UNIT-11
The p-Block Elements

NCERT–Examplar Problems with Solutions

SECTION-I: *Multiple Choice Questions (Type-I)*

Note: In the following questions, only one option is correct.

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

(i) B

(ii) Al

(iii) Ga

(iv) In

Ans. (iii)

Gallium in group 13 exists in a liquid state.

2. Which of the following is a Lewis acid?

(i) $AlCl_3$

(ii) $MgCl_2$

(iii) $CaCl_2$

(iv) $BaCl_2$

Ans. (i)

Lewis acid is electron pair acceptor.

In $AlCl_3$, Al has an incomplete octet with one empty p-atomic orbital. Hence, $AlCl_3$ is a Lewis acid.

3. The geometry of a complex species can be understood from the knowledge of type of hybridization of orbitals of central atom. The hybridisation of orbitals or central atom in $[Be(OH)_4]^-$ and the geometry of the complex are respectively

(i) sp^3, tetrahedral

(ii) sp^3, square planar

(iii) sp^3d^2, octahedral

(iv) dsp^2, square planar

Ans. (i)

In $[Be(OH)_4]^-$, Be is sp^3 hybridised, this complex ion is tetrahedral in shape.

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

(i) B_2O_3

(ii) Al_2O_3

(iii) Ga_2O_3

(iv) In_2O_3

Ans. (i)

B_2O_3 is acidic oxide. It reacts with metal oxides to form metaborates.

$$\underset{\text{cobalt oxide (base)}}{CoO} + \underset{\text{(acid)}}{B_2O_3} \longrightarrow \underset{\text{Cobalt metaborate}}{Co(BO_2)_2}$$

5. The exhibition of highest co-ordination 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-}?

(i) B

(ii) Al

(iii) Ga

(iv) In

Ans. (i)

B is from the second period with valence shell electronic configuration of $2s^2\ 2p^1$. Since B does not have d-atomic orbitals available, it does not show covalency more than 4. Hence, MF_6^{3-} ion for boron does not exist.

6. Boric acid is an acid because its molecule

(i) contains replaceable H^+ ion

(ii) gives up a proton

(iii) accepts OH^- from water releasing proton

(iv) combines with proton from water molecule

Ans. (iii)

Boric acid is a Lewis acid and not a protonic acid

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

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:

(i) C > Si > Ge > Sn

(ii) C >> Si > Ge = Sn

(iii) Si > C > Sn > Ge

(iv) Ge > Sn > Si > C

Ans. (ii)

Catenation is the ability of an atom to form a bond with itself. Down the group, atomic size increases and the tendency to catenate decreases. However, Ge and Sn have almost same tendency to catanate.

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

(i) $MeSiCl_3$

(ii) Me_2SiCl_2

(iii) Me_3SiCl

(iv) Me_4Si

Ans. (iii)

Addition of Me_3SiCl will block the chain on one side and control the polymerization of silicones.

9. Ionisation enthalpy (Δ_iH_i kJ mol^{-1}) for the elements of group 13 follows the order

(i) B > Al > Ga > ln > Tl

(ii) B < Al < Ga < ln < Tl

(iii) B < Al > Ga < ln > Tl

(iv) B > Al < Ga > ln < Tl

Ans. (iv)

Ga has a higher Δ_iH_1 than Al due to the presence of fully filled $3d^{10}$ which does not protect the valence electrons from the nucleus effectively and the electrons are tightly held by the nucleus.

Tl has a highly diffused $4f^{14}$ which has a poorest shielding effect. Hence, Tl has a higher Δ_iH_i than In.

10. In the structure of diborane

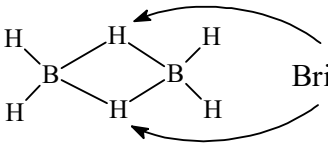
(i) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane

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

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

(iv) All the atoms are in the same plane

Ans. (ii)



Bridged H-atoms perpendicular to the plane

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

(i) B_2H_6, $B_3N_3H_6$

(ii) B_2O_3, $B_3N_3H_6$

(iii) BF_3, $B_3N_3H_6$

(iv) $B_3N_2H_6$, B_2H_6

Ans. (i)

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

$$3B_2H_6 + 6NH_3 \longrightarrow \underset{(Y)}{2B_3N_3H_6} + 12H_2$$

Inorganic benzene

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

(i) Pb

(ii) Si

(iii) Ti

(iv) Sn

Ans. (ii)

Quartz is made up of SiO_2 tetrahedral units.

13. The most commonly used reducing agent is

(i) $AlCl_3$

(ii) $PbCl_2$

(iii) $SnCl_4$

(iv) $SnCl_2$

Ans. (iv)

In $SnCl_2$, the oxidation state of Sn is +2 and it can attain stable +4 oxidation state by the loss of $2e^-$.

Hence, $SnCl_2$ act as a reducing agent.

For Pb, +2 is more stable than +4.

14. Dry ice is

(i) Solid NH_3

(ii) Solid SO_2

(iii) Solid CO_2

(iv) Solid N_2

Ans. (iii)

Dry ice is solid CO_2 which is a molecular solid, used as a refrigerant.

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?

(i) group 2

(ii) groups 2, 13 and 14

(iii) groups 2 and 13

(iv) groups 2 and 14

Ans. (ii)

Cement is a mixture of calcium and aluminium silicates (CaO. $Al_2O_3.SiO_2$) and also contains iron and sulphur Ca $\longrightarrow$ group-2, Al $\longrightarrow$ group 13, Si $\longrightarrow$ gropu14.

SECTION-II: *Multiple Choice Questions (Type II)*

Note: In the following questions two or more options may be correct.

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

(i) poor screening effect of d orbitals

(ii) increase in nuclear charge

(iii) presence of higher orbitals

(iv) higher atomic number

Ans. (i), (ii)

This is due to increased nuclear charge and poor shielding effect of the $3d^{10}$ electrons that valence electrons are very tightly held by the nucleus and atomic size of Ga is small as compared to Al.

17. The linear shape of CO_2 is due to

(i) sp^3 hybridisation of carbon

(ii) sp hybridisation of carbon

(iii) pπ-pπ bonding between carbon and oxygen

(iv) sp^2 hybridisation of carbon

Ans. (ii), (iii)

In CO_2, C form one sigma bond with each oxygen. CO_2 also contains pπ-pπ bond. C in CO_2 is sp hybridized and is linear in shape.

18. Me_3SiCl is used during polymerisation of organo silicones because

(i) the chain length of organo silicone polymers can be controlled by adding Me_3SiCl

(ii) Me_3SiCl blocks the end terminal of silicon polymer

(iii) Me_3SiCl improves the quality and yield of the polymer

(iv) Me_3SiCl acts as a catalyst during polymerization

Ans. (i), (ii)

Me_3SiCl block the polymerization of chain at one end and thereby control the chain length of organo silicone polymers.

19. Which of the following statements are correct?

(i) Fullerenes have dangling bonds.

(ii) Fullerenes are cage like molecules

(iii) Graphite is thermodynamically most stable allotrope of carbon

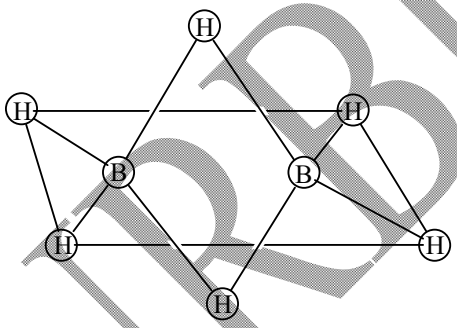
(iv) Graphite is slippery and hard and therefore used as a dry lubricant in machines.

Ans. (ii), (iii)

Fullerenes are cage like structures (called bucky ball) and contains six-membered rings as well as five membered rings.

Graphite is thermodynamically the most stable allotrope of carbon.

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



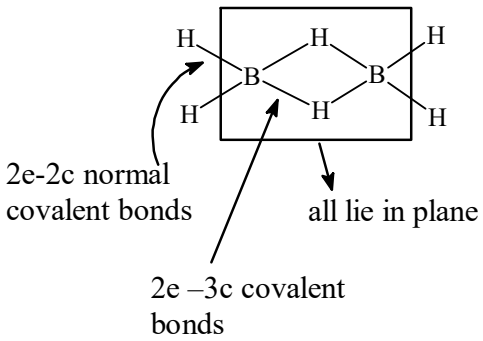
(i) The two bridged hydrogen atoms and the two boron atoms lie in one plane

(ii) Out of six B – H bonds two bonds can be described in terms of 3 centre 2-electron bonds.

(iii) Out of six B – H bonds four B– H bonds can be described in terms of 3 centre 2 electron bonds.

(iv) The four terminal B – H bonds are two centre two electron regular bonds.

Ans. (i), (ii), (iv)

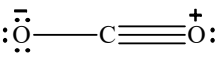


21. Identify the correct resonance structure of carbon dioxide from the ones given below:

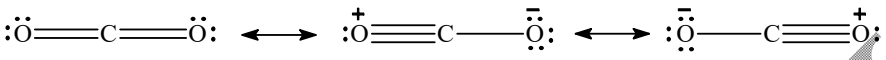
(i) O – C = O

(ii) O = C = O

(iii) $\bar{O} \equiv C - O^+$

(vi) 

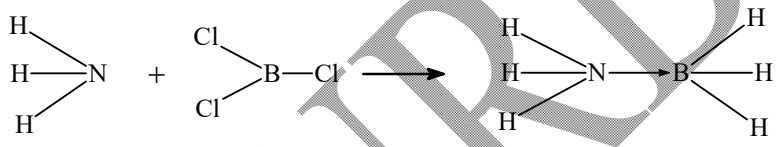
Ans. (ii), (iv)



SECTION-III: *Short Answer Type*

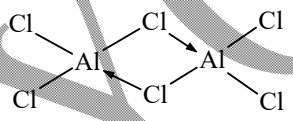
22. Draw the structures of $BCl_3.NH_3$ and $AlCl_3$ (dimer)

Ans. In BCl_3, B is sp^2 bridised with one empty p-atomic orbital. B has an incomplete octet. BCl_3 is a Lewis acid BCl_3 accepts electron pair from ammonia. NH_3 has a lone pair of electron present NH_3 is a Lewis base.



$N \rightarrow sp^3$	$B \rightarrow sp^2$	$N \rightarrow sp^3$	$B \rightarrow sp^3$
AX_3E	AX_3	AX_4	AX_4
Trigonal pyramidal	Trigonal planar	Tetrahedral	Tetrahedral

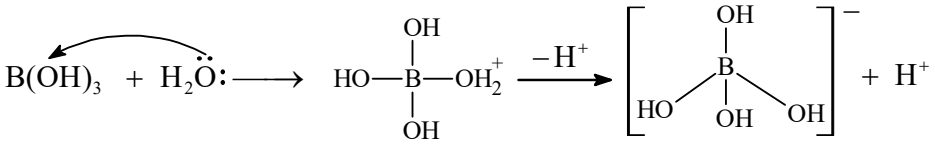
Al_2Cl_6 has a dimer structure with bridged chlorine atoms and each Al has a complete octet.



Each Al is sp^3 hybridised

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

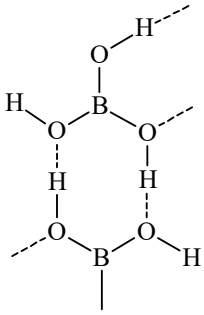
Ans. In boric acid, H_3BO_3, B has an incomplete octet. It accepts lone pair of electron from H_2O and loses H^+ from H_2O.



Boric acid is a Lewis acid and H^+ comes from H_2O.

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

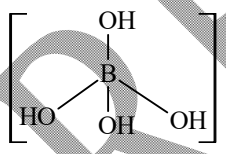
Ans. In boric acid, planar BO_3^{3-} units are joined by unsymmetrical hydrogen bonds to give a layered structure.



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

boric acid

$B(OH)_4^-$ is present in water. In this the B atom is sp^3 hybridised and has a tetrahedral structure.



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

(i) BCl_3 **(ii) $AlCl_3$**

Ans. In both BCl_3 and $AlCl_3$, the central atom is bonded with only three chlorine atoms. The central atoms has only six electrons and incomplete octet with empty p-atomic orbital. So, both BCl_3 and $AlCl_3$ are electron pair acceptor and hence both are **Lewis acids.**

26. Give reasons for the following:

(i) CCl_4 is immisible in water, whereas $SiCl_4$ is easily hydrolysed.

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

Ans. (i) In CCl_4, carbon ha a complete octet. It does not have any d-atomic orbital and cannot accept any lone pair from water. Hence, CCl_4 is inert towards water and immiscible in water. In $SiCl_4$, Si has empty d orbitals available, can accept lone pair of electron from H_2O. Si in $SiCl_4$ can expand its octet, hence gets hydrolysed by H_2O easily.

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

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

(silicic acid)

(ii) Due to small size of C and high carbon–carbon bond dissociation energy, carbon has more tendency to catenate then silicon.

27. Explain the following:

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

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

Ans. (i) In CO_2, carbon completes its octet via pπ-pπ bond formation, CO_2 is a discrete molecule and the inter molecular forces of attraction are the weak van der Waal forces. Hence, CO_2 is a gas. On the other hand, due to large size, silicon completes its octet via sigma bond formation. In SiO_2, each Si is tetrahedrally bonded to form oxygen atoms and oxygen is bonded to two silicon atom. SiO_2 has network structure. Hence, SiO_2 is a covalent network solid.

(ii) Si from SiF_6^{2-} because silicon has empty d-atomic orbitals and silicon can show higher covalency.

Carbon does not have d-atomic orbitals and carbon has a maximum covalency of 4. Hence, CF_6^{2-} does not exist.

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 group 13 elements have a valance shell electronic configuration of ns^2np^1 and the group oxidation state is +3. The heavier elements of this group have either fully filled d^{10} or f^{14} or both d^{10} and f^{14}. Due to poor shielding effect of d and f electrons, the valence electrons are held more strongly by the nucleus as we move down the group. Since ns electrons are nearer to the nucleus, held more strongly than np. So, only np electron participates in bonding. As we move down the group, the tendency of the ns electron pair to remain inert or not participate in the bond formation increases. This is known as **inert pair effect**. So, the heavier elements show an oxidation state two units less than the group oxidation state. Hence, in group 13, (ns^2 np^1), the group oxidation state is +3 but the heavier elements shows +1 similarly in group 14 (ns^2np^2), the group oxidation state is +4 but the heavier elements show +2.

Group 13 (ns^2 np^1)

B
Al
Ga
In
Tl

+3 stability decreases

+1 stability increases

Group 14 (ns^2 np^2)

C
Si
Ge
Sn
Pb

+4 stability decreases

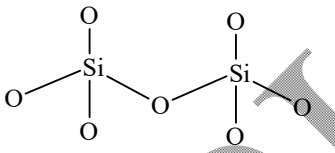
+2 stability increases

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

Ans. Carbon form CO_2 in which the C is sp hybridized and complete its octet via pπ-pπ bond formation CO_2 is a linear molecule and discrete molecule. The intermolecular forces of attraction are the weak van der Waal forces and hence CO_2 is a gas

O = C = O

Silicon form SiO_2 in which Si is sp^3 hybridised and each Si is tetrahedrally bonded to four oxygen atoms. Silicon complete its octet via sigma bond formation and SiO_2 has a three dimensional network structure. Hence, SiO_2 is a high melting solid.



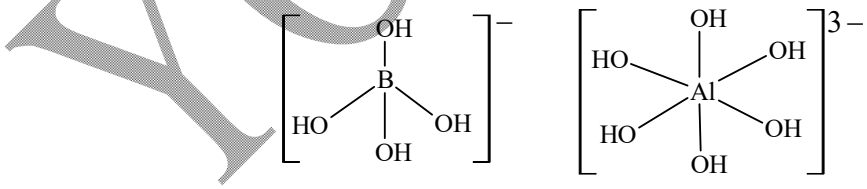
30. If a trivalent atom replaces a few silicon atoms in three dimensional network of silicon dioxide, what would be the type of charge on overall structure?

Ans. When we replace tetravalent silicon by trivalent atoms in three-dimensional network of silicon dioxide, then one valence of silicon remains free, one electron of silicon remains unused. As result, SiO_2 acquires a negative charge.

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. $BCl_3 + 4H_2O \longrightarrow [B(OH)_4]^- + 3Cl^- + 4H^+$

In $[B(OH)_4]^-$, B is sp^3 hybridised and the geometry is tetrahedral



$AlCl_3 + 6H_2O \longrightarrow [Al(OH)_6]^{3-} + 3Cl^- + 6H^+$

In $[Al(OH)_6]^{3-}$, Al is sp^3d^2 hybridised and the geometry is octehdral.

32. Aluminium dissolved 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 indicated the evolution of hydrogen gas. The same

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

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

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

with mineral aids and alkali (NaOH), H_2 gas is released

Since, HNO_3 is a strong oxidizing agent, it oxidizes Al to Al_2O_3 and itself reduced to form brown fumes of NO_2 gas.

This Al_2O_3 forms a protective layer on aluminium and prevents the further reaction of Al with conc. HNO_3.

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

33. Explain the following:

(i) Gallium has higher ionization enthalpy than aluminium

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

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

(iv) PbX_2 is more stable than PbX_4.

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

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

(vii) $Tl(NO_3)_3$ acts as an oxidizing agent.

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

(ix) BF_3 does not hydrolyse

(x) Silicon does not form graphite like structure whereas carbon does.

Ans. (i) Due to presence of fully filled $3d^{10}$ subshell in gallium 3d orbitals are highly diffused and have a poor shielding effect and do not protect the valence electrons from the nucleus effectively. The valence electrons are more strongly held by the nucleus and more energy is required to remove an electron. Hence, Gallium has higher ionization enthalpy than aluminium.

(ii) This is due to extremely small size of Boron and the sum of the first three ionization enthalpies is very-very high which is not compensated either by lattice enthalpy in the solid state or hydration enthalpy in aqueous medium. That's why B^{3+} ion does not exist.

(iii) This is due to the presence of d-atomic orbitals in aluminium and the aluminium can show higher covalency of six in AlF_6^{3-}. B does not have d-atomic orbital, B has a maximum covalency of 4, hence B forms BF_4^-.

(iv) This is due to inert pair effect. Due to the presence of fully filled $4f^{14}$, the valence $6s^2$ electrons are more tightly held than $6p^2$ electrons. So, only 6p electrons participates in the bond formation. Hence, PbX_2 is more stable than PbX_4.

(v) For lead, +2 oxidation state is more stable than +4 due to inert pair effect. Pb^{4+} will try to attain + 2 oxidation state by the gain of two electrons. So, Pb^{4+} will reduce itself to Pb^{2+}, hence Pb^{4+} is a strong oxidizing agent.

On the other hand, +4 oxidation state is more stable for Sn than +2. So, Sn^{2+} will try to attain Sn^{4+} by the loss of two electrons.

Hence. Sn^{2+} acts as a reducing agent.

(vi) Due to the large size of Cl than F, it is more faourable to add one electron to Cl atom with less repulsions than addition of one electrons to extremely small size F with high electron density. Hence, Cl has more negative electron gain enthalpy than F.

(vii) This is due to inert pair effect, Tl^{3+} is unstable and will try to attain +1 oxidation state by the gain of electrons. Hence, $Ti(NO_3)_3$ acts as an oxidising agent.

(viii) Carbon show catenation property but lead does not due to small size of carbon and high carbon-carbon bond dissociation enthalpy.

(ix) BF_3 does not hydrolyse. This is due to

(a) strong B – F bond

(b) H_3BO_3 formed reacts with HF to form tetrafluoroborate ion.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

$$H_3BO_3 + 4HF \longrightarrow H^+ + BF_4^- + 3H_2O$$

(x) Silicon does not form graphite like structure due to its large size and less electronegativity. Silicon doe not complete its octet via pπ-pπ bond formation. Carbon due to its small size and high electronegativity, has a tendency to complete octet via pπ-pπ bond formation.

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

(i) $\mathbf{A + 2HCl + 5H_2O \longrightarrow 2NaCl + X}$

(ii) $\mathbf{X \xrightarrow[370\,K]{\Delta} HBO_2 \xrightarrow[>370\,K]{\Delta} Z}$

Ans. (i) A is $Na_2B_4O_7$ (borax)

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

(ii) $$\underset{(X)}{H_3BO_3} \xrightarrow[370K]{\Delta} HBO_2 + H_2O$$

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

35. Complete the following chemical equations:

$\mathbf{Z + 3LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3}$

$\mathbf{X + 6\,H_2O \longrightarrow Y + 6H_2}$

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

Ans. $Z = BF_3$

$X = B_2H_6$

$Y = H_3BO_3$

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

$$\underset{(X)}{B_2H_6} + 6H_2O \longrightarrow \underset{(Y)}{H_3BO_3} + 6H_2$$

$$\underset{(X)}{B_2H_6} + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

SECTION-IV: *Matching Type*

Note: In some of the following questions, one option of left column may be correlated to more than one option in the right column.

36. Match the elements given in column I with the properties mentioned in column II.

	Colum-I		Column-II
(i)	BF_4^-	**(a)**	**Oxidation state of central atom is +4**
(ii)	$AlCl_3$	**(b)**	**Strong oxidizing agent**
(iii)	SnO	**(c)**	**Lewis acid**
(iv)	PbO_2	**(d)**	**Can be further oxidized**
		(e)	**Tetrahedral shape**

Ans. (i) (ii) (iii) (iv)
(e) (c) (d) (a), (b)

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

	Column-I		Column-II
(i)	**Diborane**	**(a)**	**Used as a flux for soldering matals**
(ii)	**Gallium**	**(b)**	**Crystalline form of silica**
(iii)	**Borax**	**(c)**	**Banana Bonds**
(iv)	**Aluminosilicate**	**(d)**	**Low melting, high boiling, useful for measuring high temperatures**
(v)	**Quartz**	**(e)**	**Used as catalyst in petrochemical industries.**

Ans. (i) (ii) (iii) (iv) (v)
(c) (d) (a) (e) (b)

38. Match the species given in Column-I with properties given in Column-II.

	Column-I		Column-II
(i)	**Boron in $[B(OH)_4]^-$**	**(a)**	**sp^2**
(ii)	**Aluminium in $[Al(H_2O)_6]^{3+}$**	**(b)**	**sp^3**
(iii)	**Boron in B_2H_6**	**(c)**	**sp^3d^2**
(iv)	**Carbon in Buckminsterfullerene**		
(v)	**Silicon in SiO_4^{4-}**		
(vi)	**Germanium in $[GeCl_6]^{2-}$**		

Ans. (i) (ii) (iii) (iv) (v) (vi)
(b) (c) (b) (a) (b) (c)

SECTION-V: *Assertion and Reason Type*

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

39. Assertion(A): If aluminium atoms replaced 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.

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

(ii) Both A and R are correct but R is not correct explanation of A.

(iii) Both A and R are not correct

(iv) A is not correct but R is correct

Ans. (i) Replacement of tetravalent Si by trivalent Al results in one free valence for Si, the lattice acquires a negative charge.

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

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

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

(ii) Both A and R are correct but R is not correct explanation of A.

(iii) Both A and R are not correct

(iv) A is not correct but R is correct

Ans. (ii) Silocones are water repelling because in silicones, silicon atom is surrounded by non-polar hydrophobic alkyl group.

SECTION-VI: *Long answer Type*

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

(i) Atomic size **(ii) Ionisation enthalpy**

(iii) Metallic character **(iv) Oxidation states**

(v) Nature of halides.

Ans.

	Property	Group-13	Group-14
(i)	Atomic size	Atomic size increases down the group but Ga has smaller atomic radius than Al due to poor shielding by $3d^{10}$ is Ga.	Atomic size increases down the group but the increase in size from Sn to Pb is not very large due to poor shielding effect of $4f^{14}$ in Pb.
(ii)	Ionisation enthalpy	Ionization enthalpy order is B > Tl > Ga > Al > In Tl abnormality is due to poor shielding effect of $5d^{10}$ and $4f^{14}$ while in Ga, this is due to poor shielding effect of $3d^{10}$.	Ionization enthalpy decreases down the group but Pb has slight higher $\Delta_i H_1$ than Sn due to ineffective shielding of the valence electrons by $4f^{14}$.
(iii)	Metallic character	It increases down the group.	It increases down the group. C, Si are non metals, Ge is a metalloid and Sn, Pb are metals.
(iv)	Oxidation states	The group oxidation state is +3. Down the group, stability of +3 oxidation state decreases and +1 stability increases due to inert pair effect.	The group oxidation state is +4. Down the group, stability of +4 oxidation state decreases and +2 stability increases due to inert pair effect.
(v)	Nature of halides	The halides are mainly covalent. The covalent character decreases down the group.	The halides are covalent the covalent character of halides decreases down the group.

42. Account for the following observations:

(i) $AlCl_3$ is a Lewis acid

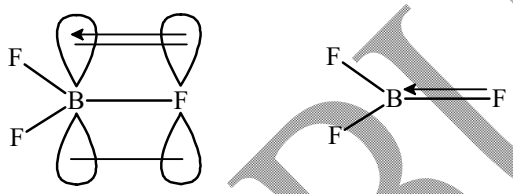
(ii) Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than BCl_3.

(iii) PbO_2 is a stronger oxidizing agent than SnO_2

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

Ans. (i) In $AlCl_3$, Al has only formed three covalent bonds, Al has incomplete octet. Al has one empty p-atomic orbital available. Al in $AlCl_3$ is electron pair acceptor. Hence $AlCl_3$ is a Lewis acid.

(ii) Due to comparable size of B and F. There is a dative π bonding takes place between B and F and B in BF_3 complete its octet.



Due to large size of Cl, there is a weak ineffective dative π bonding, between B and Cl therefore, the empty p-atomic orbital is less available in BF_3 than in BCl_3. Hence, BF_3 is a weaker Lewis acid than BCl_3.

(iii) For Pb, +2 oxidation state is more stable than +4 due to inert pair effect. Pb in PbO_2 will try to attain +2 oxidation state by the gain of two electrons. The substance which accepts electron is an oxidizing agent. Hence, PbO_2 is a stronger oxidizing agent than SnO_2.

(iv) Thallium is more stable in +1 than in +3 oxidation state due to inert pair effect. In thallium, only one electron from the p-subshell participates in bonding and the s-electron pair remain inert due to poorest shielding effect of $4f^{14}$.

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. (i) Acidification of borax with HCl.

$$Na_2B_4O_7.10H_2O + 2HCl \longrightarrow 2NaCl + 4H_3BO_3 + 5H_2O$$

Borax Boric acid

(ii) Boric acid is a white crystalline solid which has a layered structure due to hydrogen bonding. Boric acid is soapy in touch. Boric acid is not a protonic acid (not an Arrhenius or Bronsted acid)

Boric acid accepts OH^- ion from H_2O and releases H^+ ion.

Boric acid is a Lewis acid

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

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. Give reason for your choice. State the nature of bonding also.

(i) $TlCl_3$, TlCl

(ii) $AlCl_3$, AlCl

(iii) $InCl_3$, InCl

Ans. **(i)** TlCl with Tl in +1 oxidation state is more stable than $TlCl_3$. This is due to inert pair effect. TlCl has an ionic bonding.

(ii) $AlCl_3$ is more stable than AlCl. Al does not show inert pair effect.

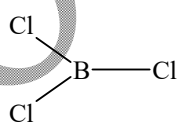
In the solid and vapour state, $AlCl_3$ is covalent but in aqueous solution, it ionize to give $Al^{3+}(aq)$ and $3Cl^-(aq)$ ions due to high hydration enthalpy.

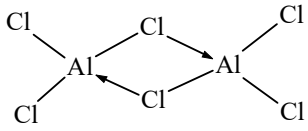
(iii) Indium shows both +1 and +3 oxidation state but $InCl_3$ is more stable than InCl due to weak inert pair effect. In $InCl_3$, the bonding is covalent.

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. BCl_3 is an electron deficient molecule and is a Lewis acid (electron pair acceptor) B in BCl_3 tries to complete its octet via dative pi bond formation. B due to its small size cannot accept electron pair from Cl- to accommodate four Cl atoms in its coordination sphere. Hence, BCl_3 exists as a monomer.

On the other hand, Al in $AlCl_3$ can accept lone pair of electron from the Cl of the second $AlCl_3$ molecule and complete its octet. Hence, $AlCl_3$ exists as a dimer with dative σ bond and bridged chlorine atom.





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.

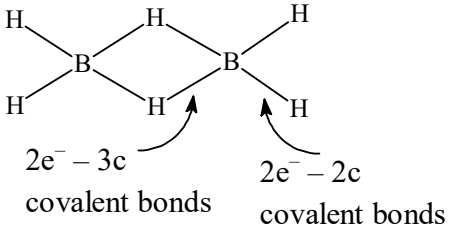
Ans. Boron fluoride exists as BF_3 in which B is sp^2 hybridised. In BF_3, there exist a dative π-bond between empty 2p atomic orbital of boron and fully filled 2p atomic orbital of fluorine. As a result, B complete its octet. This gives stability to BF_3.

BH_3 does not exist because hydrogen has no lone pair of electron and there is no dative π-bond. To gain stability BH_3 dimerise to give B_2H_6 (diborane)

Boron hydride BH_3 exist in the form of a dimer B_2H_6.

Structure of Diborane

Diborane, B_2H_6 has a structure in which B is sp^3 hybridised, there are four terminal B – H bonds which are normal $2e^-$ – 2c covalent bonds. The bridged part of the molecule contains $2e^-$ – 3c multicentre covalent bonds which are completely delocalized.



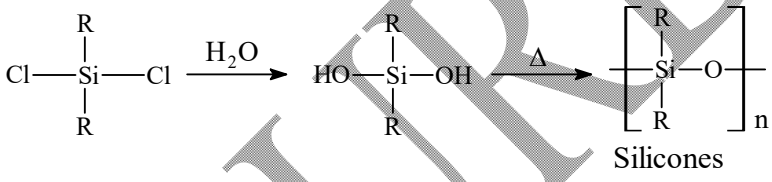
47. (i) What are silicones? State the uses of silicones.

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

Ans. (i) Silicones are organo silicon polymers.

Silicones are formed by the hydrolysis of dialkyl dichlorosilanes.

Silicones have a formula R_2SiO



Uses of Silicones

(a) Silicones are used in water proofing textiles, water proof paints.

(b) Silicones are used as lubricants.

(c) Silicones are used as insulators.

(ii) The binary compounds of boran and hydrogen are called boron hydrides. The hydrides of boron are collectively called boranes in analogy with alkanes.

Important hydride of boron is dibornae, B_2H_6.

Preparation of diborane

(a) $2NaBH_4 + I_2 \longrightarrow 2NaI + B_2H_6 + H_2$

(b) $4BF_3 + 2LiAlH_4 \longrightarrow 2B_2H_6 + 2LiF + 3AlF$

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. A $\longrightarrow$ B_2H_6

B $\longrightarrow$ $2BH_3.NMe_3$ (Me $\longrightarrow$ methyl group CH_3)

C $\longrightarrow$ H_3BO_3

Reactions

$B_2H_6 + 2NMe_3 \longrightarrow 2BH_3.NMe_3$
(A) (B)

$BH_3.NMe_3 + 3H_2O \longrightarrow H_3BO_3 + NMe_3 + 3H_2$

49. A nonmetallic 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 exhibits 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.

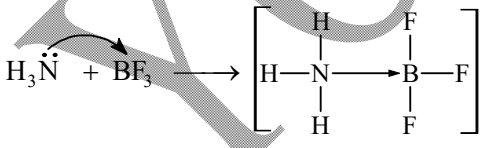
Ans. Element is boron B

Boron is extremely hard

B has only s and p orbitals present and due to absence of d-atomic orbitals, boron shows a maximum covalency of four like in BH_4^- or BF_4^-

B forms a trifluoride, BF_3

Reaction of BF_3 with NH_3



In BF_3, boron has only six electrons, boron has one empty p-atomic orbital available. B is electron pair acceptor. Hence, BF_3 is a Lewis acid.

50. A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1276 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 formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

Ans. The element is carbon, C

Formula of carbon monoxide is CO and formula of carbon dioxide is CO_2

Formation of producer gas

$$2C(s) + \underbrace{O_2(g) + N_2(g)}_{\text{air}} \longrightarrow \underbrace{2CO(g) + N_2(g)}_{\text{producer gas}}$$

Carbon monoxide is a reducing agent and it reduces Fe_2O_3 to Fe in metallurgy

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

