HINTS & SOLUTIONS

p-Block Elements

[Set-1]

SECTION-A

1. (iii): The basic structural unit of silicates is SiO_4^{4-} in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion.

2. (iii): Be_2C and Al_4C_3 both gives methane on hydrolysis

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

3. (iii): Graphite is the most stable form of carbon at 25°C and 1 bar pressure called the standard state.

4. (i): B_2H_6 has a bridged structure in which each boron uses sp^3 hydrid orbitals.

5. (iv): Inorganic benzene or Borazole or Borazine is $B_3N_3H_6$, isoelectronic and isostructural with organic benzene.

   Asbestos is type of silicate

   Tincal is a mineral called borax $Na_2B_4O_7.10H_2O$

   Acidic oxide is boron sesquioxide, B_2O_3.

6. (i): Assertion and reason both are correct and reason in the correct explanation of assertion.

   Also, the six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

7. (iii): The reason is wrong. It is not a protonic acid but acts as a Lewis acid by accepting electrons frrm a hydroxyl ion of water. It's a water which releases H^+ ions

$$B(OH)_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

8. (iii): In BCl_3, the sicleways overlapping involving vacant 2p orbital of B and fully filled 4p orbital of Br is not very effective. So, the availability of empty atomic orbital on boron is more. Hence, the Lewis acid strength order is

$$BF_3 < BCl_3 < BBr_3$$

   (ii) In this reaction, boron is using one empty 2p orbital to accept electron pair from NH_3. Hence, its hybridsation changes from sp^2 to sp^3.

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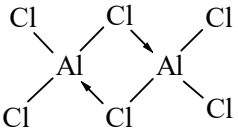
10. (i):



Each Al is bonded to 4 Cl atoms, has a covalence of 4. Also, each Al is sp^3 hybridised.

11. (i) $3BF_3 + 6LiH \rightarrow B_2H_6 + 6LiF$

(ii) $SiO_2 + 6HF \rightarrow H_2[SiF_6] + 2H_2O$

OR

(i) In diamond, each C atom is sp^3 hybridised and is linked to four toher carbon atoms in a tetrahedral fastion. This structure extends in space and produces a rigid three dimensional network of carbon atoms. The directional covalent bonds are present through out the lattice

(ii) Boron is unable to form BF_6^{3-} due to the absence of d-atomic orbitals. Boron can show a maximum covalence of four and cannot expand its octet.

12. (i) BCl_3 is more stable than $TlCl_3$ due to **inert pair effect**. In fact Tl form TlCl. Down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electron tightly and thereby restricting their participation in bonding. As a result of this only p-orbital electrons involved in bonding so, Tl shows +1 oxidation state and form TlCl and not $TlCl_3$.

(ii) In CO_2, carbon is present in its highest oxidation state of +4. This carbon can attain lower oxidation state by gain of electrons. Hence, CO_2 is acidic in nature. It dissolves in water to form a weak dibasic acid, H_2CO_2, CO is neutral oxide because it does not react with water to give neither acidic nor basic solutions.

13. (i) Electron deficient compounds are those compounds in which the central atom has an incomplete octet means less than eight electrons around the central atom or compound in which the central atom can expand its octet by using empty d-atomic orbitals. For example, in BF_3, boron has ony six electrons around it. Si can expand its octet by using empty d-orbitals.

(ii) Yes, both are electron deficient

In BCl_3, B has only six electrons and can accept one electron pair in its empty 2p-orbitals.

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In $SiCl_4$, Si has eight electrons and has an empty d-orbital, so it can expand its octet by accepting electron pair. But in fact, silicon does not accept two more Cl^- ions to form $SiCl_6^{2-}$ due to large size of Cl and weak Si – Cl bond.

14. (i) SiO_2 reacts with NaOH to form sodium silicate

$$\underset{\text{acidic oxide}}{SiO_2} + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

(ii) CO is a reducing agent and reduces ZnO to Zn

$$CO + ZnO \longrightarrow CO_2 + Zn$$

CO is used as a reducing agent in the extraction of metals.

(iii) Si on heating with CH_3Cl at high temperature in the presence of copper to give dichlorodimethyl silane.

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

OR

(i) Dilute NaOH on reaction with Al liberates hydrogen gas which helps in the opening of blocked drain.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

(ii) Diamond has a three-dimensional network structure in which each carbon atom is tetrahedraly bonded to four other carbon atoms. As a result, diamond is very hard and is used as an abrasive.

(iii) Carbon form CCl_4 but Pb form $PbCl_2$ due to inert pair effect.

Down the group 14 the stability of +2 oxidation state increases due to ineffective shielding of the valence electron by the intervering d and f orbitals. So, in lead the ns electrons are more tightly held than np electrons. Hence, Pb shows + 2 oxidation state and form $PbCl_2$.

15. (i) $X \rightarrow Na_2B_4O_7$

$Y \rightarrow H_3BO_3$

$Z \rightarrow B_2O_3$

(a) $\underset{(X)}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{(Y)}{4H_3BO_3}$

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(b) $\underset{(Y)}{H_3BO_3} \xrightarrow[370K]{Heat} HBO_2 + H_2O$

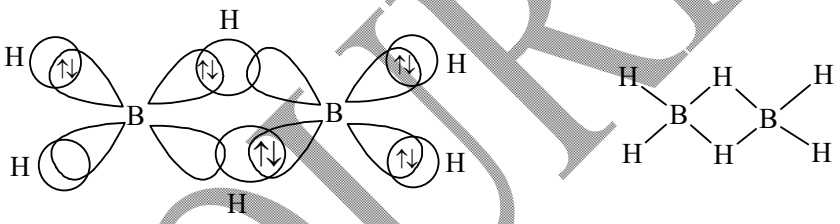
$2HBO_2 \xrightarrow[T > 370K]{Heat} \underset{(Z)}{B_2O_3} + H_2O$

(ii) (a) B is extremely small in size. The sum of the first three ionization enthalpies is very high and this cannot be compensated by hydration enthalpy in aqueous medium or lattice enthalpy in the solid state. Hence, B^{3+} ion does not exist.

(b) Due to large size, silicon cannot complete the octet via pπ-pπ bond formation. Hence, silicon does not form graphite like structure

OR

(i) (a) Diborane, B_2H_6 has a structure with two different types of hydrogen. The four terminal B – H bonds are the normal 2 electron-2-centre covalent bond. The bridged part of the molecule contains 2 electron 3 centre covalent bonds using sp^3 hybrid orbitals of boron and 1s orbital of hydrogen. The electron deficiency is present in the bridged part of the molecule. The multicenter bonds in the bridged part are also celled **banana bonds**.



(b) Diborna reacts violently with water to form boric acid and liberates hydrogen gas

$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

(ii) $X \rightarrow BF_3$

$Y \rightarrow B_2H_6$

$Z \rightarrow 2BH_3.CO$

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

$\underset{(Y)}{B_2H_6} + 2CO \longrightarrow \underset{\text{adduct}}{2BH_3.CO}$

$\underset{(Y)}{B_2H_6} + 3O_2 \xrightarrow{Heat} B_2O_3 + 3H_2O$

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