoride?
  - hydrated alumina is treated with aqueous NaOH solution?
- Q3. If the starting material for the manufacture of silicones is  $RSiCl_3$ , write the structure of the product formed.
- Q4. Write the formula of borax and basic structural unit of silicate.
- Q5.  $BF_3$  does not have proton but still acts as an acid and reacts with  $NH_3$ . Why is it so?
- Q6. (a) How borax is useful in qualitative analysis to identify cations?  
(b) A mixture of boron trichloride and hydrogen is subjected to silent electric discharge to form A and HCl. A is mixed with  $NH_3$  and heated upto  $200^\circ C$  to form B. What is the formula of B?
- Q7. A certain salt x gives the following results.
- Its aqueous solution is alkaline to litmus.
  - It swells into a glassy material y when strongly heated.
  - 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.
- Q8. (a) How would you account for the following?  
(i)  $Tl(NO_3)_3$  acts as an oxidising agent.  
(ii) Although B — Cl has a dipole moment but still  $BCl_3$  is a non-polar molecule.  
(b) Complete the following reaction
- $$PbO_2 + NaOH \longrightarrow$$
- Q9. (a) How would you account for the following?  
(i)  $PbBr_4$  and  $PbI_4$  do not exist. Explain.  
(ii) Carbon shows catenation property but lead does not.  
(b) X reacts with aqueous NaOH solution to form Y and  $H_2$ . Aqueous solution of Y is heated upto 323-333 K and on passing  $CO_2$  into it,  $Na_2CO_3$  and Z were formed. When Z is heated upto  $1200^\circ C$ ,  $Al_2O_3$  is formed. Determine X, Y and Z.
- Q10. (a) How would you account for the following?  
(i) Boron does not form ionic compounds (ii) Diamond is harder than graphite  
(b) Complete the following reaction:



Q11. (a) (i) Arrange the following in the increasing order of their basic character:



(ii) What is the mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall-Heroult process? [Atomic mass of Al = 27]



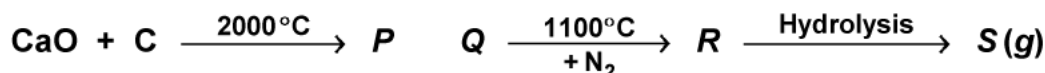
How can this reaction be made to proceed in the forward direction?

Q12. (a) Complete the following reaction:



(b) Diamond is covalent yet it has high melting point. Explain.

(c) Identify P to S in the following sequence of reactions.



(d) Explain the bonding in diborane.

(e) Graphite conducts electricity, why?

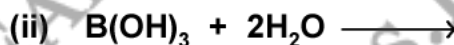
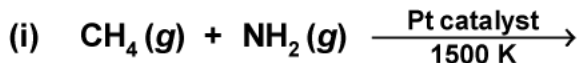
Q13. (a) Account for the following:

(i) Silicon shows a higher covalency than carbon.

(ii) Silicon forms  $\text{SiF}_6^{2-}$  ion whereas corresponding chloro compound of silicon is not known.

(iii) Boron does not form  $\text{B}^{3+}$  ion.

(b) Complete the following reactions:



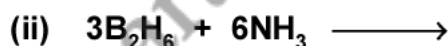
Q14. (a) Account for the following:

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

(ii) Lead does not form an iodide,  $\text{PbI}_4$ .

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

(b) Complete the following reactions:



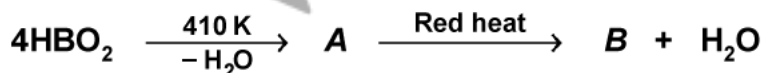
Q15. (a) The acidity of boron trihalides increases down the group. Why?

(b) The tendency to form  $p\pi-p\pi$  bonds of carbon is strong. Why?

(c) Suggest reason why the B — F bond lengths in  $\text{BF}_3$  (130 pm) and  $\text{BF}_4^-$  (143 pm) differ?

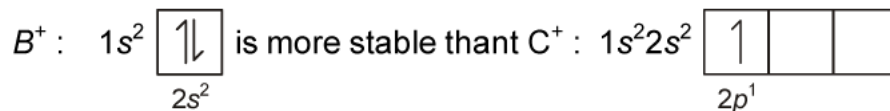
(d) Why  $\text{N}(\text{CH}_3)_3$  is more basic than  $\text{N}(\text{SiMe}_3)_3$ ?

(e) Complete the following reaction:



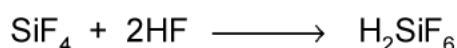
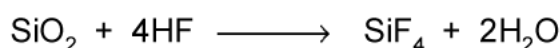


- S1.** The first ionisation energy of carbon is greater than the boron as predicted from periodic trend.

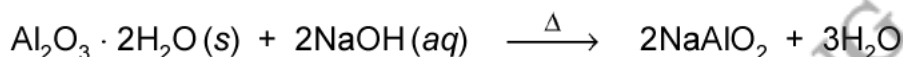


However, for 2<sup>nd</sup> ionisation energy, trend is reversed due to stability of completely filled (2s) orbital of B<sup>+</sup>.

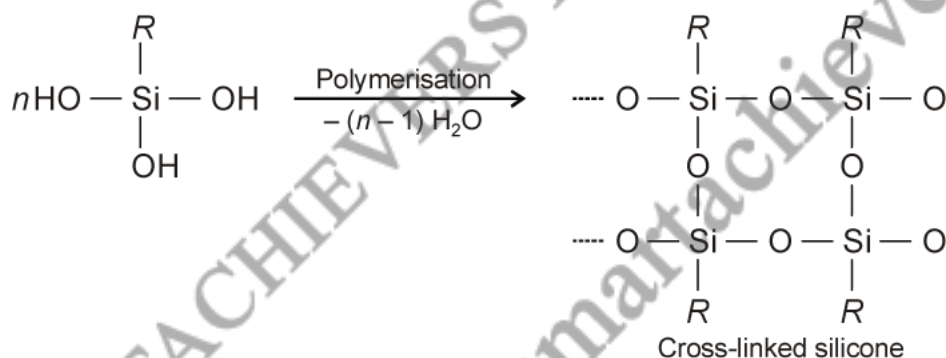
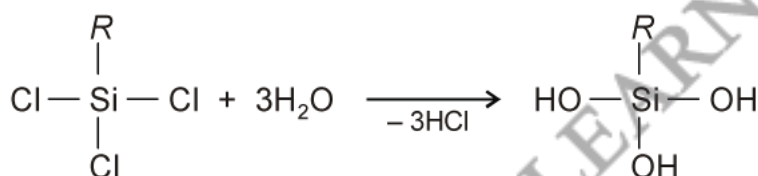
- S2.** (a) The initially formed silicon tetrafluoride (SiF<sub>4</sub>) dissolves in HF to form hydrofluorosilicic acid (H<sub>2</sub>SiF<sub>6</sub>).



- (b) Alumina dissolves to form sodium meta aluminate (NaAlO<sub>2</sub>)



- S3.** Hydrolysis of alkyltrichlorosilanes gives cross-linked silicones.



- S4.** Formula of borax = Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O.

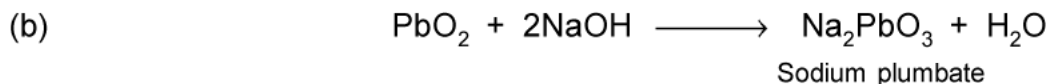
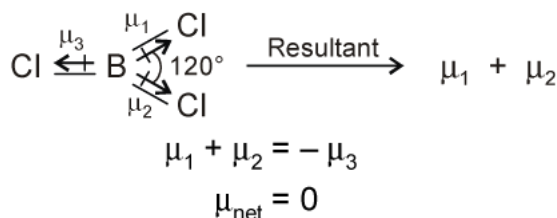
Basic structural unit of silicat = SiO<sub>4</sub><sup>4-</sup>.

- S5.** BF<sub>3</sub> is an electron deficient compound, since the valence shell of B has only six electrons and needs two more electrons to complete its octet. Hence, acts as a Lewis acid. NH<sub>3</sub> has one lone pair of electrons which can be donated to BF<sub>3</sub> to form a coordinate bond. Hence, NH<sub>3</sub> acts as a Lewis base. Thus BF<sub>3</sub> forms an adduct with ammonia. NH<sub>3</sub> → BF<sub>3</sub>.



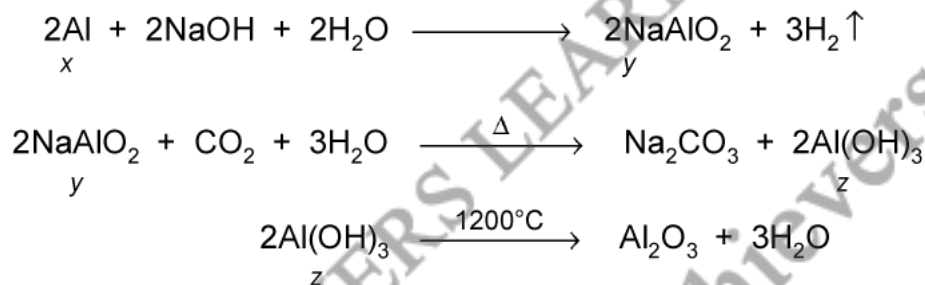


- (ii) Due to electronegativity difference between B (EN = 2.0) and Cl (EN = 3.0), the B — Cl bond is polar and hence, has a finite dipole moment. However, the overall dipole moment of a molecule depends upon its geometry. BCl<sub>3</sub> is a planar molecule in which the three B — Cl bonds are inclined at an angle of 120°. Therefore, the resultant of two B — Cl bonds is cancelled by equal and opposite dipole moment of the third B — Cl bond. Hence, overall dipole moment of BCl<sub>3</sub> is zero and it is a non-polar molecule.

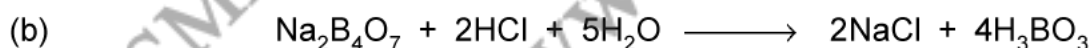


- S9.** (a) (i) The non-existing nature of PbBr<sub>4</sub> and PbI<sub>4</sub> is due to the fact that Pb<sup>4+</sup> ion is a strong oxidant while Br<sup>-</sup> and I<sup>-</sup> are strong reductants. Thus, Pb<sup>4+</sup> ion cannot survive in presence of Br<sup>-</sup> or I<sup>-</sup> and is reduced to Pb<sup>2+</sup>.
- (ii) 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 that of Pb, therefore carbon shows the property of catenation but lead does not show catenation.

(b) The reactions are as follows:



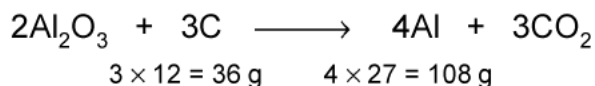
- S10.** (a) (i) Boron, due to its small size and high sum of first three ionisation enthalpies, does not lose its three valence electrons to form B<sup>3+</sup> ions. Therefore, it does not form ionic compounds. Instead, boron always forms covalent compounds by sharing its valence electrons.
- (ii) Graphite has a layered structure of hexagonal carbon rings stacked one over other which makes it slippery. On the other hand, in diamond, each carbon is tetrahedrally bonded to four other carbons extended in three dimensional space, giving a giant, network structure. Due to this reason, diamond is harder than graphite.



- S11.** (a) (i) On moving down the group, the basic character increases because down the group, ionisation enthalpy decreases. Consequently, M — O bond weakens and is easily broken resulting in increased basic strength down the group. Hence, the order would be:



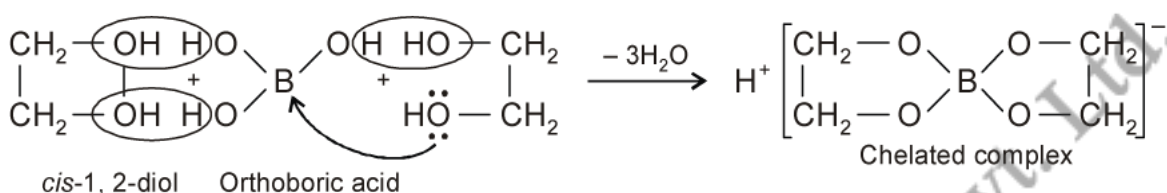
(ii) In Half-Heroult's process,



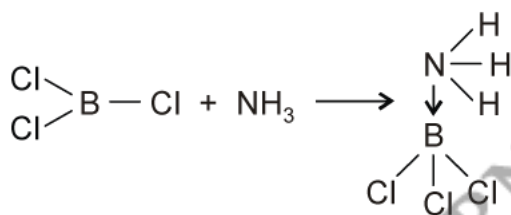
∴ For 108 g of Al, 36 g of C is required in the above reaction.

$$\begin{aligned} \therefore \text{For } 270 \times 10^3 \text{ g of Al, required amount of C} &= \frac{36}{108} \times 270 \times 10^3 \\ &= 90 \times 10^3 \text{ g.} \end{aligned}$$

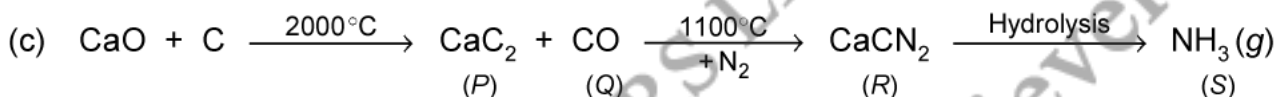
- (b) If some quantity of polyhydroxy compounds like *cis*-1,2-diol, catechol, glycerol etc., is added to the reaction mixture,  $\text{B}(\text{OH})_3$  combines with such polyhydroxy compounds to give chelated compound. Due to formation of complex compound, stability increases and due to higher stability of complex, reaction moves in forward direction.



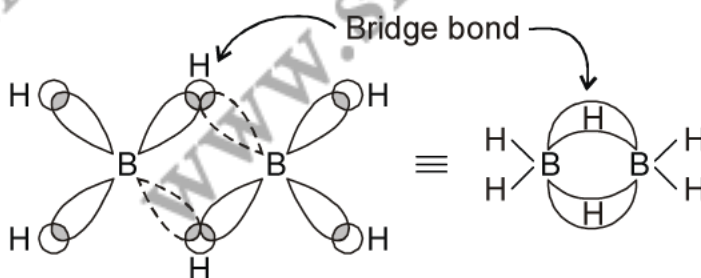
**S12.** (a)



- (b) Diamond is covalent yet it has high melting point because diamond has a three-dimensional network involving strong C — C bonds, which are very difficult to break.

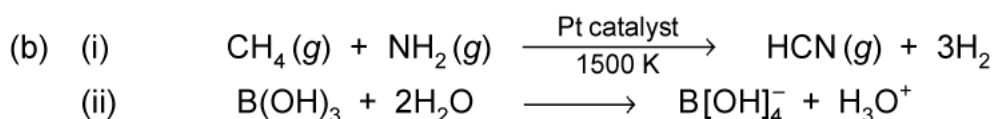


- (d) **Bonding in diborane** In diborane, each B-atom utilises its  $sp^3$ -hybrid orbitals for bonding. Out of four  $sp^3$ -hybrid orbitals, one orbital which is empty, *i.e.*, without any electron is shown with broken lines in the figure. Thus, the involvement of one half-filled orbital of one B-atom with one empty orbital of other B-atom and half-filled orbital of hydrogen atom results in formation of bridge bonds, also called banana bond. Thus, diborane has four terminal B — H bonds and two bridge bonds.

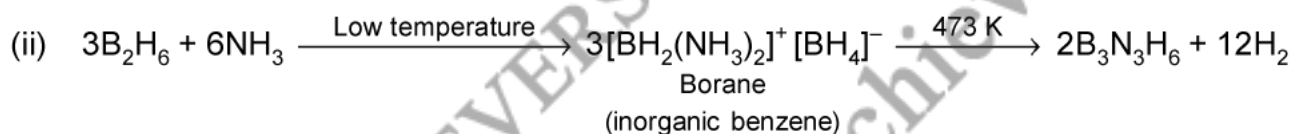
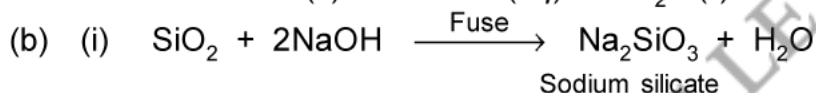


- (e) In graphite each carbon atom is bonded to three other C-atoms and is  $sp^2$ -hybridised. The fourth valence electron of C-atom does not participate in bonding and remains free, hence is responsible for electrical conductivity of graphite.

- S13.** (a) (i) Carbon has four valence electrons which are shared with four more electrons to form four single covalent bonds to attain inert gas configuration. Carbon cannot exhibit covalency of more than four, as it cannot expand its octet because of non-availability of  $d$ -orbitals.
- (ii)  $\text{SiF}_6^{2-}$  is known whereas  $\text{SiCl}_6^{2-}$  is not known because due to smaller size of F as compared to Cl, six small atoms of F can be easily accommodated around Si-atom but six large Cl-atoms cannot. The lone pair electrons on F are present in smaller  $2p$ -orbital but in Cl, they are present in a large  $3p$ -orbital. Therefore, interaction of lone pair electrons with  $d$ -orbitals of Si are stronger than that of Cl lone pairs.
- (iii) Due to small size, the sum of the first three ionisation enthalpies of B is very high. Thus, the total enthalpy required to produce  $\text{B}^{3+}$  ions is much higher and would be compensated by lattice enthalpies of ionic compounds or by hydration enthalpy of  $\text{B}^{3+}$  ions in solution. Due of this reason, B does not form  $\text{B}^{3+}$  ion.



- S14.** (a) (i) Aluminium possesses high electrical conductivity. Moreover, it is much lighter metal in comparison of Cu, which also has high electrical conductivity. Therefore, it is used in making transmission cables.
- (ii) Due to strong oxidising power of  $\text{Pb}^{4+}$  ion and reducing power of  $\text{I}^-$  ion,  $\text{PbI}_3$  does not exist.
- (iii) NaOH reacts with Al to evolve dihydrogen gas. The pressure of the hydrogen gas can be used to open jammed drains.



- S15.** (a) Due to the presence of only six electrons in their respective valence shell, all boron trihalides are Lewis acids. Their Lewis acid character however increases in the order.



This order of acidic strength can be explained on the basis of the tendency of the halogen atom to back donate its lone pair of electrons to the boron atom through  $p\pi-p\pi$  bonding. As the size of the halogen atom increases from F to I, the tendency to  $p\pi-p\pi$  back bonding decreases and consequently, the electron deficiency of B increases and thus, the Lewis acid character increases from  $\text{BF}_3$  to  $\text{BI}_3$ .

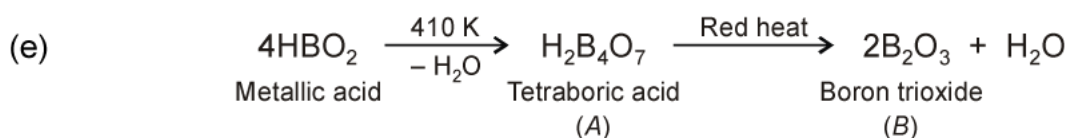
- (b) Due to small size and high electronegativity of carbon atom, it has strong tendency to form  $p\pi-p\pi$  multiple bonds either with itself ( $\text{C} \equiv \text{C}$ ,  $\text{C} = \text{C}$ ) or with other atoms of similar size such as nitrogen ( $\text{C} = \text{N}$ ,  $\text{C} \equiv \text{N}$ ) and oxygen ( $\text{C} = \text{O}$ ).



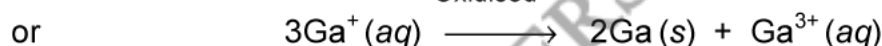
- (c) In  $\text{BF}_3$ , boron is  $sp^2$ -hybridised. It has vacant  $2p$ -orbitals. Each fluorine in  $\text{BF}_3$  has completely filled unutilised  $2p$ -orbitals. Since, both of these orbitals belong to same energy level so,  $p\pi-p\pi$  back bonding occurs in which a lone pair of electrons is transferred from unutilised completely filled  $2p$ -orbital of  $F$  to vacant  $2p$ -orbital of  $B$ . This type of bond formation is known as back bonding. Therefore,  $B-F$  bond has some double bond character. That's why, all the three boron-fluorine bonds are shorter than the usual single boron-fluorine bond.

In  $[\text{BF}_4]^-$  ion,  $B$  is  $sp^3$ -hybridised and hence, does not have any empty  $p$ -orbital available to accept the electrons donated by  $F$ -atom consequently. In  $[\text{BF}_4]^-$ , all the four  $B-F$  bonds are purely single bonds and are larger (143 pm) than  $B-F$  bonds in  $\text{BF}_3$  (130 pm) which have double bond character.

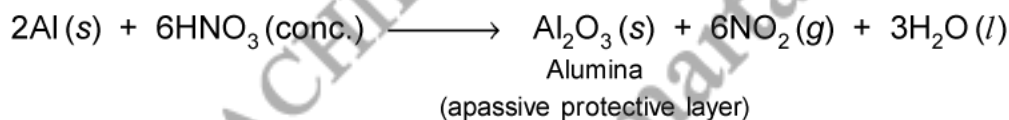
- (d) The lone pair of electrons of  $N$  (present in the  $2p$ -orbital) is transferred to the empty  $d$ -orbital of  $Si$  ( $p\pi-p\pi$  overlapping) and hence, it is not available for donation. As a result,  $N(\text{SiMe}_3)_3$  is a weaker base than  $N(\text{CH}_3)_3$ .



- S16.** (a) Gallium shows both +1 and +3 oxidation states due to inert pair effect. However, its +3 oxidation state is more stable than +1 oxidation state. Therefore, +1 oxidation state of gallium is less stable than +3 oxidation state of gallium and hence, undergoes disproportionation to form gallium and more stable +3 oxidation state of gallium ions in aqueous solution as shown below:



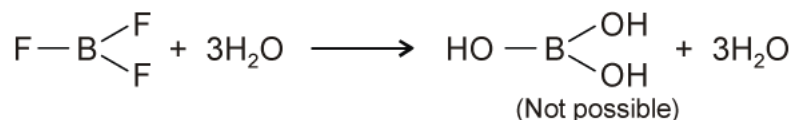
- (b)  $\text{Al}$  reacts with conc.  $\text{HNO}_3$  to form a protective layer of aluminium oxide on its surface which prevents it from further reaction.



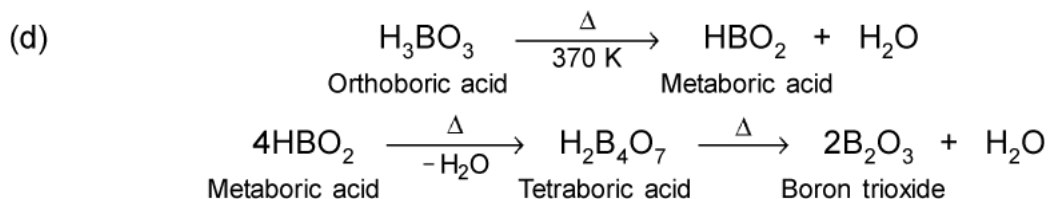
Thus,  $\text{Al}$  becomes passive and hence, aluminium containers can be used to transport conc.  $\text{HNO}_3$ .

- (c)  $\text{BF}_3$  is not easily hydrolysed by water. It forms an adduct  $\text{BF}_3 \cdot \text{OH}_2$  whereas,  $\text{BCl}_3$  and  $\text{BBr}_3$  are hydrolysed to boric acid and  $\text{HCl}$  or  $\text{HBr}$ , respectively.

This is because the  $B-F$  bond in  $\text{BF}_3$  is very strong due to extensive  $p\pi-p\pi$  back bonding. As a result, it is not hydrolysed by water. The  $B-F$  bond energy is far larger than  $B-OH$  bond energy and cannot be compensated.



However, in  $\text{BCl}_3$  and  $\text{BBr}_3$ , the corresponding  $\text{B}-\text{Cl}$  and  $\text{B}-\text{Br}$  bond energy is relatively less than  $\text{B}-\text{F}$  because of inefficient  $p\pi-p\pi$  back bonding. Therefore, these compounds get hydrolysed easily.

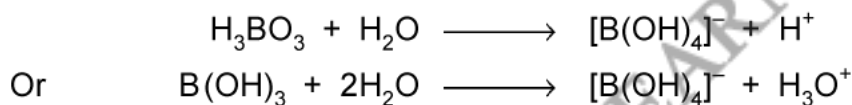


(e) Both tin and lead show two oxidation states of +2 and +4 due to inert pair effect. But the inert pair effect is more prominent in case of Pb than in Sn. In other words, +2 oxidation state of Sn is less stable than its +4 oxidation state. Therefore, Sn (II) acts as a reducing agent and gets converted into more stable Sn (VI) by losing two electrons. e.g. It reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions.



In contrast, +2 oxidation state of Pb is more stable than its +4 oxidation state. In other words, Pb (II) does not lose electrons easily and hence, does not act as a reducing agent.

**S17.** (a) (i) Boric acid is a weak monobasic acid. It does not ionise in water to liberate  $\text{H}^+$  ion but accepts electrons from  $\text{OH}^-$  ion of water by behaving as Lewis acid and in turn releases  $\text{H}^+$  ion.

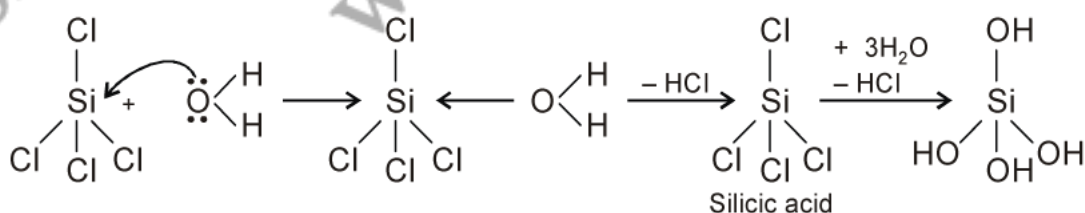


(ii)  $\text{CO}_2$  has linear structure and thus has zero dipole moment. So, the only interaction present between two  $\text{CO}_2$  molecules is weak van der Waals' forces which are not capable of binding  $\text{CO}_2$  molecules at normal condition and thus  $\text{CO}_2$  exists as gas.

In case of  $\text{SiO}_2$ , there is considerable polarity in the molecule due to significance difference in electronegativities of Si and O-atoms. Hence,  $\text{SiO}_2$  molecules form three-dimensional network structure and exist as solid.

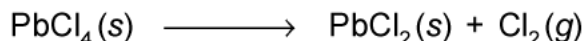
(iii) In silicon, vacant 3d-orbitals are available due to which it can accommodate electrons from 6 fluorine atoms, thereby forming  $\text{SiF}_6^{2-}$  ion. However, in case of C, only  $2p^2$ -filled orbitals are available thus, it cannot expand its covalency more than 4. Thus  $\text{CF}_6^{2-}$  is not known.

(b) (i) The hydrolysis of  $\text{SiCl}_4$  occurs due to coordination of  $\text{OH}^-$  with empty 3d-orbitals in silicon atom of  $\text{SiCl}_4$  molecule.



- (ii) The highly poisonous nature of CO molecule arises because of its ability to form a complex with haemoglobin, which reduces the oxygen transport of haemoglobin and thus can be fatal.

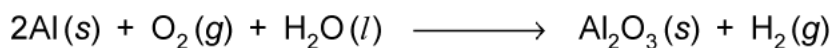
- S18.** (a) Due to greater stability of +2 over +4 oxidation state (or inert pair effect) lead (IV) chloride on heating decomposes to give lead (II) chloride and  $\text{Cl}_2$ .



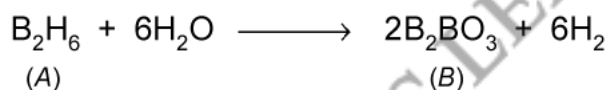
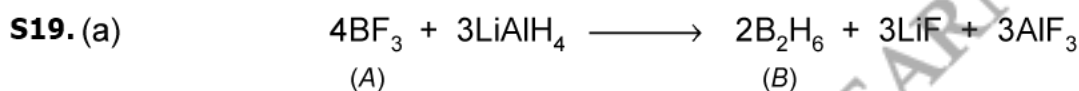
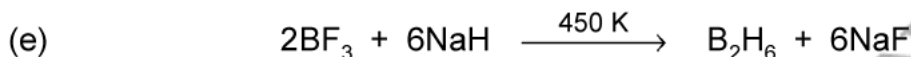
- (b) Boron halides do not dimerise like  $\text{BH}_3$ . This is because halogens are much more electronegative than H. They cannot donate electrons to form three-centre two electron bonds for dimerisation. Moreover, the bigger size of the halogen might prevent the formation of two units of  $\text{BX}_3$ .
- (c) Carbon atoms are small in size. It is difficult for C-atom to lose tightly held electrons or accommodate more electrons in the small atom.

On the other hand due to large size of Pb-atom outer most electrons are loosely held, thus Pb can easily lose two electrons to form  $\text{Pb}^{2+}$  ions and forms ionic compounds.

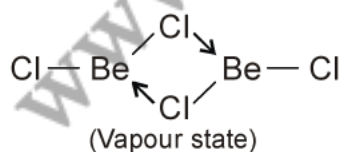
- (d) Al reacts with  $\text{H}_2\text{O}$  and dissolved  $\text{O}_2$  to form a thin film of  $\text{Al}_2\text{O}_3$ .



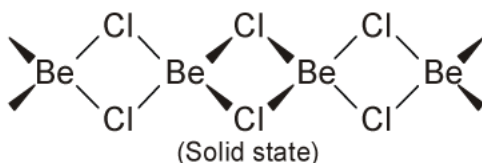
A very small amount of  $\text{Al}_2\text{O}_3$  may dissolve to give a few amount of  $\text{Al}^{3+}$  in the solution. Since  $\text{Al}^{3+}$  ions are injurious to health, therefore drinking water should not be kept in aluminium vessels.



- (b) (i) Al has vacant *d*-orbitals and hence, can expand its coordination number from 4 to 6 and hence, forms octahedral  $[\text{AlF}_6]^{3-}$  ion in which Al undergoes  $sp^3d^2$ -hybridisation. In contrast, B does not have *d*-orbitals. Therefore, it can have a maximum coordination number of 4. Hence, B forms  $[\text{BF}_4]^-$  in which B is  $sp^3$ -hybridised but not  $[\text{BF}_6]^{3-}$ .
- (ii) Due to ineffective shielding of valence electrons by the intervening 3*d* electrons, the effective nuclear charge of Ga is slightly higher than that of Al and hence, the ionisation enthalpy of gallium is higher than that of aluminium.
- (c) (i) In the vapour state, it exists as a chlorine bridged dimer.



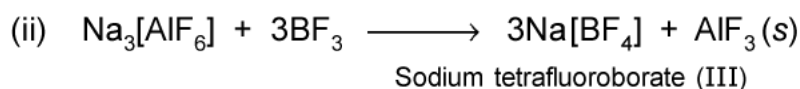
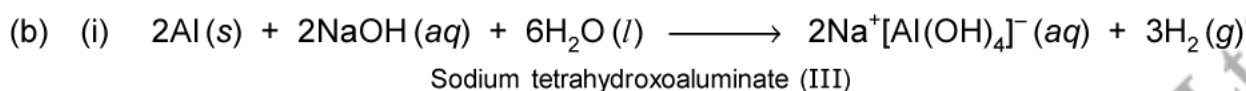
- (ii) In the solid state,  $\text{BeCl}_2$  has polymeric chain structure with chlorine bridges.



**S20.** (a) (i) The Al atom in  $\text{AlCl}_3$  has six electrons in the valence shell. Therefore, it is an electron deficient molecule and needs two more electrons to complete its octet. Therefore, it easily accepts a pair of electrons from electron rich species and thus, behaves as a Lewis acid.

(ii) The outer electronic configuration of thallium is  $6s^26p^1$ . But due to inert pair effect, the  $6s^2$ -electrons are strongly attracted by the nucleus than  $6p^1$ -electron. Therefore,  $6s^2$ -electrons do not participate in bond formation. Instead, only  $6p^1$ -electron takes part in bond formation and thallium shows an oxidation state of +1. Thus +1 oxidation state of thallium is more stable than +3 oxidation state.

(iii) In  $\text{SnO}_2$  and  $\text{PbO}_2$ , both tin and lead have +4 oxidation state. But due to inert pair effect,  $\text{Pb}^{2+}$  ion is more stable than  $\text{Sn}^{2+}$  ion.  $\text{PbO}_2$  is more easily reduced to  $\text{Pb}^{2+}$  ion than  $\text{Sn}^{4+}$  ions are reduced to  $\text{Sn}^{2+}$  ion. Hence,  $\text{PbO}_2$  acts as a stronger oxidising agent than  $\text{SnO}_2$ .



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