

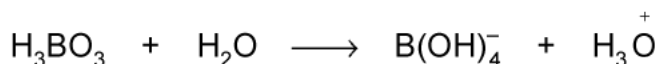
- Q1. Borax is used in qualitative analysis. Explain.
- Q2. The $p\pi - p\pi$ back bonding occurs in the halides of boron but not in the halides of aluminum. Explain.
- Q3. The first ionisation energies of boron and aluminum are lesser than those of Be and Mg respectively. Explain.
- Q4. Why does boron trifluoride behave as a Lewis acid?
- Q5. Boron has high m.pt. and b.pt. Explain.
- Q6. The B — X distance is shorter than what is theoretically expected BX_3 molecules; e.g., calculated bond length in BF_3 is 152 pm whereas the observed bond length is 130 pm. Explain.
- Q7. Write the probable reaction for tetraborate ion in acidic solution of water.
- Q8. Aqueous solution of borax containing one mole requires two moles of acid. Explain.
- Q9. Why borax can be used as a buffer?
- Q10. $Na_2B_4O_7 + \text{conc. } H_2SO_4 \longrightarrow A \xrightarrow[\text{(ii) ignite}]{\text{(i) } C_2H_5OH} B$
- Q11. The correct equivalence point of boric acid and NaOH titration can not be determined. Why?
- Q12. How can BI_3 or BCl_3 be converted to pure boron.
- Q13. Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion. why?
- Q14. Why does anhydrous $AlCl_3$ fume in air?
- Q15. $AlCl_3$ form a dimer but BCl_3 does not form dimer. Explain.
- Q16. Boron and aluminum halides behave as Lewis acid. Explain.
- Q17. Why do aluminum and boron generally form covalent compounds?
- Q18. $B(OH)_3$ is an acid, $Al(OH)_3$ is amphoteric and $Tl(OH)_3$ is basic, Explain.
- Q19. Boron nitride is slippery solid. Explain on the basis of structure.
- Q20. How will you distinguish between inorganic and organic benzene?
- Q21. What happens when any two of the BF_3 , BCl_3 and BBr_3 are mixed at room temperature? and what happens when all the three are mixed?
- Q22. BX_3 is known but BH_3 is not known. Explain.
- Q23. Boron tribromide is stronger acid than boron trifluoride.

- Q24. Aluminium containers can be used to store conc. HNO_3 or Al becomes passive in conc. HNO_3 . Explain.
- Q25. For what of air-crafts aluminium metal is used in air-craft parts?
- Q26. Aluminium fluoride is ionic while AlCl_3 is covalent?
- Q27. What is emery and for what purpose it is used?
- Q28. Which type of cations are capable of replacing aluminium in alums?
- Q29. Aluminium does not react readily with conc. HNO_3 . Why?
- Q30. What purposes does chrome plating of steel serve? what Ni plating serves?
- Q31. Explain why a homeowner should avoid attaching aluminium downspouts to galvanised steel gutters.
- Q32. Aluminium is a very reactive metal, but is still used for marking pans. Explain.
- Q33. Alum is often used to stop bleeding from cuts. why?
- Q34. How is lithium aluminium hydride (LiAlH_4) prepared? What is its important use?
- Q35. AlF_3 is a high m.pt. solid while AlCl_3 is low m.pt. volatile solid. Explain.
- Q36. TlCl_3 is unstable whereas TlCl is stable. Explain.
- Q37. What is the most important ore of Al. Give its formula. Give the reactions involved in its purification and its electrolysis.
- Q38. IE_1 of Al is lower than IE_1 of Mg, explain.
- Q39. $\text{Al}(\text{OH})_3$ is amphoteric. Explain.
- Q40. Certain metallic oxides are reduced with aluminium but not with carbon during extraction. Explain.
- Q41. Molten AlBr_3 is a poor conductor of current. Explain.
- Q42. Discuss the pattern of variation in the oxidation states of Al to Tl.
- Q43. Anhydrous AlCl_3 cannot be prepared by heating $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Why?
- Q44. Suggest a reason why the B — F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ?
- Q45. Describe the shapes of BF_3 and $[\text{BF}_4]^-$. Assign the hybridization of boron in these species.
- Q46. Explain what happens when boric acid is heated?
- Q47. How can you explain higher stability of BCl_3 as compared to TlCl_3 ?
- Q48. Write reactions to justify amphoteric nature of aluminium.
- Q49. Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

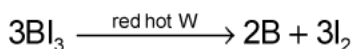
- Q50. If B — Cl bond has a dipole moment, why does BCl_3 have zero dipole moment?
- Q51. BCl_3 and BBr_3 fume in moist air while BF_3 not, explain.
- Q52. B_2H_6 reacts with NH_3 to form different product Explain.
- Q53. Discuss the changes in coordination number when crystalline AlCl_3 is heated.
- Q54. Discuss the pattern of variation in the oxidation states of (i) B to Tl (ii) C to Pb.
- Q55. Is boric acid a protic acid? Explain.
- Q56. What are electron deficient compounds? Are BCl_3 and SiCl_4 electron deficient species? Explain.
- Q57. Arrange in the increasing order of Lewis acid strength (with pyridine donor)
(a) BX_3 , GaX_3 , AlX_3 (b) AlCl_3 , AlBr_3 , AlI_3 (c) B, Tl, Ga, In, Al
- Q58. When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.
- Q59. What happens when
(a) Borax is heated strongly (b) Boric acid is added to water
(c) Aluminium is treated with dilute NaOH (c) BF_3 is reacted with ammonia
- Q60. Explain structure of diborane and boric acid.

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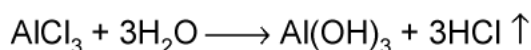
S11. H_3BO_3 or $\text{B}(\text{OH})_3$ is weak mono-basic acid and partially reacts with H_2O to form H_3O^+ and $\text{B}(\text{OH})_4^-$ ion.



S12. $3\text{BCl}_3 + 3\text{H}_2 \xrightarrow{\text{red hot W}} 2\text{B} + 6\text{HCl}$



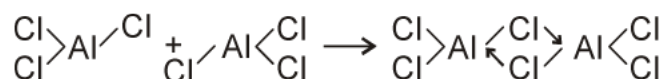
S13. Anhydrous AlCl_3 hydrolyses in moist air and gives fumes of HCl .



S14. $4\text{LiH} + \text{AlCl}_3 \xrightarrow{\text{Et}_2\text{O}} \text{LiAlH}_4 + 3\text{LiCl}$

LiAlH_4 is a reducing agent for organic compounds.

S15. AlCl_3 form dimer by completing octet for Al involving p-orbitals to accept electron pair from Cl atoms as:



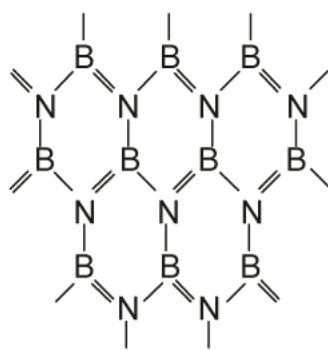
The non-existence of the dimer of boron trifluoride is that the energy released by the formation of an additional bond to another boron atom (as required for the formation of a dimer) is not sufficient to compensate for the loss energy to the system. The B — F form $p\pi - p\pi$ back bonding in the monomer itself.

S16. Both boron and aluminum atoms in their halides possess six electrons in their valence shell and thus possess tendency to accept a lone pair to act as Lewis acid.

S17. B and Al have high I.E. and high amount of energy required to form B^{3+} and Al^{3+} cation. *i.e.*, they form 3-covalent bond by outer most 3-unpaired electrons.

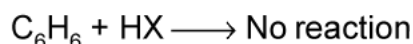
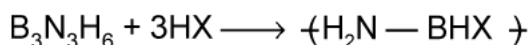
S18. The electropositive or metallic character of group 13 elements increases from B to Tl. B being nonmetal and thus acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic forms basic hydroxides.

S19. $(\text{BN})_x$ has sheet like structure as graphite, with sheets made up of hexagonal rings of alternate B and N atoms joined together. The sheets are stacked one on top of the other giving a layer structure. One B-atom and one N-atom together have same number of valency electrons as two C-atoms in graphite.

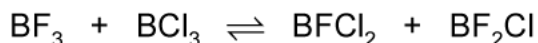


Boron nitride

- S20.** Borazine ($B_3N_3H_6$) is known as inorganic benzene. Unlike benzene borazine adds HX , H_2O , ROH etc. It is hydrolysed to boric acid and NH_3 at elevated temperatures.



- S21.** Redistribution of halogen atoms occurs to produce a mixture of original pure halides with the mixed halides in about statistical proportions, thus an equilibrium established.



In mixture of three halides, existence of $BFCIBr$ has been reported.

- S22.** BH_3 undergoes dimerization to form B_2H_6 giving rise to hydrogen bridge bond forced by electron deficiency of the compound. No such bonds exist in BX_3 . Because due to back bonding ($p\pi - p\pi$ bonding) in $B - X$ bond, B atom in BX_3 is not as much electron deficient as in BH_3 .

- S23.** Back bonding occurs in boron halides to compensate the electron deficiency and hence Lewis acidity is decreased. The tendency of back bonding is maximum in BF_3 and decreases from BF_3 to BI_3 as the size of the halogen increases. p -orbitals of high energy shells in bromine overlap less effectively with vacant p -orbital of boron in BBr_3 . Thus, BBr_3 is stronger acid than BF_3 as it has still tendency to accept electrons to remove electron deficiency.

- S24.** Aluminium can be used with good results in air-craft parts if the speed of air-craft does not exceed 2.4 times the speed of sound.

- S25.** The size of chloride ion is larger than fluoride ion. Due to higher polarisation in $AlCl_3$, it behaves as a covalent compound. The electronegativity difference between Al and Cl is 1.5 while between Al and F it is 2.5. Thus, the bond between Al and F is ionic and between Al and Cl covalent in nature.

- S26.** Impure form of Al_2O_3 containing Fe_2O_3 and silica is called emery. It is coated over paper to produce sand paper or emery paper, used for polishing metals.

- S27.** The trivalent metal cations of about the same size as that of Al^{3+} are capable of replacing aluminium in alums e.g. Ti^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , and Co^{3+} .

- S28.** The aluminium while protecting steel by cathodic protection, would itself be more susceptible to oxidation.

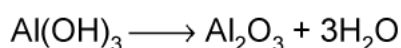
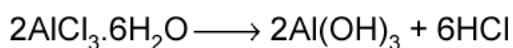
- S29.** Due to the formation of a protective oxide film on the surface. It does not corrode easily.

S30. Al surface gets oxidised covered by an oxide film which prevents and concentrated HNO_3 does not react with Al_2O_3 .

S31. Chrome plating protects steel by cathodic protection, Ni protects by covering the entire surface with a less active metal (as long as no scratches or imperfections develops.)

S32. Al^{3+} ions liberated from alum are highly effective in coagulating negatively charged colloids like blood, muddy water etc. due to their high valency. Blood coagulates and makes a clot and thus the bleeding stops.

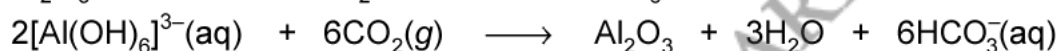
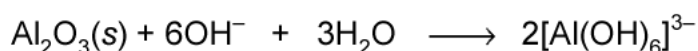
S33. Hydrated aluminium chloride undergoes hydrolysis to form Al_2O_3 on heating



S34. Al forms $[\text{AlF}_6]^{3-}$ ion because $\text{Al}(3s^23p^1)$ can achieve co-ordination number of six by using d -orbitals of 3^{rd} shell. On the other hand, boron ($2s^22p^1$) cannot extend its co-ordination number by four (it has vacant p -orbitals and no d -orbitals in 2^{nd} shell). Also due to small size B^{3+} can not show six coordination number.

S35. Al on coming in contact with conc. HNO_3 becomes passive due to the coating of aluminium oxide on its surface and thus Al containers can be used store conc. HNO_3 .

S36. Bauxite ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$). The various reactions for purification are

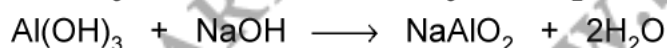
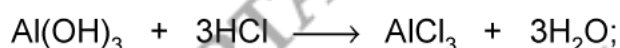


The electrolysis of Al_2O_3 involves:



S37. $\text{Al}(3s^23p^1)$ involves removal of $3p$ -electron to give Al^+ ion, whereas $\text{Mg}(3s^2)$ involves removal of $3s$ -electron to give Mg^+ ion, s -orbitals being closer to nucleus and thus it requires more energy to liberate electron.

S38. $\text{Al}(\text{OH})_3$ reacts with acids and alkalies both



S39. Metals oxides which during reaction with carbon form carbides are not reduced by carbon. Al which has great affinity for oxygen is used to reduce such metal oxides to metals.

S40. AlBr_3 is covalent in nature and thus during fusion does not produce Al^{3+} and Br^- ions. Hence it is poor conductor of current.

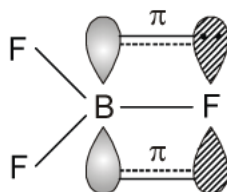
S41. Smaller anion F^- in AlF_3 is least polarized in comparison to large anion Cl^- in AlCl_3 by Al^{3+} cation. Thus AlF_3 is more ionic in comparison to AlCl_3 and has high m.pt. is solid state.

S42. $Tl(3d^{10}, 4s^2 4p^1)$ shows inert pair effect and thus tendency to show higher oxidation state decreases. *i.e.*,

Tl^+ is more stable than Tl^{3+} .

S43. Al to Tl common states are +3 and +1. Stability order in +1 follows $Al < Ga < In < Tl$. Tl^+ is more stable than Tl^{3+} .

S44. BF_3 is a planar molecule in which B is sp^2 -hybridized. It has an empty $2p$ -orbital. F-atom has three lone pairs of electrons in the $2p$ -orbitals. Because of its small size and strong inter electronic repulsions, $p\pi$ - $p\pi$ back bonding or back donation occurs in which a lone pair is transferred from F to B.

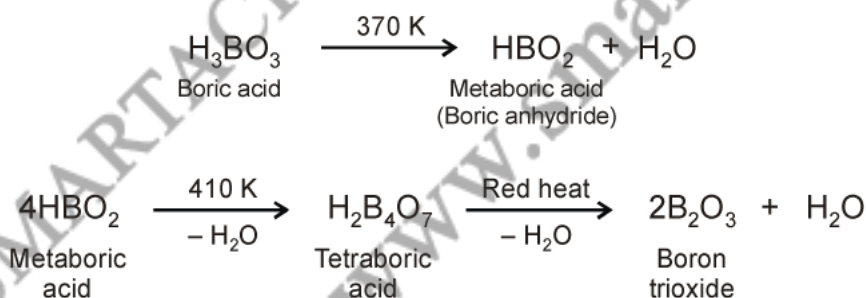


As a result of this back bonding, B — F bond acquires some double bond character. In contrast, in $[BF_4]^-$ ion, B is sp^3 -hybridized and hence does not have an empty p -orbital available to accept the electrons donated by the F atom. Consequently, in $[BF_4]^-$, B — F is a purely single bond. Since double bonds are shorter than single bonds. Therefore, the B — F bond length in BF_3 is shorter (130 pm) than B — F bond length (143 pm) in $[BF_4]^-$.

S45. In BF_3 , boron is sp^2 -hybridized and, therefore, BF_3 is a planar molecule. On the other hand, in $[BF_4]^-$, boron is sp^3 -hybridized and hence $[BF_4]^-$ is a tetrahedral species.



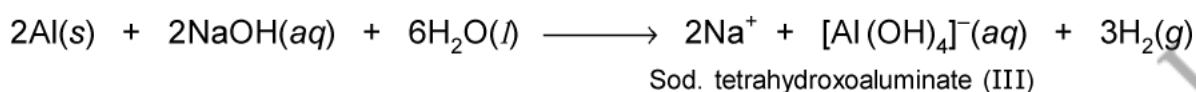
S46. Boric acid, on heating, loses water in there different stages at different temperatures ultimately giving boron trioxide or boric anhydride.



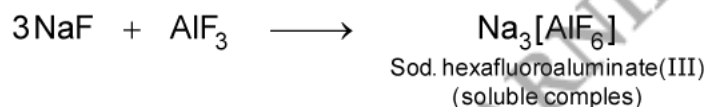
S47. Boron and thallium belong to group 13 of the periodic table. On moving from top to bottom in a group the increases in nuclear charge is not neutralised by the poor shielding effect of electrons in inner orbitals (*i.e.*, $3d$, $4d$, $5d$, $4f$, etc.). As a result, the inert pair effect becomes more predominant. Thus, the valence s electrons experience strong force of attraction. The inert pair effect is maximum in Tl. As a result, only $6p^1$ electron participates in bond formation and thus the most stable state of Tl is +1 and not +3. Therefore, $TlCl$ is stable but $TlCl_3$ is unstable. In contrast, due to the absence of d - and f -electrons in B, all the three valence electrons (*i.e.*, to $2s$ and one $2p$) take part in bond formation and hence B exhibits an oxidation state of +3 and thus forms BCl_3 . Thus, BCl_3 is more stable than $TlCl_3$.

S48. An amphoteric substance is the one which can react with both acid as well as base. Aluminium dissolves both in acids and alkalies evolving dihydrogen.

The following reactions justify the amphoteric nature of aluminium.

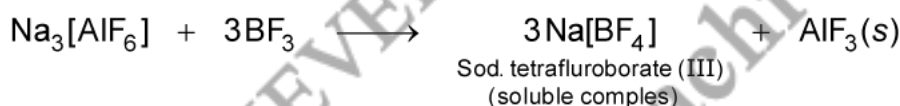


S49. (i) Anhydrous HF is a covalent compound and is strongly H-bonded. Therefore, it does not give free F^- ions and hence AlF_3 does not dissolve in HF. In contrast, NaF is an ionic compound and hence F^- ions are easily available. As a result these combines with AlF_3 to form the soluble complex.

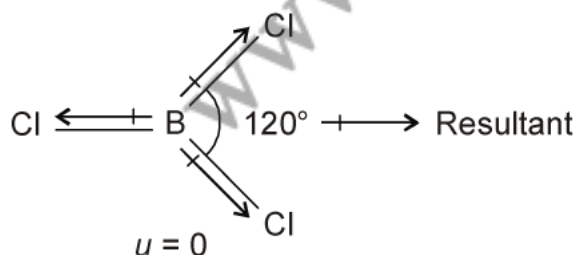


(ii) On bubbling gaseous BF_3 , AlF_3 is precipitated.

It is because BF_3 is a stronger Lewis acid than AlF_3 . This is attributable to smaller size and higher electronegativity of Boron. As a result of this B has higher tendency to form complexes than Al, therefore when BF_3 is added to the above solution, AlF_3 gets precipitated.



S50. B — Cl bond has a dipole moment due to electronegativity difference between B and Cl. The overall dipole moment of a molecule, however, depends upon its geometry. Now BCl_3 is a planar molecule in which the three B — Cl bonds are inclined at an angle of 120° . Therefore, the resultant of two B — Cl bonds is cancelled by equal and opposite dipole moment of the third B — Cl bond.

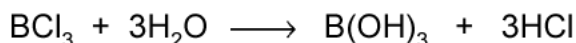


As a result, overall dipole moment of BCl_3 is zero.

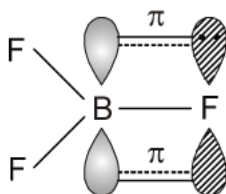
S51. Electron acceptor strength of boron halides is in the order



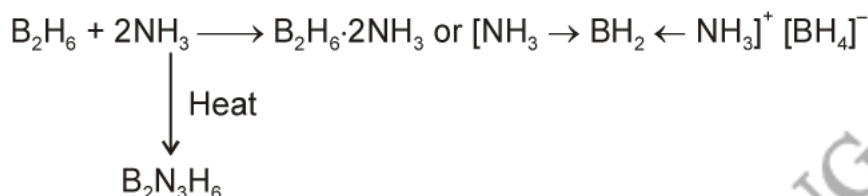
So the same will be the order of ease of hydrolysis. Due to rapid hydrolysis BBr_3 and BCl_2 fume in moist air.



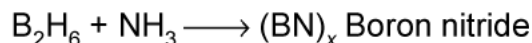
BF_3 has $p\pi - p\pi$ back bonding and boron has not empty orbital to accept electron pair from H_2O .



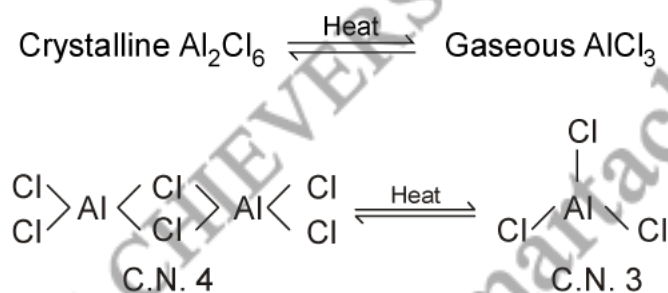
S52. (a) Excess of NH_3 and low temperature



(b) Excess of NH_3 and higher temperature.



S53. Crystalline AlCl_3 is found in dimer Al_2Cl_6 having 4-co-ordination number on heating it convert into gaseous monomer having 3-co-ordination number.



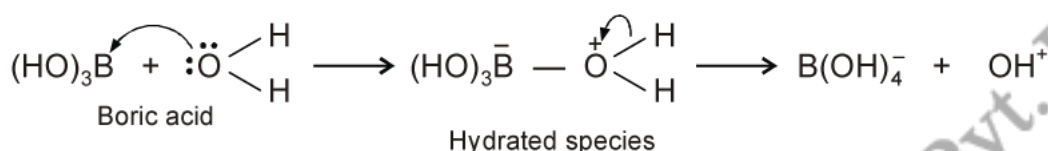
S54. (i) The oxidation state in a group depends upon the presence of electrons in valence shell of an element. B and Al have no d - or f -electrons. Therefore, they do not exhibit *inert pair effect*. Consequently, they show only one oxidation state of +3 due to the presence of two electrons in the s - and one electron in the p -orbital of the valence shell. In contrast, all other elements from Ga to Tl contain only d - or d - and f -electrons and hence show two oxidation states of +1 and +3 due to inert pair effect. Further, on moving down the group, the inert pair effect becomes more and more pronounced. In other words, as we move down the group from Ga to Tl, the stability of +1 oxidation state increases (i.e., $\text{Ga} < \text{In} < \text{Tl}$) while that of +3 oxidation state decreases (i.e., $\text{Ga} > \text{In} > \text{Tl}$). Thus, +1 oxidation state of Tl is more stable than its +3 oxidation state.

- (ii) Carbon and silicon do not contain *d*- or *f*-electrons and hence do not exhibit *inert pair effect*. Consequently, they show an oxidation state of +4 due to the presence of two electrons in the *s*- and two electrons in the *p*-orbital of the valence shell. In contrast, all other elements from Ge to Pb contain either *d*- or *d*- and *f*-electrons and hence show an oxidation state of +2 moving down the group, the inert pair effect becomes more and more pronounced. In other words, *as we move down the group from Ge to Pb, the stability of +2 oxidation state increases (i.e., Ge < Sn < Pb) while that of +4 oxidation state decreases (i.e., Ge > Sn > Pb). Thus, +2 oxidation state of Pb is more stable than its +4 oxidation state.*

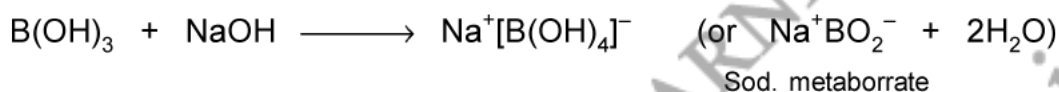
S55. A protic acid is the one which can ionise in solutions to produce protons or hydronium ions. Boric acid is not a protic acid since it does not ionize in H₂O to give a proton.



On the contrary, because of the small size of boron atom and due to presence of only six electrons in its valence shell, B(OH)₃ accepts a lone pair of electrons from oxygen atom of the H₂O molecule to form a hydrated species.



The +ve charge on the O-atom, in turn, pulls the σ -electrons of the O—H bond towards itself thereby facilitating the release of proton. As a result, B(OH)₃ acts as a weak monobasic Lewis acid and thus reacts with NaOH solution to form sodium metaborate.



S56. Species in which the central atom either does not have eight electrons in the valence shell or those which have 8 electrons in the valence shell but can expand their covalency beyond 4 due to the presence of *d*-orbitals, are called **electron deficient molecules**.

- (i) In BCl₃, the central boron atom has only six electrons. Therefore, it is an electron deficient compound. As such it accepts a pair of electrons from nucleophiles like NH₃ to form an adduct.

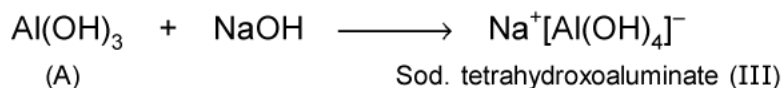
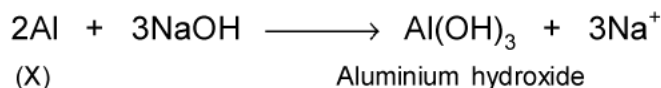


- (ii) In SiCl₄, the central Si atom has 8 electrons but it can expand its covalency beyond 4 due to the presence of vacant *d*-orbitals. Therefore, in principle, SiCl₄ should also be an electron deficient molecule. It is not worthy to mention here that SiCl₄ cannot accept two more Cl⁻ ions to form [SiCl₆]²⁻ because of the following two reasons:

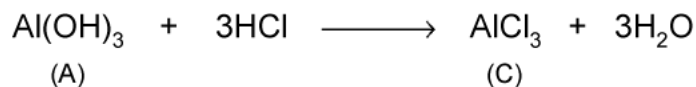
- Six large sized Cl atom cannot be accommodated around small Si atom.
- Interaction between lone pairs of chlorine atom and silicon atom is weak.

S57. (a) AlX₃ > BX₃ > GaX₃ (b) AlCl₃ > AlBr₃ > AlI₃ (c) B < Al > Ga > In > Tl

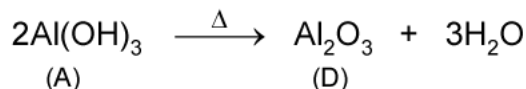
S58. Since metal X reacts with NaOH to first give a white ppt. (A) which dissolves in excess of NaOH to give a soluble complex (B), therefore, metal (X) must be Al; ppt (A) must be Al(OH)₃ and complex (B) must be sodium tetrahydroxoaluminate (III)



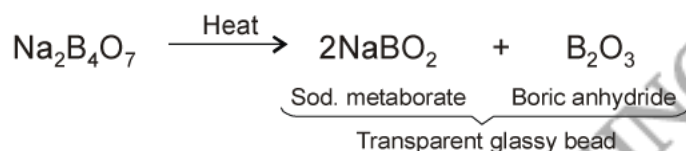
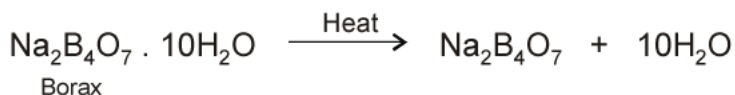
Since (A) is amphoteric in nature, it reacts with dil. HCl to form (C) which is AlCl_3



Since (A) on heating gives (D) which is used to extract metal, therefore, (D) must be alumina (Al_2O_3)



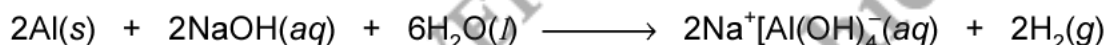
- S59.** (a) When borax is heated strongly, a transparent glassy bead which consists of sodium metaborate (NaBO_2) and boric anhydride is formed.



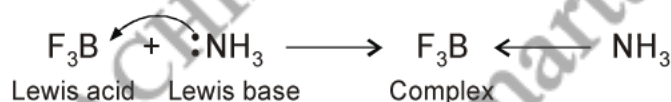
- (b) Boric acid acts as a weak Lewis acid. When boric acid is added to water it accepts the hydroxyl ion of water and releases a proton into the solution as shown:



- (c) Aluminium when treated with dil NaOH dissolves in it forming sodium tetrahydroxoaluminate complex along with evolution of dihydrogen gas.



- (d) BF_3 is a Lewis acid and accepts a pair of electrons from NH_3 to form a complex.



S60. The structure of diborane, is given in figure (a), and the structure of boric acid is given in figure (b).

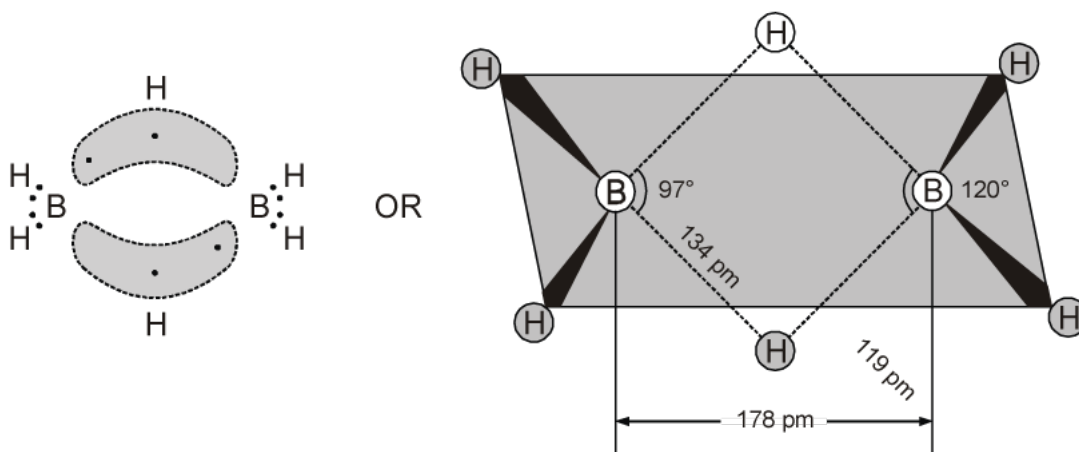


Figure (a): The Structure of Diborane

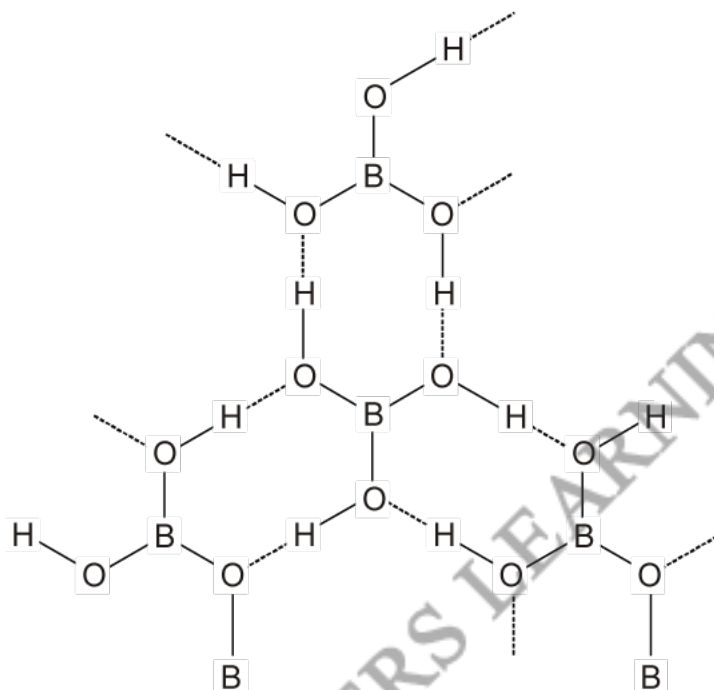


Figure (b): The Structure of Boric Acid

- Q1. C — C bond length in graphite is shorter than C — C bond of diamond. Explain.
- Q2. Diamond (impure) is used as abrasive. Explain.
- Q3. Diamond is used as precious stone. Explain.
- Q4. Diamond is bad conductor of current. Explain.
- Q5. Diamond is the hardest substance but graphite is soft in nature. Explain.
- Q6. How would you explain the lower atomic radius of Ga as compared to Al?
- Q7. Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon?
- Q8. What is the state of hybridization of carbon in (a) CO_3^{2-} (b) diamond (c) graphite?
- Q9. Gaseous fuels are better fuels than solid and liquid fuels. Explain.
- Q10. Graphite is good conductor of current. Explain.
- Q11. Carbon acts as an abrasive and also as a lubricant. Explain.
- Q12. Diamond is covalent yet its p.pt. is very high. Explain.
- Q13. Carbon monoxide is poisonous. Explain.
- Q14. Carbon never shows coordination number greater than four while other members of carbon family show coordination number as high as six.
- Q15. Solid CO_2 is known as dry ice. Explain.
- Q16. When CO_2 under high pressure is released from a fire extinguisher, particles of solid CO_2 are formed, despite the low sublimation temperature of CO_2 (1 atm P, -77°C). Explain.
- Q17. Point out some gases responsible for green house effect.
- Q18. Point out the number of σ and π bonds in (a) C_2^{2-} (b) C_3^{4-} (c) CN_2^{2-}
- Q19. List a property in which CO acts as Lewis base.
- Q20. CO_2 can not be used for extinguishing fires caused by the burning of Mg metal.
- Q21. CO_2 is sparingly soluble in water but its solubility increases with increase in pressure. Explain.
- Q22. Write down the structure of C_3O_2 .
- Q23. Graphite is thermodynamically more stable than diamond but naturally diamond is not converted into graphite, why?
- Q24. The first ionisation energy of carbon atom is greater than that of boron atom whereas the reverse is true for second ionisation energy. Explain.

- Q25. When graphite is heated at approximately 673 K with vapours of K, Rb or Cs, bronze colour is developed. Explain the chemical changes involved.
- Q26. What are “Acetylides”? Why are they so called?
- Q27. CS_2 is stored in dark coloured bottles, why?
- Q28. CO_2 is chief gas responsible for global warming (Green house effect), why?
- Q29. Name a complex in which CO_2 acts as ligand.
- Q30. Producer gas is less efficient fuel than water gas, why?
- Q31. In atomic pile, graphite is used as moderator, why?
- Q32. Pure diamond is colourless and electrical insulator, why?
- Q33. Diamond is colourless while graphite is black in colour, explain.
- Q34. The chemical reactivity of Si — C bond is generally greater than that of C — C bonds, why?
- Q35. What happens when CS_2 liquid is passed through Zn arc?
- Q36. A mixture of $\text{CS}_2(l)$ and $\text{NO}(g)$ gives a vivid blue flame on ignition and a yellow solid is left as residue. Identify it and write reactions.
- Q37. Why is SiH_4 more reactive than CH_4 ?
- Q38. CCl_4 is used as fire extinguisher but CS_2 not.
- Q39. Why does element silicon not form a graphite like structure, whereas carbon does?
- Q40. SiF_6^{2-} is known but SiCl_6^{2-} is not, why?
- Q41. Carbon and silicon are always tetravalent but germanium and lead show divalency, Explain.
- Q42. Why $(\text{CH}_3)_3\text{COH}$ is less acidic than $(\text{CH}_3)_3\text{SiOH}$ although carbon is more electronegative than Si
- Q43. Alkanes are more stable and less reactive in comparison to silanes. Explain.
- Q44. Like CO, why its analogue SiO is not stable?
- Q45. Ge^{2+} is strong reducing agent while Pb^{4+} is strong oxidising agent, why?
- Q46. SnCl_2 is ionic solid but SnCl_4 is covalent liquid. Explain.
- Q47. Germanium and tin are reducing agents while lead is an oxidant. Explain.
- Q48. PbBr_4 and PbI_4 do not exist. Explain.
- Q49. CO_2 is an acidic anhydride while PbO_2 is basic anhydride. Explain.
- Q50. Why are Pb (IV) salts in less abundance?
- Q51. Carbon atoms are tetra valent inspite of the fact that there are only two unpaired electron in $2p$ -orbitals.

- Q52. Graphite is a better lubricant on Moon than on the surface of Earth. Explain.
- Q53. Carbon does not form divalent ionic compounds. Explain.
- Q54. How is excessive content of CO_2 responsible for global warming?
- Q55. Write the resonance structures of CO_3^{2-} and HCO_3^- .
- Q56. Suggest a reason as to why CO is poisonous?
- Q57. Explain the difference in properties of diamond and graphite on the basis of their structures.
- Q58. The reaction of an aqueous solution of carbon dioxide with base is slow, why?
- Q59. In phosgene, C — O bond length is longer than expected while C — Cl bond length is shorter, Explain.
- Q60. CO_2 is gas while silica is solid. Explain.
- Q61. CCl_4 does not act as Lewis acid, while SiCl_4 and SnCl_4 acts as Lewis acid as well as their aqueous solutions are acidic. Explain.
- Q62. SnI_4 is orange coloured solid while CCl_4 and SiBr_4 are colourless liquids, why?
- Q63. Trimethylamine $[(\text{CH}_3)_3\text{N}]$ is pyramidal while trimethyl silane $[(\text{SiH}_3)_3\text{N}]$ is planar, Explain.
- Q64. Why a base PbO is not dissolved in HCl and H_2SO_4 but dissolves in HNO_3 .
- Q65. Arrange hydrides of gp. 14 elements in increasing order of: (a) Thermal stability. (b) Reducing nature.
- Q66. Rationalise the given statements and give chemical reactions:
- Lead (II) Chloride reacts with Cl_2 to give PbCl_4 .
 - Lead (IV) chloride is highly unstable towards heat.
 - Lead is known not to form an iodide, PbI_4 .
- Q67. Write balanced equations for the following reactions:
- Aqueous sodium hydroxide is added dropwise to a solution of gallium chloride in water. A precipitate formed initially which dissolves on further addition of NaOH solution.
 - SnO is treated with dilute HNO_3 .
 - Lead sulphide is heated in air.
- Q68. Explain the following reactions
- Silicon is heated with methyl chloride at high temperature in the presence of copper.
 - Silicon dioxide is treated with hydrogen fluoride.
 - C is heated with ZnO .
 - Hydrated alumina is treated with aqueous NaOH solution.

- S1.** Graphite has sp^2 hybridization and C — C bond involves $sp^2 - sp^2$ hybridized carbon. Diamond has sp^3 hybridization and C — C bond involves $sp^3 - sp^3$ hybridization. Furthermore, more s character (in sp^2) in hybridized atom, smaller is size of hybridized orbital, more is overlapping shorter is bond length.
- S2.** Diamond (black) an impure form is the hardest substance known and thus used as abrasive and for cutting glass.
- S3.** Diamond has a very high refractive index and possesses the ability of reflection and refraction. Moreover, the refraction of different colours of light is not equal and therefore white light passing through it give rise to brilliant play of colours which makes diamond as a valuable gem stone.
- S4.** All valence electrons of each carbon are used in bond formation with four neighbouring atoms and there is no mobile electron in the system and hence the diamond crystal is bad conductor of current.
- S5.** Diamond possesses very big three dimensional polymeric structure involving each carbon of sp^3 hybridized nature linked to four other neighbouring carbon atoms which makes it hardest. On the other hand, graphite has layer structure involving each carbon of sp^2 hybridized nature having wide separation and weak interlayer bonds and thus two adjacent layers can easily slide over each other to produce soft nature. This makes the graphite to show lubricant nature.
- S6.** Due to poor shielding of the valence electrons of Ga by the inner 3d-electrons, the effective nuclear charge of Ga is greater in magnitude than that of Al. As a result, the electrons in gallium experience greater force of attraction by the nucleus than in Al and hence atomic size of Ga (135 pm) is slightly less than that of Al (143 pm).
- S7.** Due to increase in atomic size and screening effect, the force of attraction of the nucleus for the valence electron decreases considerably in Si as compared to C. As a result, there is a phenomenal decrease in ionization enthalpy from carbon to silicon.
- S8.** (a) In CO_3^{2-} ion, it is sp^2 (b) In diamond, it is sp^3 (c) In graphite, it is sp^2 .
- S9.** Gaseous fuels leave no residue after burning, also they have high calorific value because their combustion is complete.
- S10.** Graphite has sp^2 hybridized carbons with layer structure along with π electrons ($p - p$ bond) free to move throughout the entire layers hence graphite is good conductor of current.
- S11.** Carbon has two crystalline allotropic forms; one is diamond, the hardest substance used as a abrasive and the other is graphite, the softer one used as lubricant.
- S12.** Diamond has three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence diamond possesses high p.pt. inspite of covalent nature.

S13. The poisonous nature of CO is due to the fact that it combines with haemoglobin (a red colouring matter of blood which is oxygen carrier) to form a stable compound carboxyhaemoglobin. Thus oxygen transportation is disturbed and tissues do not get necessary oxygen and ultimately death occurs.

A victim of CO gas poisoning (people sleeping in closed rooms with charcoal fire inside), if unconscious, should be brought in the open place and give artificial respiration with carbogen (mixture of O₂ + 5-10% CO₂).

S14. Except carbon, all the elements of group 14 can expand their coordination number from four to six due to the availability of 'd' sub-shells in them. Carbon, however, possesses no 'd' sub-shell in its outermost shell and thus cannot expand its coordination number greater than four.

S15. Solid CO₂ is technically known as dry ice because it sublimates without leaving any stain on surface.

S16. The gas does work pushing the atmosphere. The energy for doing work is provided by the gas itself and thus kinetic energy of gas molecules is lowered and hence the temperature is lowered.

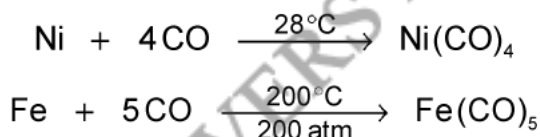
S17. CO₂ (main gas for green house effect), 50% contribution towards it. CH₄, O₃, N₂O, CFC's (other gases).

S18. (a) 1 σ and two π ($\bar{C} \equiv C$)

(b) 2 σ and two π ($\bar{C} \equiv C - C^{3-}$)

(c) 2 σ and two π ($\bar{N} = C = N^-$)

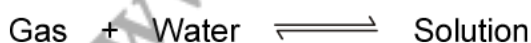
S19. CO also shows Lewis base nature and acts as ligands in many of its complexes with transition metals usually in zero oxidation state.



S20. Fire obtained by Mg is highly exothermic reaction and Mg continuously burns in CO₂ also



S21. CO₂ being covalent molecule is little soluble in water. However, the solubility of CO₂ in water increases with increase in pressure. This is Henry law. Alternatively in terms of Le chatelier principle, an increase in pressure at equilibrium brings the change in the direction where volume decrease.



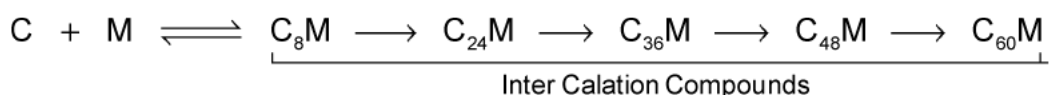
S22. O = C = C = C = O; Each carbon is sp hybridised having delocalisation of π electrons from one end to other.

S23. Because activation energy for the reaction is very high.

S24. The first ionisation energy of carbon ($1s^2, 2s^2 2p_x^1 2p_y^1$) is higher than boron ($1s^2 2s^2 2p_x^1$) as the nuclear charge in carbon is higher than boron (At. no. C = 6; B = 5).

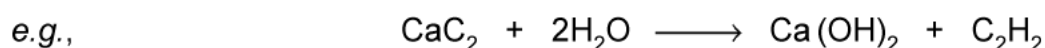
The second ionisation energy of carbon is less than that of boron because in carbon the second electron is to be removed from $2p$ -orbital while in boron the second electron is to be removed from paired $2s$ -orbital which requires higher energy in comparison to singly occupied p -orbital.

S25. Due to larger difference between layers of graphite. The metal atoms invade the space between sheets forming '**Inter Calation Compounds**' of different composition. In the compounds formed, inter sheet distance increases making π electrons more free.



Bronze colour is developed due to formation of metal atom clusters.

S26. Those carbides which react with water and liberate acetylene (C_2H_2) are called acetylides. They contain C_2 unit. Carbides of gp. 1 metals (M_2C_2) gp. 2 metals (MC_2), contain metals (Cu, Ag & Au), Zn and Cd and some of lanthanoids are acetylides. They are colourless ionic compounds.



They have NaCl like structure.

S27. Because sun light changes CS_2 into CS.

S28. CO_2 absorbs strongly heat in IR region and its increased concentration in atmosphere decreases the loss of heat from earth by radiation.

S29. $[\text{Co}(\text{CO})_2 \cdot (\text{PPh}_3)_3]$, here CO_2 acts as bidentate ligand.

S30. In water gas ($\text{CO} + \text{H}_2$), both components burn and evolve heat while in producer gas ($\text{CO} + \text{N}_2$), only CO burns, i.e., why former has higher calorific value and is good fuel.

S31. The capture cross section of graphite for thermal neutrons is extremely low (3.4×10^{-3} barn) so it can be used as moderator.

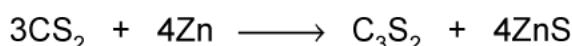
S32. In the absence of impurities there is large gap (≈ 6 eV) between filled electron band and next vacant band.

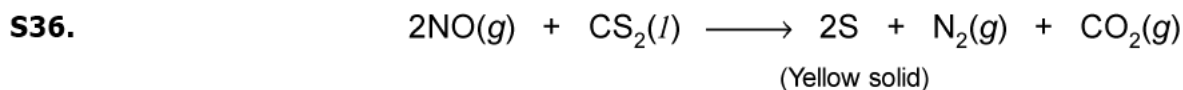
S33. In graphite C-atom is sp^2 hybridized and non-bonded p_z orbitals overlap to give completely delocalized systems of molecular orbitals. Due to excitation of these delocalised electrons graphite appear black.

S34. (a) $\overset{+\delta}{\text{Si}}-\overset{-\delta}{\text{C}}$ bond is more polar than $\text{C}-\text{C}$ bond.

(b) displacement reactions at Si are facilitated by its ability to form 5-coordinate transition states by utilization of d -orbitals.

S35. A red coloured liquid carbon subsulphide is obtained.



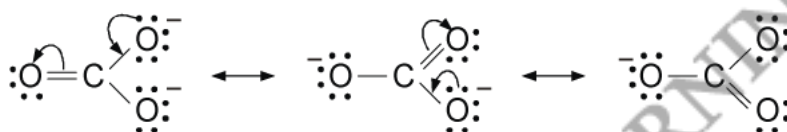


- S37.** SiH_4 is more reactive than CH_4 due to the polarity of the Si — H bond and the availability of d -orbitals with silicon.
- S38.** CCl_4 is heavy non combustible liquid but CS_2 is highly combustible liquid.
- S39.** $p_\pi - p_\pi$ multiple bonding is not prominent for silicon and other heavier elements of group 14 and this reluctance for $p_\pi - p_\pi$ bonds in silicon does not allow to form graphite like structure in silicon.
- S40.** (a) Smaller size of F give rise to less steric repulsion in SiF_6^{2-} .
(b) Interaction of lone pair of F with Si stronger than that of chlorine lone pair.
- S41.** Inert pair effect is more pronounced in Ge and Pb, as it increases down the group. This results in divalent ionic nature of Ge and Pb.
- S42.** In $(\text{CH}_3)_3\text{SiOH}$, d -orbitals of Si give rise to $p\pi - d\pi$ back bonding and thus it can easily accommodate lone pair of electron from a base.
- S43.** The C — C bond energy is appreciably higher than Si — Si bond energy and thus alkanes are relatively more stable or less reactive than silane.
- S44.** CO is more stable because of multi-bonding nature of carbon. On the other hand Si having larger size is unable to form multiple-bonding and thus SiO is unstable.
- S45.** Ge^{2+} is less stable than Ge^{4+} thus it is readily converted into Ge^{4+} when brought in contact of oxidising agent. On the other hand Pb^{4+} is less stable than Pb^{2+} so Pb^{4+} behaves as oxidising agent. Stabilities of $\text{Ge}^{2+}/\text{Ge}^{4+}$ and $\text{Pb}^{2+}/\text{Pb}^{4+}$ pairs can be explained on the basis of inert pair effect.
- S46.** SnCl_2 has ionic character (Sn^{2+} ion) and thus has higher m. pt. and exists as solid. On the other hand, SnCl_4 involves sp^3 hybridization in Sn atom leading to covalent character and thus is a liquid.
- S47.** Ge and tin are non-metals and metal respectively and thus possess more reduction potential in comparison to lead which being metal possess less reduction potential or higher oxidation potential. Hence Ge and tin possess the tendency to accept electron and acts as reducing agent while lead having more tendency to lose electron acts as oxidant.
- S48.** The non-existence nature of PbBr_4 and PbI_4 is due to the fact that Pb^{4+} ion is a strong oxidant while Br^- and I^- are strong reductants. Thus Pb^{4+} ion cannot survive in presence of Br^- or I^- and is reduced to Pb^{2+} .
- S49.** Carbon is non metal and thus its oxide (CO_2) is acidic which reacts with water to form its oxyacid H_2CO_3 . On the other hand Pb being metal and thus its oxide (PbO_2) is basic.
- S50.** Due to inert pair effect the ns electrons of lead are more deeply penetrated to $(n - 1)$ d -orbitals and thus tendency to show + 4 state becomes less.

- S51.** 2s electron pair becomes unpaired by excitation of 2s electron to 2p empty orbital giving rise to four unpaired electron in excited state.
- S52.** Graphite is a better lubricant on Moon because of lack of gravity on Moon where friction is already less than the Earth.
- S53.** For divalent ionic compounds to be formed, the lattice energy of the reaction leading to the formation of divalent ionic compound must be sufficiently high so as to contribute for that required for the first two ionization energies and the sublimation energy. In the case of carbon lattice energy is not very high and divalent ionic compounds of carbon are not formed.
- S54.** CO₂ is produced during combustion. It is utilized by plants during photosynthesis and O₂ is released into the atmosphere. As a result of this CO₂ cycle, a constant percentage of 21% O₂ in the atmosphere is maintained. However, if the concentration of CO₂ increases beyond a certain level due to excessive combustion, some of the CO₂ will always remain unutilized. This excess CO₂ absorbs heat radiated by the Earth. Some of it is dissipated into the atmosphere while the remaining part is radiated back to the earth and other bodies present on the Earth. As a result, temperature of the Earth and other bodies on the Earth increases. This is called **greenhouse effect** and CO₂ is called a **greenhouse gas**.

As a result of greenhouse effect, global warming occurs which has series consequences.

- S55.** Resonance structures of CO₃²⁻ ion:



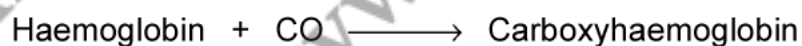
Resonance structures of HCO₃⁻ ion:



- S56.** In the lungs, haemoglobin present in red bloodcells combines with molecular oxygen loosely and reversibly to form oxyhaemoglobin.



Oxyhaemoglobin, thus, formed in the lungs then travels to different parts of the body through blood stream and deliver O₂ to the various tissues of the body. On the contrary, CO combines with haemoglobin irreversibly to form carboxyaemoglobin is about 300 times more stable than the oxyhaemoglobin.



As a result, it destroys the oxygen carrying capacity of haemoglobin and ultimately the man dies of suffocation. Thus, *the highly poisonous nature of CO arises due to its ability to form a complex with haemoglobin which is about 300 times more stable than the oxygen-haemoglobin complex.*

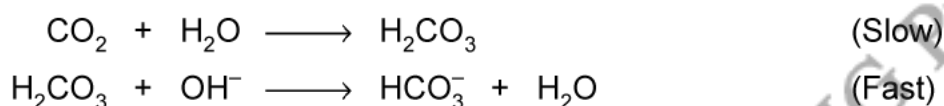
- S57.** The important differences in properties between **diamond** and **graphite**

Diamond	Graphite
1. Due to its high refractive index, it is a transparent substance.	1. Although it is black and opaque, yet it has metallic lustre.
2. It has high density (3.51 g cm^{-3}).	2. It has relatively low density (2.26 g cm^{-3}).
3. It is very hard.	3. It is soft.
4. It is bad conductor of heat and electricity.	4. It is good conductor of heat and electricity.
5. It possesses three dimensional network structure.	5. It possesses a sheet type structure.
6. Chemical reactivity is low.	6. Chemical reactivity is high.

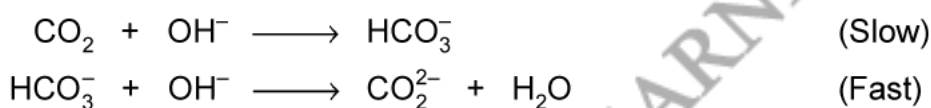
S58. It is due to two reasons.

- Only small amount of aqueous carbon dioxide exists in the hydrated form.
- Interconversion of carbon dioxide hydrated species is slow.

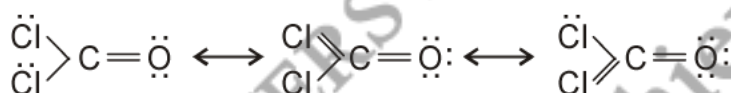
The nature of hydrated species depends upon pH. At Ph < 8 the important reaction are



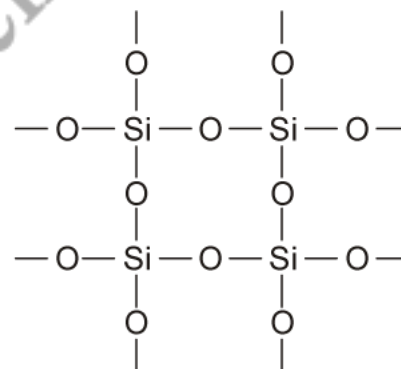
and at pH > 10, the predominant reactions are



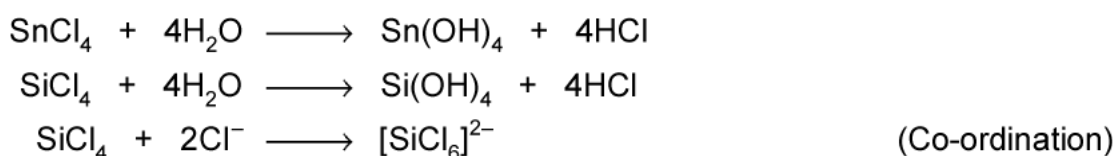
S59. Due to resonance, C — Cl acquires partial double bond character and *i.e.*, why shortened.



S60. Due to large electronegativity difference in Si and O atoms, Si — O bond possess considerable ionic nature and thus silica has three dimensional infinite structure having silicon atom tetrahedrally bonded to four oxygen atoms and each oxygen atom is bound to two silicon atoms by covalent bonds. The entire crystal of silica shows a giant molecule and thus is a high melting solid. On the other hand, CO₂ shows simple covalent nature having carbon atom *sp* hybridized. The molecules of CO₂ are held together by weak van der Waals forces and thus it exists as gas.



S61. SiCl₄ and SnCl₄ are hydrolysed to form acidic solution as well as they can act as Lewis acid because they can increase their co-ordination number beyond four due to availability of *d*-orbitals.

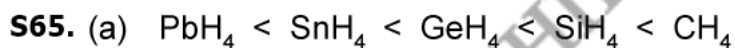
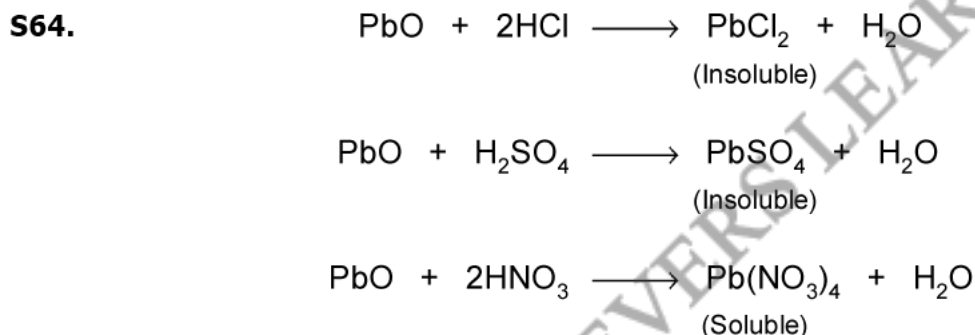
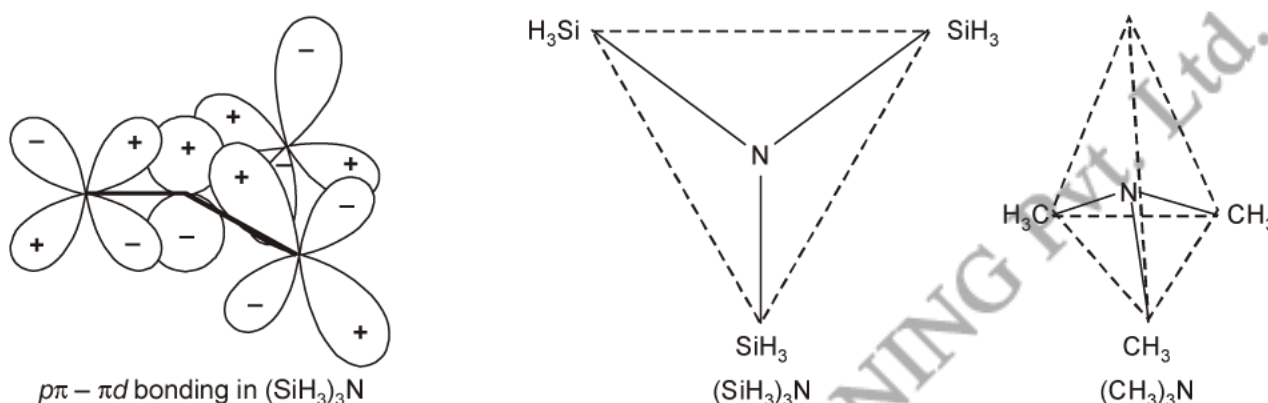


On the other hand C can not increase its co-ordination number beyond four due to non availability of *d*-orbitals and thus not hydrolysed.

S62. Colour is associated with electrons being promoted from one energy level to another. The colour is developed generally when electronic transition occurs between energy levels of same shell. If transition involves different shell (say $2p \rightarrow 3p$), that appear while as energy required is quite high. Because in CCl_4 and SiBr_4 , *s* and *p* subshells are filled so they appear white.

In SnI_4 , the energy absorbed causes transfer of electron from iodine to Sn^{4+} , causing temporary reduction of Sn^{4+} into Sn^{3+} . This charge transfer spectra is responsible for colour of SnI_4 .

S63. In trimethyl silane, N-atom forms 3Si-N σ bonds and lone pair of electron occupy a *p*-orbital which forms $p\pi - d\pi$ bond (a bond formed between full *p*- and empty *d*-orbital). $p\pi - d\pi$ bonding is not possible in $(\text{CH}_3)_3\text{N}$ because N- does not contain *d*-orbitals and so molecule is pyramidal.



S66. (a) Pb can exist in its compounds in two different oxidation states of +2 and +4.

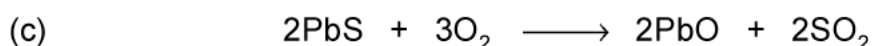
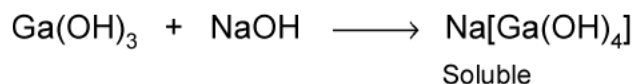
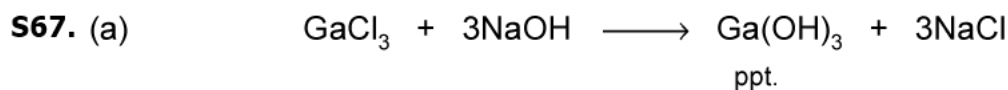


Due to *inert pair effect*, Pb is more stable in +2 than in +4 oxidation state. Therefore, lead (II) chloride is more stable than lead (IV) chloride and hence *lead (II) chloride does not react with Cl_2 to form lead (IV) chloride.*

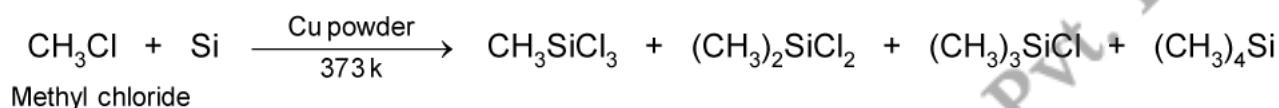
(b) Lead (IV) chloride on heating decomposes to give lead (II) chloride and Cl_2 .



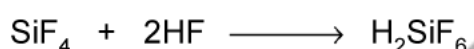
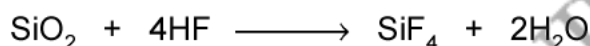
- (c) PbI_4 is unstable to heat because the Pb – I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ to have four unpaired electrons around lead atom needed for formation of PbI_4 . In addition to this Pb^{+4} ion acts as a good oxidising agent (*i.e.*, readily changes to stable Pb^{+2} ion) and I^- ion has good reducing power. Hence PbI_4 does not exist.



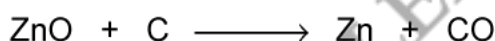
- S68.** (a) The reaction of silicon with CH_3Cl in the presence of Cu, at high temperature produces a mixture of mono-, di- and trimethylchlorosilanes along with a small amount of tetramethylsilane.



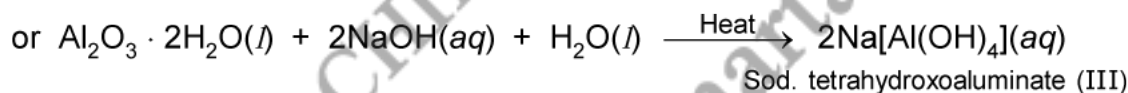
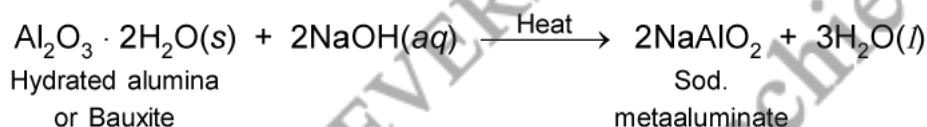
- (b) Silicon tetrafluoride dissolves in HF to form hydrofluorosilicic acid



- (c) ZnO is reduced to zinc metal



- (d) Alumina dissolves to form sodium metaaluminate



Name :

M.M.: 12

Time : 05:00

Date: 16/10/2021

- Q1. Classify following oxides as neutral, acidic, basic or amphoteric** **2**
 CO , B_2O_3 , SiO_2 , CO_2 , Al_2O_3 , PbO_2 , Ti_2O_3 .
- Q2. Consider the compounds, BCl_3 and CCl_4 . How will they behave with water?** **2**
- Q3. Write the formulae of the following compounds:** **3**
- | | | | |
|-------------------|-------------------|-------------------|--------------|
| (a) Nutter of tin | (b) White lead | (c) Sugar of lead | (d) Litharge |
| (e) Red lead | (f) Carborundum | (g) Phosgene | (h) Dry cold |
| (i) Water glass | (j) Chrome yellow | | |
- Q4. Give reasons:** **5**
- (a) Conc. HNO_3 can be transported in aluminium container.
 - (b) A mixture of dilute NaOH and aluminium pieces is used to open drain.
 - (c) Graphite is used as lubricant.
 - (d) Diamond is used as an abrasive.
 - (e) Aluminium alloys are used to make aircraft body.
 - (f) Aluminium utensils should not be kept in water overnight.
 - (g) Aluminium wire is used to make transmission cables.

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Name :

Time : 05:00

Total Marks = 12

Date: 16/10/2021

S1. The given oxides can be classified as: **2**

Neutral oxides:	CO
Acidic oxides:	B ₂ O ₃ , SiO ₂ , CO ₂
Amphoteric oxides:	Al ₂ O ₃ , PbO ₂
Basic oxide:	Tl ₂ O ₃ .

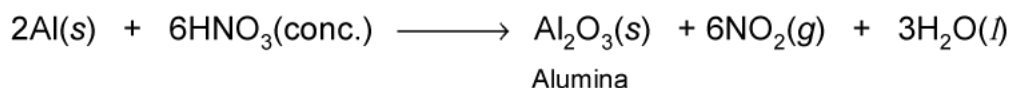
S2. The B atom in BCl₃ has only six electrons in the valence shell and hence is an **electron-deficient molecule**. It easily accepts a pair of electrons donated by water and hence BCl₃ undergoes hydrolysis to form boric acid (H₃BO₃) and HCl. **2**



In contrast, C atom in CCl₄ has 8 electrons in the valence shell. Therefore, it is an **electron-precise molecule**. As a result, it neither accepts nor donates a pair of electrons. In simple words, it does not accept a pair of electrons from H₂O molecule and hence CCl₄ does not undergo hydrolysis in water.

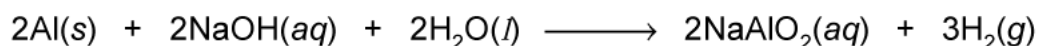
- S3.** (a) SnCl₄ · 5H₂O (Stannic chloride) **3**
 (b) 2PbCO₃ · Pb(OH)₂ (Basic lead carbonate)
 (c) Pb(CH₃COO)₂ (Lead acetate)
 (d) PbO (Lead monoxide)
 (e) Pb₃O₄ (Trilead tetra-oxide)
 (f) SiC (Silicon carbide)
 (g) COCl₂ (Carbonyl chloride)
 (h) CO₂ (Carbon dioxide is solid state)
 (i) Na₂SiO₃ (Sodium silicate)
 (j) PbCrO₄ (Lead chromate)

S4. (a) Al reacts with conc. HNO₃ to form a very thin film of aluminium oxide on its surface which protects it from further action. **5**

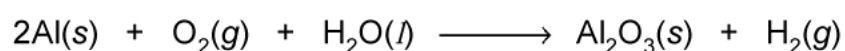


Thus, Al becomes passive and hence aluminium containers can be used to transport conc. HNO_3 .

- (b) NaOH reacts with Al to evolve dihydrogen gas whose high pressure is enough to open clogged drains.



- (c) Graphite has layered structure in which the different layers are held together by weak van der Waals forces and hence can be made to slip over one another. Therefore, graphite acts as a lubricant.
- (d) Diamond is very hard because it is a network solid and hence can be used as an abrasive.
- (e) Aluminium alloys such as duralumin is light, tough and resistant to corrosion and hence is used to make aircraft body.
- (f) Al reacts with H_2O and dissolved O_2 to form a thin film of aluminium oxide.



A very very small amount of Al_2O_3 may also dissolve to give a few ppm of Al^{3+} ions in the solution. Since Al^{3+} ions are injurious to health, therefore, drinking water should not be kept in aluminium utensils overnight.

- (g) On weight to weight basis, aluminium conducts twice as Cu. Therefore, it is used in transmission cables.

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