

# Chapter

# The p-Block Elements

## (Group-13 and 14)



### Topic-1: Group-13 Elements (Boron Family)



#### 1 MCQs with One Correct Answer

- The increasing order of atomic radii of the following Group 13 elements is [Adv. 2016]
  - Al < Ga < In < Tl
  - Ga < Al < In < Tl
  - Al < In < Ga < Tl
  - Al < Ga < Tl < In
- How can the following reaction be made to proceed in forward direction? [2006 - 3M, -1]  
$$\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$$
  - addition of borax
  - addition of *cis*-1,2-diol
  - addition of  $\text{Na}_2\text{HPO}_4$
  - addition of *trans*-1,2-diol
- $\text{H}_3\text{BO}_3$  is: [2003S]
  - Monobasic and weak Lewis acid
  - Monobasic and weak Bronsted acid
  - Monobasic and strong Lewis acid
  - Tribasic and weak Bronsted acid
- Which of the following statements about anhydrous aluminium chloride is correct? [1981 - 1 Mark]
  - it exists as  $\text{AlCl}_3$  molecules
  - it is not easily hydrolysed
  - it sublimes at  $100^\circ\text{C}$  under vacuum
  - it is a strong Lewis base



#### 2 Integer Value Answer

- Three moles of  $\text{B}_2\text{H}_6$  are completely reacted with methanol. The number of moles of boron containing product formed is [Adv. 2015]
- The coordination number of Al in the crystalline state of  $\text{AlCl}_3$  is [2009]



#### 4 Fill in the Blanks

- Hydrogen gas is liberated by the action of aluminium with concentrated solution of ..... [1987 - 1 Mark]



#### 5 True / False

- All the Al-Cl bonds in  $\text{Al}_2\text{Cl}_6$  are equivalent. [1989 - 1 Mark]



#### 6 MCQs with One or More than One Correct Answer

- The compound(s) which react(s) with  $\text{NH}_3$  to give boron nitride (BN) is(are) [Adv. 2022]
  - B
  - $\text{B}_2\text{H}_6$
  - $\text{B}_2\text{O}_3$
  - $\text{HBF}_4$
- Among the following, the correct statement(s) is (are) [Adv. 2017]
  - $\text{Al}(\text{CH}_3)_3$  has the three-centre two-electron bonds in its dimeric structure
  - $\text{BH}_3$  has the three-centre two-electron bonds in its dimeric structure
  - $\text{AlCl}_3$  has the three-centre two-electron bonds in its dimeric structure
  - The Lewis acidity of  $\text{BCl}_3$  is greater than that of  $\text{AlCl}_3$
- The crystalline form of borax has [Adv. 2016]
  - tetranuclear  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  unit
  - all boron atoms in the same plane
  - equal number of  $sp^2$  and  $sp^3$  hybridized boron atoms
  - one terminal hydroxide per boron atom
- The correct statement(s) for orthoboric acid is/are [Adv. 2014]
  - It behaves as a weak acid in water due to self-ionization.
  - Acidity of its aqueous solution increases upon addition of ethylene glycol
  - It has a three dimensional structure due to hydrogen bonding
  - It is a weak electrolyte in water





 7 Match the Following

13. Match the following : [2006 - 6M]

## Column I

## Column II

- |   |                       |
|---|-----------------------|
| (A) $\text{Bi}^{3+} \longrightarrow (\text{BiO})^+$                       | (p) Heat              |
| (B) $[\text{AlO}_2]^- \longrightarrow \text{Al}(\text{OH})_3$             | (q) Hydrolysis        |
| (C) $[\text{SiO}_4]^{4-} \longrightarrow [\text{Si}_2\text{O}_7]^{6-}$    | (r) Acidification     |
| (D) $[\text{B}_4\text{O}_7]^{2-} \longrightarrow [\text{B}(\text{OH})_3]$ | (s) Dilution by water |

 9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- (c) If Statement -1 is correct but Statement -2 is incorrect.
- (d) If Statement -1 is incorrect but Statement -2 is correct.
14. **Statement-1** : Boron always forms covalent bond.  
**Statement-2** : The small size of  $\text{B}^{3+}$  favours formation of covalent bond. [2007]
15. **Statement-1** : In water, orthoboric acid behaves as a weak monobasic acid.  
**Statement-2** : In water, orthoboric acid acts as a proton donor. [2007]
16. **Statement-1** :  $\text{Al}(\text{OH})_3$  is amphoteric in nature  
**Statement-2** :  $\text{Al-O}$  and  $\text{O-H}$  bonds can be broken with equal ease in  $\text{Al}(\text{OH})_3$ . [1998 - 2 Marks]

 10 Subjective Problems

17.  $\text{AlF}_3$  is insoluble in anhydrous HF but it becomes soluble in presence of little amount of KF. Addition of boron trifluoride to the resulting solution causes reprecipitation of  $\text{AlF}_3$ . Explain with balanced chemical equations. [2004 - 2 Marks]
18. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of  $\text{B}_2\text{H}_6$  and its reaction with HCl. [2002 - 5 Marks]
19. Compound (X) on reduction with  $\text{LiAlH}_4$  gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Draw the structure of (Y). [2001 - 5 Marks]
20. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced : Alumina from aluminium. [1983 - 1 Mark]
21. State with balanced equations what happens when :  
(i) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. [1997 - 2 Marks]  
(ii) Reaction of aluminium with aqueous sodium hydroxide. [1997 - 1 Mark]
22. Give reason of the following :  
The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other. [1991 - 1 Mark]
23. Complete the following equations (no balancing is needed)  
(i)  $\text{HCO}_3^- + \text{Al}^{3+} \longrightarrow \text{Al}(\text{OH})_3 + \dots$  [1981 - 1 Mark]  
(ii)  $\text{AlBr}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_3\text{PO}_4 \longrightarrow \text{K}_3\text{PO}_4 + \text{AlPO}_4 + \text{H}_2\text{O} + \dots + \dots$  [1981 - 1 Mark]



### Topic-2: Group-14 Elements (Carbon Family)

 1 MCQs with One Correct Answer

1. Name the structure of silicates in which three oxygen atoms of  $[\text{SiO}_4]^{4-}$  are shared. [2005S]  
(a) Pyrosilicate  
(b) Sheet silicate  
(c) Linear chain silicate  
(d) Three dimensional silicate
2.  $(\text{Me})_2\text{SiCl}_2$  on hydrolysis will produce [2003S]  
(a)  $(\text{Me})_2\text{Si}(\text{OH})_2$  (b)  $(\text{Me})_2\text{Si}=\text{O}$   
(c)  $-\text{O}-(\text{Me})_2\text{Si}-\text{O}-$  (d)  $\text{Me}_2\text{SiCl}(\text{OH})$
3. Which one of the following oxides is neutral? [1996 - 1 Mark]  
(a) CO (b)  $\text{SnO}_2$   
(c) ZnO (d)  $\text{SiO}_2$
4. Which of the following halides is least stable and has doubtful existence? [1996 - 1 Mark]  
(a)  $\text{Cl}_4$  (b)  $\text{GeI}_4$  (c)  $\text{SnI}_4$  (d)  $\text{PbI}_4$
5. Moderate electrical conductivity is shown by [1982 - 1 Mark]  
(a) silica (b) graphite  
(c) diamond (d) carborundum





6. Lead pencil contains [1980]  
 (a) Pb (b) FeS  
 (c) Graphite (d) PbS

2 Integer Value Answer

7. The value of  $n$  in the molecular formula  $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$  is [2010]

4 Fill in the Blanks

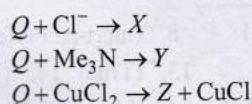
8. Compounds that formally contain  $\text{Pb}^{4+}$  are easily reduced to  $\text{Pb}^{2+}$ . The stability of the lower oxidation state is due to ..... [1997 - 1 Mark]  
 9. A liquid which is permanently supercooled is frequently called a ..... [1997 - 1 Mark]  
 10. One recently discovered allotrope of carbon (e.g.,  $\text{C}_{60}$ ) is commonly known as ..... [1994 - 1 Mark]  
 11. The hydrolysis of trialkylchlorosilane  $\text{R}_3\text{SiCl}$ , yields ..... [1994 - 1 Mark]  
 12. The hydrolysis of alkyl substituted chlorosilanes gives ..... [1991 - 1 Mark]

5 True / False

13. The tendency for catenation is much higher for C than for Si. [1993 - 1 Mark]  
 14. Diamond is harder than graphite. [1993 - 1 Mark]  
 15. Graphite is better lubricant on the moon than on the earth. [1987 - 1 Mark]  
 16. Carbon tetrachloride is inflammable. [1985 - ½ Mark]  
 17. Carbon tetrachloride burns in air when lighted to give phosgene. [1983 - 1 Mark]  
 18. When  $\text{PbO}_2$  reacts with a dilute acid, it gives hydrogen peroxide. [1982 - 1 Mark]

6 MCQs with One or More than One Correct Answer

19. Choose the correct statement(s) among the following.  
 (a)  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is a reducing agent. [Adv. 2020]  
 (b)  $\text{SnO}_2$  reacts with  $\text{KOH}$  to form  $\text{K}_2[\text{Sn}(\text{OH})_6]$ .  
 (c) A solution of  $\text{PbCl}_2$  in  $\text{HCl}$  contains  $\text{Pb}^{2+}$  and  $\text{Cl}^-$  ions.  
 (d) The reaction of  $\text{Pb}_3\text{O}_4$  with hot dilute nitric acid to give  $\text{PbO}_2$  is a redox reaction.  
 20. A tin chloride  $Q$  undergoes the following reactions (not balanced) [Adv. 2019]



$X$  is a mono anion having pyramidal geometry. Both  $Y$  and  $Z$  are neutral compounds. Choose the correct option(s).

- (a) The oxidation state of the central atom in  $Z$  is +2  
 (b) The central atom in  $Z$  has one lone pair of electrons  
 (c) The central atom in  $X$  is  $sp^3$  hybridized  
 (d) There is a coordinate bond in  $Y$   
 21. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are [Adv. 2015]  
 (a)  $\text{CH}_3\text{SiCl}_3$  and  $\text{Si}(\text{CH}_3)_4$   
 (b)  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$   
 (c)  $(\text{CH}_3)_2\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$   
 (d)  $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$   
 22. With respect to graphite and diamond, which of the statement(s) given below is (are) correct? [2012]  
 (a) Graphite is harder than diamond.  
 (b) Graphite has higher electrical conductivity than diamond.  
 (c) Graphite has higher thermal conductivity than diamond.  
 (d) Graphite has higher C-C bond order than diamond.  
 23. The material used in the solar cells contains  
 (a) Cs (b) Si [1993 - 1 Mark]  
 (c) Sn (d) Ti

7 Match the Following

24. Match gases under specified conditions listed in **Column I** with their properties/laws in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [1995S]

Column I	Column II
(A) Explosive	(p) $\text{NaN}_3$
(B) Artificial gem	(q) $\text{Fe}_3\text{O}_4$
(C) Selfreduction	(r) Cu
(D) Magnetic material	(s) $\text{Al}_2\text{O}_3$
	(t) $\text{Pb}(\text{N}_3)_2$
	(u) $\text{Fe}_2\text{O}_3$
	(v) Cu
	(w) SiC

25. Each entry in column **X** is in some way related to the entries in column **Y** and **Z**. Match the appropriate entries : [1989]

X	Y	Z
A. Mica	(a) Graphite crystallite	(i) Abrasive
B. Superphosphate	(b) Cubic	(ii) Insulator
C. Carbon fibres	(c) Layer structure	(iii) Fertilizer
D. Rock salt	(d) Diamond structure	(iv) Reinforced plastics
E. Carborundum	(e) Bone ash	(v) Preservative





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26. **Statement-1** :  $\text{Pb}^{+4}$  compounds are stronger oxidising agents than  $\text{Sn}^{+4}$  compounds [2008]  
**Statement-2** : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.  
 27. **Statement-1** : Between  $\text{SiCl}_4$  and  $\text{CCl}_4$ , only  $\text{SiCl}_4$  reacts with water.  
**Statement-2** :  $\text{SiCl}_4$  is ionic and  $\text{CCl}_4$  is covalent. [2001S]



## 10 Subjective Problems

28. Starting from  $\text{SiCl}_4$ , prepare the following in steps not exceeding the number given in parentheses (give reactions only):

- (i) Silicon (1)  
 (ii) Linear silicone containing methyl groups only (4)  
 (iii)  $\text{Na}_2\text{SiO}_3$  (3) [2001 - 5 Marks]
29. Draw the structure of a cyclic silicate,  $(\text{Si}_3\text{O}_9)^{6-}$  with proper labelling. [1998 - 4 Marks]
30. Complete and balance the following chemical reactions :  
 $\text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \longrightarrow \dots + \dots$  [1994 - 1 Mark]
31. State with balanced equations what happens when :  
 (i)  $\text{SnCl}_4 + \text{C}_2\text{H}_5\text{Cl} + \text{Na} \rightarrow$  [1998 - 1 Mark]  
 (ii) Write balanced equations for the preparation of crystalline silicon from  $\text{SiCl}_4$ . [1990 - 1 Mark]
32. Give reasons for the following :  
 (i)  $(\text{SiH}_3)_3\text{N}$  is a weaker base than  $(\text{CH}_3)_3\text{N}$ . [1995 - 2 Marks]  
 (ii) The molecule of magnesium chloride is linear whereas that of stannous chloride is angular. [1987 - 1 Mark]  
 (iii) Graphite is used as a solid lubricant; [1985 - 1 Mark]  
 (iv) Solid carbon dioxide is known as dry ice. [1983 - 1 Mark]  
 (v) Carbon acts as an abrasive and also as a lubricant. [1981 - 1 Mark]
33. State with balanced equations, what happens when :  
 (i) Tin is treated with moderately concentrated nitric acid.  
 (ii) Aluminium is reacted with hot concentrated caustic soda solution. [1979]



## Answer Key

## Topic-1 : Group-13 Elements (Boron Family)

1. (b) 2. (b) 3. (a) 4. (c) 5. (6) 6. (6) 7. (sodium hydroxide) 8. (False)  
 9. (a,b,c) 10. (a,b,d) 11. (a,c,d) 12. (b,d) 13. (A)-(q), (B)-(s), (C)-(p), (D)-(r) 14. (a) 15. (c) 16. (c)

## Topic-2 : Group-14 Elements (Carbon Family)

1. (b) 2. (c) 3. (a) 4. (d) 5. (b) 6. (c) 7. (3) 8. (inert-pair effect) 9. (glass)  
 10. (fullerence) 11. (trialkylchlorosilanol) 12. (silicones) 13. (True) 14. (True) 15. (True)  
 16. (False) 17. (False) 18. (False) 19. (a,b) 20. (c,d) 21. (b) 22. (b,d) 23. (b)  
 24. A-(t); B-(s); C-(v); D-(q) 25. A-(c)-(ii); B-(e)-(iii); C-(a)-(iv); D-(b)-(v); E-(d)-(i). 26. (c) 27. (c)



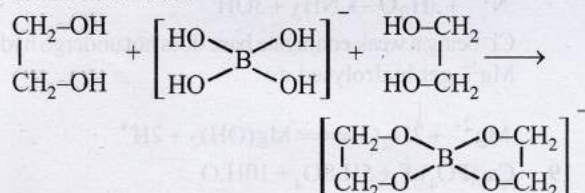


# Hints & Solutions



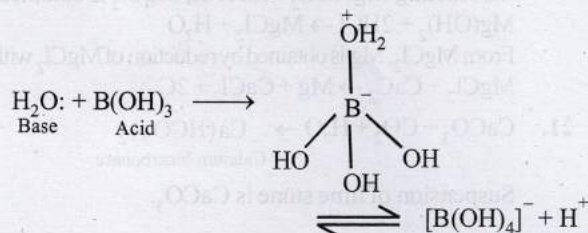
## Topic-1: Group-13 Elements (Boron Family)

- (b) Atomic radii increases on moving down a group. However, due to poor shielding effect of  $d$  orbital, atomic radius of Ga is smaller than Al (**anomaly**). Thus, the correct order is  $Ga < Al < In < Tl$ .
- (b) *cis*-1,2-diol forms chelated complex ion with the product,  $[B(OH)_4]^-$  causing the reaction to proceed in forward direction.

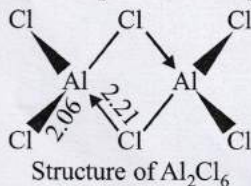


Stable chelated complex ion

- (a) The central boron atom in boric acid,  $H_3BO_3$  is electron-deficient. Boric acid is a Lewis acid with one  $p$ -orbital vacant. There is no  $d$ -orbital of suitable energy in boron atom. So, it can accommodate only one additional electron pair in its outermost shell.



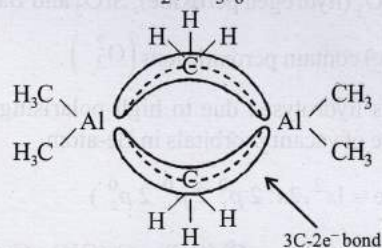
- (c)  $AlCl_3$  exists as a dimer ( $Al_2Cl_6$ ). It is a strong Lewis acid as it has an incomplete octet and has a tendency to gain electrons.  $AlCl_3$  undergoes hydrolysis easily and forms an acidic solution.  $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$ . Option (c) is true that  $AlCl_3$  sublimes at  $100^\circ C$  under vacuum.  $AlCl_3$  is a **Lewis acid**.
- (6)  $3B_2H_6 + 18CH_3OH \rightarrow 6B(OCH_3)_3 + 18H_2$
- (6) Coordination number of Al is 6. It exists in *ccp* lattice with 6 coordinate layer structure.
- sodium hydroxide;**  
 $Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
- False:**



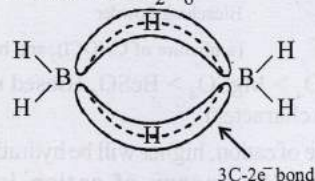
Bond distance between aluminium-chlorine bond forming bridge is greater (2.21 Å) than the distance between aluminium-chlorine bond present in the end (2.06 Å).

- (a, b, c)
  - $2B + 2NH_3 \longrightarrow 2BN + 3H_2$   
amorphous
  - $3B_2H_6 + 6NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2 \xrightarrow{\Delta} (BN)_x$
  - $B_2O_3 + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2O$
  - $HBF_4 + NH_3 \longrightarrow [NH_4]^+ [BF_4]^-$
- (a, b, d)

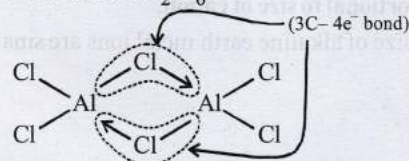
(a) Structure of  $Al_2(CH_3)_6$



(b) Structure of  $B_2H_6$

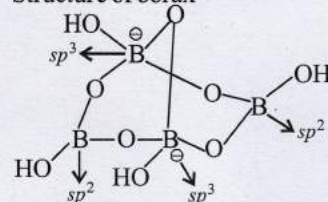


(c) Structure of  $Al_2Cl_6$



(d) Towards hard Lewis bases such as water, the Lewis acidity would decrease down the group as the hardness of acceptor element decreases, i.e.,  $BCl_3 > AlCl_3$ .

- (a, c, d) Structure of borax

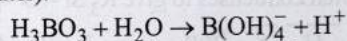


Correct formula of borax is  $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

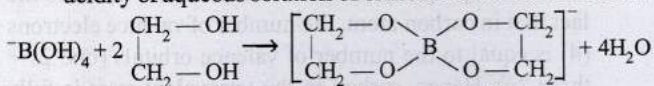
- Borax has tetranuclear  $[B_4O_5(OH)_4]^{2-}$  unit
- Only two 'B' atom lie in same plane
- two Boron are  $sp^2$  and two are  $sp^3$  hybridised.
- one terminal hydroxide per boron atom.



12. (b, d)  $H_3BO_3$  does not undergo self ionization. However, it acts as a weak acid in water (hence it is a weak electrolyte in water).



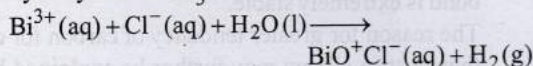
Addition of *cis*-diols (e.g., ethylene glycol) to aqueous solution of orthoboric acid leads to complex formation, thus acidity of aqueous solution of orthoboric acid is increased.



It arranges to planar sheets due to H-bonding.

13. (A)-(q), (B)-(s), (C)-(p), (D)-(r)

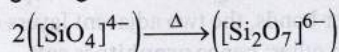
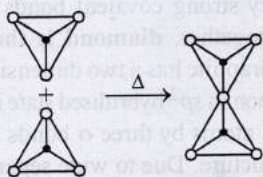
(A) Hydrolysis of  $BiCl_3$



(B)  $Al + 3NaOH \longrightarrow Al(OH)_3 \downarrow$   
white ppt

$Al(OH)_3 + NaOH(\text{excess}) \rightleftharpoons NaAlO_2 + 2H_2O$   
Upon dilution by water, we will again get the white ppt of  $Al(OH)_3$ .

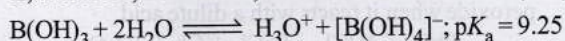
(C) Pyrosilicates are formed from 2 moles of orthosilicates as :



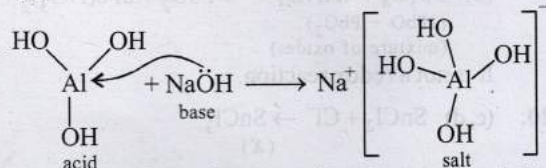
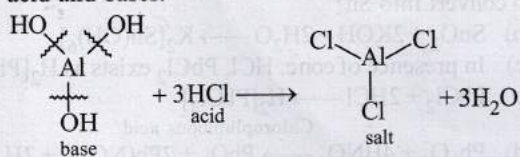
(D)  $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3$

14. (a) Both statements are true. Boron forms only covalent compounds (bonds) because small sized B ion polarizes the corresponding anion largely.

15. (c) Orthoboric acid ( $H_3BO_3$ ) is soluble in water and behaves as weak monobasic acid. It does not donate protons like most acids, but rather it accepts  $OH^-$  ions. It is, therefore, Lewis acid, and is better written as  $B(OH)_3$ .

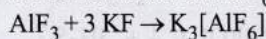


16. (c) Assertion is correct because  $Al(OH)_3$  can react with acid and bases.

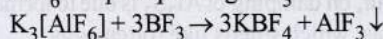


Reason is incorrect because the electronegativity difference between Al-O and O-H are different.

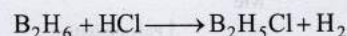
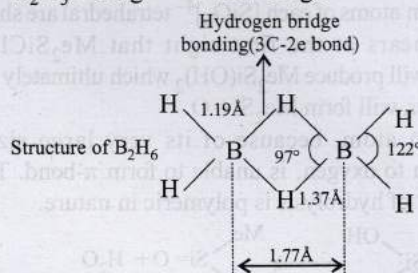
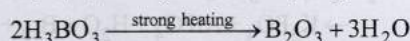
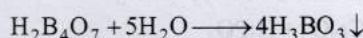
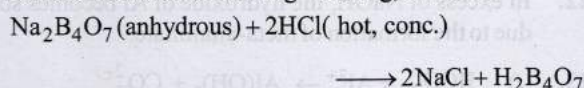
17. HF is weakly dissociated, while KF is highly dissociated giving a high concentration of  $F^-$  which leads to the formation of soluble  $AlF_6^{3-}$ .



Since  $BF_3$  is more acidic than  $AlF_3$ , it pulls out  $F^-$  from  $AlF_6^{3-}$  reprecipitating  $AlF_3$ .

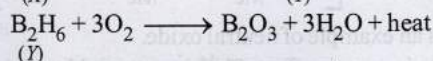
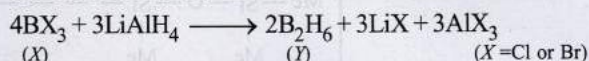


18. When hot concentrated HCl is added to borax ( $Na_2B_4O_7 \cdot 10H_2O$ ) the sparingly soluble  $H_3BO_3$  is formed which on subsequent heating gives  $B_2O_3$  which is reduced to boron on heating with Mg, Na or K.

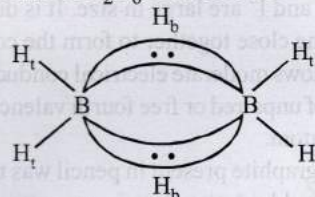


[Normally this reaction takes place in the presence of Lewis acid ( $AlCl_3$ )]

19. Since  $B_2O_3$  is formed by reaction of (Y) with air, (Y) therefore should be  $B_2H_6$  in which % of hydrogen is 21.72. The compound (X) on reduction with  $LiAlH_4$  gives  $B_2H_6$ . Thus it is boron trihalide. The reactions are shown as:



Structure of  $B_2H_6$  is as follows:



Thus, the diborane molecule has **four** two-centre-two-electron bonds ( $2c - 2e$  bonds) also called usual bonds and **two** three-centre-two-electron bonds ( $3c - 2e$ ) also called **banana bonds**. Hydrogen attached to usual and banana bonds are called  $H_t$  (terminal H) and  $H_b$  (bridged H) respectively.



20.  $\text{Al} + \text{NaOH} \xrightarrow{\text{aq.}} \text{NaAlO}_2$   
 $\xrightarrow{2\text{H}_2\text{O}} \text{Al}(\text{OH})_3 \xrightarrow{\text{heat}} \text{Al}_2\text{O}_3 \text{ (Alumina)}$
21. (i)  $\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 \downarrow + 3\text{H}_2\text{S} \uparrow$   
 (foul odour)  
 Foul odour, on damping of  $\text{Al}_2\text{S}_3$  is due to formation of  $\text{H}_2\text{S}$  gas, which smells like rotten eggs.
- (ii)  $2\text{Al} + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2$   
 Sodium meta-aluminate
22. In excess of  $\text{NaOH}$ , the hydroxide of  $\text{Al}$  becomes soluble due to the formation of meta-aluminate.
23. (i)  $\text{HCO}_3^- + \text{Al}^{3+} \rightarrow \text{Al}(\text{OH})_3 + \text{CO}_3^{2-}$   
 (ii)  $\text{AlBr}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_3\text{PO}_4 \rightarrow \text{K}_3\text{PO}_4 + \text{AlPO}_4 + \text{H}_2\text{O} + \text{Br}_2 + \text{Cr}^{3+}$

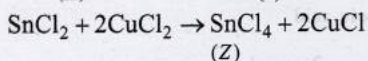
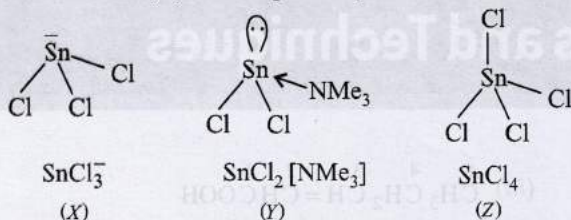
### Topic-2: Group-14 Elements (Carbon Family)

1. (b) Two dimensional sheet structures are formed when three oxygen atoms of each  $[\text{SiO}_4]^{4-}$  tetrahedral are shared.
2. (c) It appears at the first sight that  $\text{Me}_2\text{SiCl}_2$  on hydrolysis will produce  $\text{Me}_2\text{Si}(\text{OH})_2$  which ultimately upon loss of water, will form  $\text{Me}_2\text{Si}=\text{O}$ .  
 But silicon atom, because of its very large size in comparison to oxygen, is unable to form  $\pi$ -bond. Thus, the product of hydrolysis is polymeric in nature.
- $$\begin{array}{c} \text{Me} \quad \text{OH} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{Me} \quad \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{Me} \quad \text{O} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{Me} \quad \text{O} \end{array} + \text{H}_2\text{O}$$
- ↓ Polymerisation
- $$\left[ \begin{array}{c} \text{Me} \quad \text{Me} \\ | \quad | \\ \text{Me}-\text{Si}-\text{O}-\text{Si}- \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{Me}-\text{Si}-\text{O}-\text{Si}- \\ | \quad | \\ \text{Me} \quad \text{Me} \end{array} \right]_n$$
3. (a)  $\text{CO}$  is an example of neutral oxide.
4. (d) Due to inert pair effect,  $\text{Pb}^{4+}$  is not a stable oxidation state. Both  $\text{Pb}^{4+}$  and  $\text{I}^-$  are large in size. It is difficult for the atoms to come close together to form the compound.
5. (b) Graphite shows moderate electrical conductivity due to the presence of unpaired or free fourth valence electron on each carbon atom.
6. (c) Earlier the graphite present in pencil was thought to be lead, as it resembles to graphite in appearance.
7. (3) Total cationic charge = Total anionic charge  
 $2n + 6 + 24 = 36 \Rightarrow n = 3$
8. **inert-pair effect**; When  $ns^2$  electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect.
9. **glass**
10. **Fullerene**
11. **Trialkylchlorosilanol**; The hydrolysis of  $\text{R}_3\text{SiCl}$ , yields  $\text{R}_3\text{Si}(\text{OH})$  which condenses to give  $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$   
 $\text{R}_3\text{Si}-\text{O}-\text{H} + \text{H}-\text{O}-\text{SiR}_3 \longrightarrow \text{R}_3\text{Si}-\text{O}-\text{SiR}_3 + \text{H}_2\text{O}$
12. **Silicones**;
13. **True**: The property of catenation in carbon is due to the fact that in carbon atom, the number of valence electrons (4) is equal to the number of valence orbitals (one  $2s$  + three  $2p$ ). Hence, carbon in the tetravalent state is fully saturated, i.e., it has neither any vacant orbital nor any lone pair of electrons on its atom due to which the  $\text{C}-\text{C}$  bond is extremely stable.  
 The reason for greater tendency of carbon for catenation than that in silicon may further be explained by the fact that the  $\text{C}-\text{C}$  bond energy is approximately of the same magnitude as the energies of the bond between  $\text{C}$  and other elements. On the other hand, the  $\text{Si}-\text{Si}$  bond is weaker than the bonds between silicon and other elements.
14. **True**: In diamond, each carbon atom is in  $sp^3$  hybridised state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds. Owing to very strong covalent bonds by which the atoms are held together, **diamond is the hardest substance known**. Graphite has a two dimensional sheet like structure and carbon in  $sp^2$  hybridised state is attached to three other carbon atoms by three  $\sigma$  bonds forming a hexagonal planar structure. Due to wide separation and weak interlayer bonds, the two adjacent layers can easily slide over each other; hence **graphite is soft**.
15. **True**: Graphite is better lubricant on the moon than on the earth because of lack of gravitation pull on the moon, where friction is already less than earth.
16. **False**:  $\text{CCl}_4$  is most stable as compared to other tetrachlorides of the group because of its high thermal stability.
17. **False**:  $\text{CCl}_4$  gives phosgene with superheated steam  
 $\text{CCl}_4 + \text{H}_2\text{O} \rightarrow \text{COCl}_2 + 2\text{HCl}$
18. **False**:  $\text{PbO}_2$  is a dioxide and it *does not* give hydrogen peroxide when it reacts with a dilute acid.  
 $\text{PbO}_2 + 4\text{HCl} \rightarrow \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
19. (a, b) (a)  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is a reducing agent since  $\text{Sn}^{2+}$  tends to convert into  $\text{Sn}^{4+}$ .  
 (b)  $\text{SnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O} \longrightarrow \text{K}_2[\text{Sn}(\text{OH})_6]$   
 (c) In presence of conc.  $\text{HCl}$ ,  $\text{PbCl}_2$  exists as  $\text{H}_2[\text{PbCl}_4]$   
 $\text{PbCl}_2 + 2\text{HCl} \longrightarrow \text{H}_2[\text{PbCl}_4]$   
 Chloroplumbous acid  
 (d)  $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \longrightarrow \text{PbO}_2 + 2\text{Pb}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$   
 (2 $\text{PbO} + \text{PbO}_2$ )  
 (mixture of oxides)  
 It is not a redox reaction.
20. (c, d)  $\text{SnCl}_2 + \text{Cl}^- \rightarrow \text{SnCl}_3^-$  (X)  
 $\text{SnCl}_2 + \text{Me}_3\text{N} \rightarrow \text{SnCl}_2[\text{NMe}_3]$  (Y)



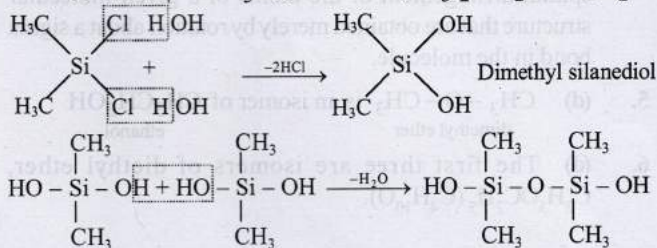
There is a coordinate bond between  $\text{NMe}_3$  and  $\text{SnCl}_2$  due to sharing of lone pairs of  $\text{NMe}_3$  with  $\text{SnCl}_2$ .

Structure of X, Y, Z are respectively :

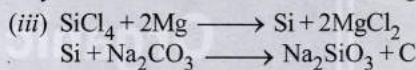


21. (b)  $(\text{CH}_3)_2\text{SiCl}_2$  form linear polymer on hydrolysis and  $(\text{CH}_3)_3\text{SiCl}$  is a chain terminator.
22. (b, d) (a) Diamond is harder than graphite.  
(b) Graphite is good conductor of electricity as each carbon is attached to three C-atoms leaving one valency free, which is responsible for electrical conduction, while in diamond, all the four valencies of carbon are satisfied, hence insulator.  
(c) Diamond is better thermal conductor than graphite. Whereas electrical conduction is due to availability of free electrons; thermal conduction is due to transfer of thermal vibrations from atom to atom. A compact and precisely aligned crystal like diamond thus facilitates fast movement of heat.  
(d) In graphite, C - C bond acquires double bond character, hence higher bond order than in diamond.
23. (b) Silicon is used in solar cells.
24. (A)-(t),  $\text{Pb}(\text{N}_3)_2$  is an explosive  
(B)-(s),  $\text{Al}_2\text{O}_3$  is used to prepare artificial gem.  
(C)-(v), Extraction of copper involves self-reduction process.  
(D)-(q),  $\text{Fe}_3\text{O}_4$  is a magnetic material.
25. A-(c)-(ii); B-(e)-(iii); C-(a)-(iv); D-(b)-(v); E-(d)-(i).
26. (c) In group 14 elements, the lower (and not higher) oxidation states are more stable for heavier members of the group due to inert pair effect.  
Thus,  $\text{Pb}^{4+}$  is less stable as compared to  $\text{Sn}^{4+}$  (lead is heavier than Tin). Therefore,  $\text{Pb}^{4+}$  acts as a strong oxidising agent than  $\text{Sn}^{4+}$ . Hence, statement 1 is false and statement 2 is true.
27. (c)  $\text{SiCl}_4$  undergoes hydrolysis due to the presence of empty *d* orbitals in the valence shell of Si, while C has no vacant *d* orbitals to accommodate electron pairs donated by water molecules during hydrolysis.  
 $\text{SiCl}_4$  is a covalent compound because the difference in electronegativity of Si and C is not high.

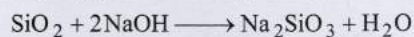
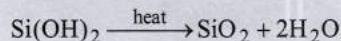
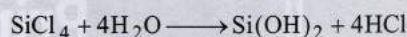
28. (i)  $\text{SiCl}_4 + 2\text{Mg}$  (or Zn)  $\longrightarrow$   $\text{Si} + 2\text{MgCl}_2$  (or  $\text{ZnCl}_2$ )  
(ii)  $\text{SiCl}_4 + 2\text{CH}_3\text{MgCl} \longrightarrow (\text{CH}_3)_2\text{SiCl}_2 + 2\text{MgCl}_2$



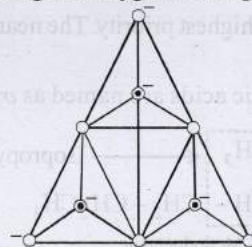
Polymerisation continues on both ends to give linear silicone.



OR



29. In cyclic  $\text{Si}_3\text{O}_9^{6-}$ , three tetrahedra of  $\text{SiO}_4^{2-}$  are joined together sharing two oxygen atoms per tetrahedron.



Structure of  $\text{Si}_3\text{O}_9^{6-}$

Dark circle represents Si and open circle represents oxygen atom/ion

30.  $\text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \rightarrow \text{K}_2\text{Sn}(\text{OH})_6 + 2\text{H}_2$
31. (i)  $\text{SnCl}_4 + 2\text{C}_2\text{H}_5\text{Cl} + \text{Na} \rightarrow \text{C}_4\text{H}_{10} + \text{Na}_2[\text{SnCl}_6]$   
(ii)  $3\text{SiCl}_4 + 4\text{Al} \xrightarrow{\Delta} 4\text{AlCl}_3 \uparrow + 3\text{Si}$   
(molten)
32. (i) In  $(\text{SiH}_3)_3\text{N}$ , lone pair of electrons on nitrogen is involved in  $p\pi - d\pi$  back bonding, while in  $(\text{CH}_3)_3\text{N}$  no such  $p\pi - d\pi$  back bonding is possible because of absence of *d* orbitals in carbon, so  $(\text{CH}_3)_3\text{N}$  is more basic than  $(\text{SiH}_3)_3\text{N}$ .  
(ii) In  $\text{MgCl}_2$ , Mg is *sp* hybridised while in  $\text{SnCl}_2$ , Sn is *sp*<sup>2</sup> hybridised (hence the molecule is angular).  
(iii) In graphite, out of four valence electrons, only three form covalent bonds (*sp*<sup>2</sup> hybridisation) with three other carbon atoms. This forms hexagonal rings as sheets of one atom thickness. These sheets are held together by weak attractive forces. One electron of each carbon atom is free and this enables these thin sheets to slide over one another. For this reason, graphite is a soft material with lubricating properties.  
(iv) Solid  $\text{CO}_2$  is technically known as **dry ice** because it sublimates without leaving any stain on surface.  
(v) Carbon exists in various allotropic forms like diamond, graphite, coal, etc. Diamond consists of a three-dimensional structure of *sp*<sup>3</sup> hybridised carbon atoms bonded through very strong covalent bonds. It makes it hard and useful as an abrasive.  
Graphite, on the other hand, is made up of a two dimensional sheet like structure made of *sp*<sup>2</sup> hybridised carbon atoms. These layers of carbon atoms are held together by relatively weak van der Waals forces and can, therefore, slip over one another imparting lubricating properties to graphite.
33. (i)  $\text{Sn} + 4\text{HNO}_3 \longrightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$   
Metastannic acid  
(ii)  $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$   
Sod. aluminate