

p-BLOCK ELEMENTS [JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

JEE Advanced

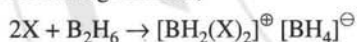
Group 13 (The Boron Family)

Single Correct Answer Type

- H_3BO_3 is
 - a monobasic and weak Lewis acid.
 - a monobasic and weak Bronsted acid.
 - a monobasic and strong Lewis acid.
 - a tribasic and weak Bronsted acid. (IIT-JEE 2003)
- Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is
 - pyrosilicate
 - sheet silicate
 - linear-chain silicate
 - three-dimensional silicate (IIT-JEE 2005)
- $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$
How can this reaction be made to proceed in the forward direction?
 - Addition of borax
 - Addition of cis-1, 2-dial
 - Addition of Na_2HPO_4
 - Addition of trans-1, 2-dial (IIT-JEE 2006)

Multiple Correct Answers Type

- In the following reaction,



The amine(s) X is/are

- NH_3
- CH_3NH_2
- $(CH_3)_2NH$
- $(CH_3)_3N$ (IIT-JEE 2009)

- The correct statement(s) for orthoboric acid is/are
 - 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 (JEE Advanced 2014)

Integer Answer Type

- The coordination number of Al in the crystalline state of $AlCl_3$ is _____. (IIT-JEE 2009)
- Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is (JEE Advanced 2015)

Assertion-Reasoning Type

In each of the following question, an Assertion (A) is followed by a corresponding Reason (R). Use the following keys to choose the appropriate answer.

- If both assertion and reason are correct, and reason is the correct explanation of the assertion.
 - If both assertion and reason are correct, but reason is not the correct explanation of the assertion.
 - If assertion is correct but reason is incorrect
 - If assertion is incorrect but reason is correct.
- Assertion:** $Al(OH)_3$ is amphoteric in nature.
Reason: Al – O and O – H bonds can be broken with equal ease in $Al(OH)_3$. (IIT-JEE 1998)



2. **Assertion:** Between SiCl_4 and CCl_4 , only SiCl_4 reacts with water.

Reason: SiCl_4 is ionic and CCl_4 is covalent.

(IIT-JEE 2001)

3. **Assertion:** In water, orthoboric acid behaves as a weak monobasic acid.

Reason: In water, orthoboric acid acts as a proton donor.

(IIT-JEE 2007)

4. **Assertion:** Boron always forms covalent bonds.

Reason: The small size of B^{3+} favours formation of covalent bond.

(IIT-JEE 2007)

Fill in the Blanks Type

1. The two types of bonds present in B_2H_6 are covalent and _____.

(IIT-JEE 1994)

True / False Type

1. All the Al - Cl bonds in Al_2Cl_6 are equivalent.

(IIT-JEE 1989)

(IIT-JEE 1993)

Subjective Type

1. State with balanced equations, what happens when aluminium is reacted with hot concentrated caustic soda solution.

(IIT-JEE 1979)

(IIT-JEE 1983)

(IIT-JEE 1997)

$$\Delta_{\text{hydration}} \text{ for } \text{Al}^{3+} = -4665 \text{ kJ mol}^{-1}$$

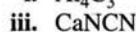
$$\Delta_{\text{hydration}} \text{ for } \text{Cl}^- = -381 \text{ kJ mol}^{-1}$$

(IIT-JEE 1997)

(IIT-JEE 2000)

(IIT-JEE 2001)

(IIT-JEE 2002)



(IIT-JEE 2002)

(IIT-JEE 2004)

Group 14 (The Carbon Family)

Single Correct Answer Type

1. Moderate electrical conductivity is shown by
- silica
 - graphite
 - diamond
 - carborundum

(IIT-JEE 1982)

(IIT-JEE 1996)

(IIT-JEE 2003)

Multiple Correct Answers Type

1. When PbO_2 reacts with conc. HNO_3 , the gas(es) evolved is/are
- NO_2
 - O_2
 - N_2
 - N_2O

(IIT-JEE 2005)

(IIT-JEE 2012)

Matching Column Type

1. Match the following:

Column I	Column II
a. $\text{Bi}^{3+} \rightarrow (\text{BiO})^{\oplus}$	p. Heat
b. $[\text{AlO}_2]^- \rightarrow \text{Al}(\text{OH})_3$	q. Hydrolysis
c. $\text{SiO}_4^{4-} \rightarrow \text{Si}_2\text{O}_7^{6-}$	r. Acidification
d. $[\text{B}_4\text{O}_7]^{2-} \rightarrow [\text{B}(\text{OH})_3]$	s. Dilution of water

(IIT-JEE 2006)

Assertion-Reasoning Type

In the following question, an Assertion (A) is followed by a corresponding Reason (R). Use the following keys to choose the appropriate answer.

- If both (A) and (R) are correct, and (R) is the correct explanation of (A).
- If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
- If (A) is correct but (R) is incorrect.
- If (A) is incorrect but (R) is correct.

1. **Assertion (A):** Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.

Reason (R): The higher oxidation states for group 14 elements are more stable for the heavier members of the group due to inert pair effect. (IIT-JEE 2008)

Fill in the Blanks Type

- The hydrolysis of alkyl-substituted chlorosilanes gives _____. (IIT-JEE 1991)
- The hydrolysis of trialkylchlorosilane, R_3SiCl , gives _____. (IIT-JEE 1994)
- One recently discovered allotrope of carbon (e.g. C_{60}) is commonly known as _____. (IIT-JEE 1994)
- A liquid which is permanently supercooled is frequently called a _____. (IIT-JEE 1998)

True / False Type

- When PbO_2 reacts with a dilute acid, it gives hydrogen peroxide. (IIT-JEE 1982)
- Carbon tetrachloride burns in air when lighted to give phosgene. (IIT-JEE 1983)
- Graphite is a better lubricant on the moon than on the earth. (IIT-JEE 1987)
- Diamond is harder than graphite. (IIT-JEE 1993)
- The tendency for catenation is much higher for C than for Si. (IIT-JEE 1993)

Subjective Type

- Write the chemical equations involved in the extraction of lead from galena by self-reduction process. (IIT-JEE 1979)

- State with balanced equations, what happens when
 - Ammonium dichromate is heated.
 - Silver is treated with hot concentrated sulphuric acid.
 - H_2S is passed through a solution of potassium permanganate acidified with dilute sulphuric acid.
 - Tin is treated with moderately concentrated nitric acid.

(IIT-JEE 1979)

- Give reason for the following in one or two sentences: 'Solid carbon dioxide is known as dry ice'.

(IIT-JEE 1983)

- Give reasons for the following in one or two sentences: 'Graphite is used as a solid lubricant'. (IIT-JEE 1985)

- Each entry in column X is in some way related to the entries in columns Y and Z. Match the appropriate entries.

X	Y	Z
Yeast	Fermentation	Ethanol
Mica	Graphite	Abrasive
Superphosphate	Crystallite cubic	Insulator
Carbon fibres	Layer structure	Fertiliser
Rock salt	Diamond structure	Reinforced plastics
Carborundum	Bone ash	Preservative

(IIT-JEE 1989)

- Write balanced equations for the preparation of crystalline silicon from SiCl_4 . (IIT-JEE 1990)
- Complete and balance the following reactions: $\text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \rightarrow$ (IIT-JEE 1994)
- Draw the structure of a cyclic silicate $(\text{Si}_3\text{O}_9)^{6-}$ with proper labeling. (IIT-JEE 1998)
- Complete the reaction: $\text{SnCl}_4 + \text{C}_2\text{H}_5\text{Cl} + \text{Na} \rightarrow$ (IIT-JEE 1998)
- Starting from SiCl_4 , prepare the following in steps not exceeding the number given in parenthesis (give reactions only).
 - Silicon (1)
 - Linear silicone containing methyl group only (4)
 - Na_2SiO_3 (3)

(IIT-JEE 2001)

Answer Key

JEE Advanced

Group 13 (The Boron Family)

Single Correct Answer Type

1. a. 2. b. 3. b.

Multiple Correct Answers Type

1. a., b., c. 2. b., d.

Integer Answer Type

1. (6) 2. (6)

Assertion-Reasoning Type

1. c. 2. c. 3. c. 4. a.

Fill in the Blanks Type

1. banana bonds

True/False Type

1. False 2. False

Group 14 (The Carbon Family)

Single Correct Answer Type

1. b. 2. d. 3. c

Multiple Correct Answers Type

1. b. 2. b., d.

Matching Column Type

1. (a) → (q, s); (b) → (s); (c) → (r); (d) → (q, r)

Assertion-Reasoning Type

1. c.

Fill in the Blanks Type

1. silicones 2. $R_3Si(OH)$
3. Buckminsterfullerene
4. glass

True/False Type

1. False 2. False 3. True 4. True 5. True

THROUGH PERSEVERANCE
MANY PEOPLE WIN
SUCCESS OUT OF WHAT SEEMED DESTINED
TO BE CERTAIN FAILURE."
BENJAMIN DISRAELI
#RKMALIKSNEWTONCLASSES

Hints and Solutions

ABILITY
IS WHAT YOU'RE CAPABLE OF DOING

MOTIVATION
DETERMINES WHAT YOU DO

ATTITUDE
DETERMINES HOW WELL YOU DO IT

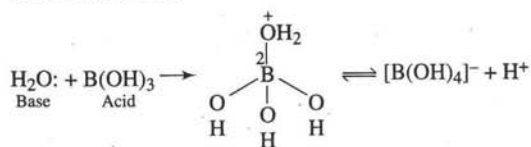
NEWTONCLASSES.NET

JEE Advanced

Group 13 (The Boron Family)

Single Correct Answer Type

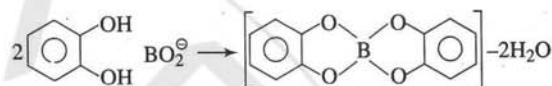
1. a. The central boron atom in boric acid, H_3BO_3 is electron-deficient. Boric acid is a Lewis acid with one p-orbital vacant. There is no d-orbital of suitable energy in boron atom. So, it can accommodate only one additional electron pair in its outermost shell.



H_3BO_3 is a monobasic acid and acts as a weak Lewis acid by accepting OH^- ions.

2. b. The dimensional sheet structures are formed when three oxygen atoms of each $[SiO_4]^{4-}$ tetrahedral are shared.
3. b. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na^+ [B(OH)_4]^- + H_2O$
This reaction is reversible due to the hydrolysis of sodium metaborate ($NaBO_2$).

In the presence of complexing agents such as cis-1, 2-diol, catechol, glycerol, etc. a complex is formed, and it prevents hydrolysis from taking the reaction in the forward direction.

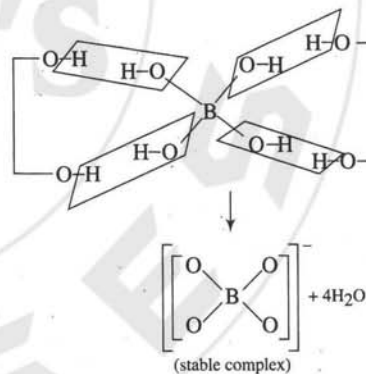


Multiple Correct Answers Type

1. a., b., c.
Tertiary amines do not react in this reaction due to bulky methyl groups.
2. b., d.
a. H_3BO_3 does not ionize on over rather it is Lewis acid due to electron deficiency on B it accepts OH^- from water



b.



- c. It has a planar sheet like structure due to hydrogen bonding. It has three-dimensional structure.
- d. H_3BO_3 is a weak electrolyte in water

Integer Answer Type

1. (6) $AlCl_3$ in acidified aqueous solution crystallizes as octahedral $[Al(H_2O)_6]^{3+} Cl_3^-$. In this complex, the 3d orbitals of Al are involved and hybridization state of Al is sp^3d^2 . Hence, the coordination number of Al is six. It exists in ccp lattice with six coordinate layer structure.
2. (6) $3B_2H_6 + 18CH_3OH \rightarrow 6B(OCH_3)_3 + 18H_2$

Assertion-Reasoning Type

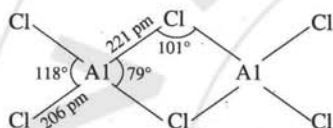
- c. Assertion (A) is true; Reason (R) is false.
The O – H bond is stronger than the Al – O bond in aluminium hydroxide.
- c. Assertion (A) is correct, but Reason (R) is incorrect, SiCl₄ also has covalent bonds. CCl₄ does not get hydrolysed because carbon does not have vacant d-orbitals, so water cannot donate lone pair of electrons to start the reaction.
- c. Assertion (A) is true; Reason (R) is false.
B(OH)₃ + H₂O → [B(OH)₄][⊖] + H[⊕]
H₃BO₃ is a monobasic weak Lewis acid.
- a. Boron always forms covalent bonds because boron requires very high energy to form a tripositive ion. Due to its very small size, B³⁺ has high polarizing power; so it forms covalent linkage according to Fajan's rule.

Fill in the Blanks Type

- The two types of bonds present in B₂H₆ are covalent and **banana bonds** (three-centre two-electron bonds).

True / False Type

- False:**



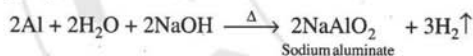
Bridging chlorine bonds are different than terminal chlorine bonds.

- False:**

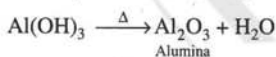
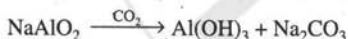
The basic nature of the hydroxides of group 13 increases progressively down the group because the electropositive character of elements increases.

Subjective Type

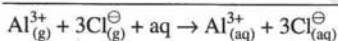
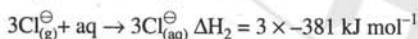
- Hydrogen gas is evolved.



- Al + NaOH $\xrightarrow{\text{Aqueous}}$ NaAlO₂ + H₂O



- Al_(g)³⁺ + aq → Al_(aq)³⁺ ΔH₁ = -4665 kJ mol⁻¹

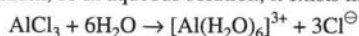


Therefore,

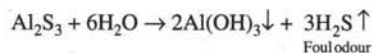
The total hydration energy of AlCl₃ = Hydration energy of Al³⁺ + 3 × Hydration energy of Cl⁻

$$= -4665 + 3(-381) = -5808 \text{ kJ mol}^{-1}$$

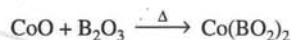
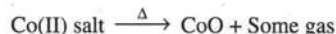
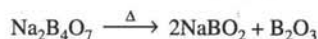
The above hydration energy is more than ionization energy of aluminium, so in aqueous solution, it exists in ionic form.



- Aluminium sulphide gives a foul odour when it becomes damp because it is a salt of weak acid and weak base. So upon hydrolysis, hydrogen sulphide is produced which has a rotten egg-like smell.

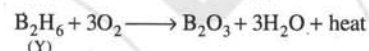
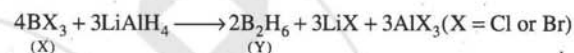


- When borax is heated, a colourless glassy bead is formed of the following composition:

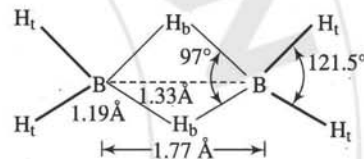


Blue-coloured bead of cobalt metaborate is formed.

- Since B₂O₃ is formed by reaction of (Y) with air, (Y) therefore should be B₂H₆ in which % of hydrogen is 21.72. The compound (X) on reduction with LiAlH₄ gives B₂H₆. Thus it is boron trihalide. The reactions are shown as:

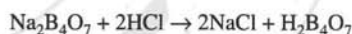


Structure of B₂H₆ is as follows:

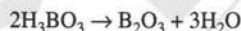


Thus the diborane molecule has **four** two-centre -two-electron bonds (2c – 2e bonds) also called usual bonds and **two** three-centre-two-electron bonds (3c – 2e) also called **banana bonds**. Hydrogen attached to usual and banana bonds are called H_t (terminal H) and H_b (bridged H) respectively.

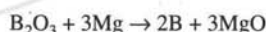
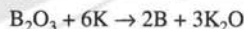
- The finely ground borax is heated with concentrated hydrochloric acid when sparingly soluble orthoboric acid separates out.



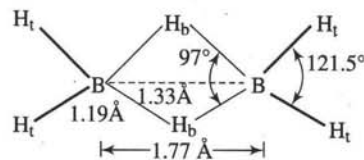
Orthoboric acid is strongly heated to get B₂O₃.

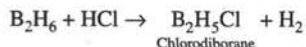


The reduction of boric anhydride (B₂O₃) can be done with sodium, potassium or magnesium.



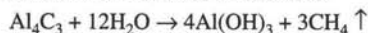
The structure of diborane



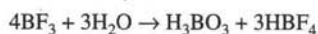


Note: Normally this reaction takes place in the presence of Lewis acid (AlCl_3)

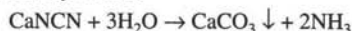
8. i. With aluminium carbide, methane is formed.



- ii. With boron trifluoride, boric acid is formed.



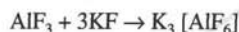
- iii. With calcium cyanamide,



Ammonia formed dissolves in water to form NH_4OH



9. 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-} .



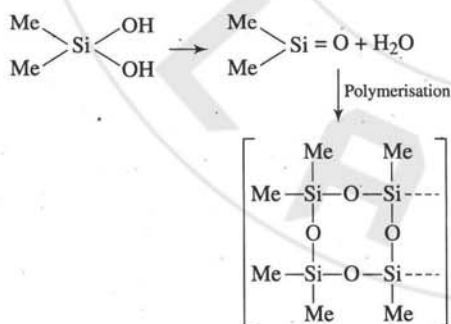
Since BF_3 is more acidic than AlF_3 , it pulls out F^- from AlF_6^{3-} reprecipitating AlF_3 .



Group 14 (The Carbon Family)

Single Correct Answer Type

1. b. Graphite shows moderate electrical conductivity due to the presence of unpaired or free fourth valence electron on each carbon atom.
2. d. Due to strong inert pair effect, Pb^{2+} is more stable than Pb^{4+} . Non-existence of PbI_4 can be explained on the basis of strong oxidizing nature of Pb^{4+} . The iodide ions are reducing agents. In the presence of these ions, Pb^{4+} ions are reduced to Pb^{2+} ions.
- $$\text{Pb}^{4+} + 2\text{I}^- \rightarrow \text{Pb}^{2+} + \text{I}_2$$
3. c. Me_2SiCl_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 π -bond. Thus, the product of hydrolysis is polymeric in nature.



Multiple Correct Answers Type

1. b.

When PbO_2 reacts with conc HNO_3 the gas evolved is oxygen ($2\text{PbO}_2 + 4\text{HNO}_3 \rightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{O}_2 + 2\text{H}_2\text{O}$).

2. b., d.

- a. Diamond has a three-dimensional network structure, whereas graphite is soft due to layered structure.
- b. In graphite only three valence electrons are involved in bonding and one electron remains free, giving electrical conductivity. In diamond all the four valence electrons are covalently bonded hence insulator.
- c. Diamond is a better thermal conductor than graphite. Electrical conductivity is due to availability of free electrons. Thermal conductance is due to transfer of thermal vibrational energy from one atom to another atom. A compact and precisely aligned crystals such as diamond thus facilitate better movement of heat.
- d. In graphite, C-C bond acquires some double bond character, and hence has higher bond order than in diamond.

Bond order of graphite = 1.33

Bond order of diamond = 1.0

Matching Column Type

1. (a) \rightarrow (q, s); (b) \rightarrow (s); (c) \rightarrow (r); (d) \rightarrow (q, r)

- a. $\text{Bi}^{3+} + \text{H}_2\text{O} \rightarrow [\text{BiO}]^{\oplus} + 2\text{H}^{\oplus}$ (Hydrolysis and dilution by H_2O)
- b. $\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$ (Dilution by H_2O)
- c. $2\text{SiO}_4^{4-} + 2\text{H}^{\oplus} \rightarrow \text{Si}_2\text{O}_7^{6-} + \text{H}_2\text{O}$ (Acidification)
- d. $\text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\text{Acid}} \text{H}_3\text{BO}_3$ (Acidification)

Assertion-Reasoning Type

1. c. Assertion (A) is true; Reason (R) is false.

Down the group, the inert pair effect increases; therefore, the higher oxidation state becomes less stable, and the lower oxidation state becomes more stable down the group. Pb^{4+} has a higher tendency to pass into Pb^{2+} and is, therefore, a good oxidizing agent compared to Sn^{4+} .

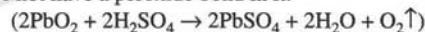
Fill in the Blanks Type

- The hydrolysis of alkyl-substituted chlorosilanes gives silicones.
- The hydrolysis of trialkylchlorosilane, R_3SiCl , yields $\text{R}_3\text{Si}(\text{OH})$ which may further form a dimer.
- One recently discovered allotrope of carbon (e.g. C_{60}) is commonly known as Buckminsterfullerene.
- A liquid which is permanently supercooled is frequently called a glass.

True / False Type

1. False:

PbO_2 with dilute acid does not give hydrogen peroxide because it does not have a peroxide bond in it.



2. False:

CCl_4 gives phosgene gas (COCl_2) with superheated steam only. $\text{CCl}_4 + \text{H}_2\text{O} \rightarrow \text{COCl}_2 + 2\text{HCl}$

3. True:

Graphite is a better lubricant on the moon than on the earth because of less gravitational attraction on moon as compared to earth.

4. True:

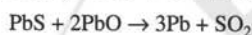
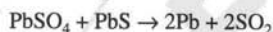
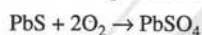
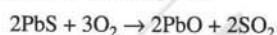
5. True:

The tendency for catenation is much higher for C than for Si. Due to smaller size and high EN of carbon, bonds are stronger. Catenation also depends upon the strength of element-element bond. Since the bond energy of C-C bond is very high (355 kJ mol^{-1}), C forms long straight chains or branched C-C chains or rings of different sizes and shape. Elements-element bond energies decrease rapidly down the group (\downarrow), viz.

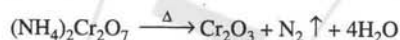
C-C (355 kJ mol^{-1}) > Si-Si (200 kJ mol^{-1}) > Ge-Ge (167 kJ mol^{-1}) and therefore the tendency for the catenation decreases in the order, C > Si > Ge > Sn.

Subjective Type

1. Lead is mainly extracted from its sulphide ore called galena. Roasting is done followed by reduction with carbon. Self-reduction finally takes place.



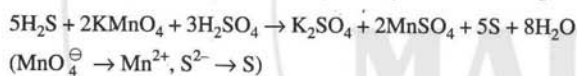
2. a. Nitrogen gas is evolved.



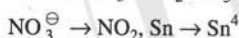
- b. Sulphur dioxide gas is evolved.



- c. Pink colour of acidified potassium permanganate is discharged.



- d. Meta stannic acid is formed.



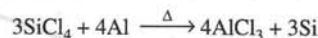
3. Carbon dioxide solidifies at very low temperature. If CO_2 under pressure is allowed to escape through a nozzle, a white solid called dry ice is obtained. Solid CO_2 is a soft, white snow-like substance. It sublimates and leaves no residue. So it is known as dry ice.

4. Graphite has a two-dimensional sheet structure. Each carbon atom is in sp^2 -hybridised state and is linked to three other carbon atoms in a hexagonal planar structure. After forming three C-C bonds, each carbon atom is left with one electron in its p-orbital. This electron then overlaps with the other to form a p-bond. Hexagonal planes are held by weak van der Waals forces. These planes can slide over one another. Therefore, graphite is a good lubricant.

5.

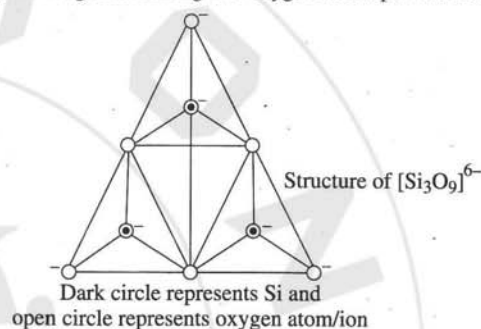
X	Y	Z
Yeast	Fermentation	Ethanol
Mica	Layer structure	Insulator
Superphosphate	Bone ash	Fertiliser
Carbon fibres	Graphite	Reinforced plastics
Rock salt	Cubic	Preservative
Carborundum (SiC)	Diamond structure	Abrasive

6. By passing vapours of SiCl_4 through molten aluminium.



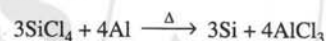
7. $\text{Sn} + 2\text{KOH} + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SnO}_3 + 2\text{H}_2$

8. In cyclic silicate (Si_3O_9)⁶⁻, three tetrahedral of SiO_4 ²⁻ are joined together sharing two oxygen atoms per tetrahedron.



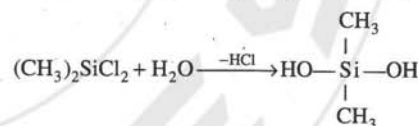
9. $\text{SnCl}_4 + 2\text{C}_2\text{H}_5\text{Cl} + 2\text{Na} \rightarrow \text{Na}_2\text{SnCl}_6 + \text{C}_4\text{H}_{10}$

10. a. With aluminium, it can be reduced to silicon. Mg and Zn may also be used.

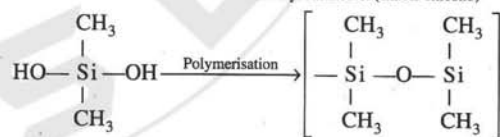


(Due to higher reducing character of Al)

- b. $3\text{SiCl}_4 + 2\text{CH}_3\text{MgCl} \rightarrow (\text{CH}_3)_2\text{SiCl}_2 + 2\text{MgCl}$



dimethyl silanediol (Linear silicone)



- c. $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4 + \text{HCl}$

