The *p*-Block Elements (Group 13 and 14)

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence

(a) Al < Ga < In < Tl (b) Tl < In < Ga < Al
(c) In < Tl < Ga < Al (d) Ga < In < Al < Tl

2. In group 13, electronegativity first decreases from B to Al and then increases marginally down the group. This is because of

(a) non-metallic nature of B
(b) discrepancies in atomic size of elements
(c) ability of B and Al to form $p\pi$ - $p\pi$ multiple bonds
(d) irregular trend in electronegativity throughout the periodic table.

3. Choose the correct statement.

(a) Non-metals have higher ionisation enthalpies and higher electronegativities than the metals.
(b) Non-metals and metalloids exist only in the *p*-block of the periodic table.
(c) Change of non-metallic to metallic character can be illustrated by the nature of oxides they form.
(d) All are correct.

4. What is the hybridisation of B in BCl_3?

(a) sp^3 (b) sp^2
(c) sp (d) dsp^2

5. Elements of group 14

(a) exhibit oxidation state of +4 only
(b) exhibit oxidation state of +2 and +4 only
(c) form M^{2-} and M^{4+} ions
(d) form M^{2+} and M^{4-} ions.

6. Carbon-60 contains

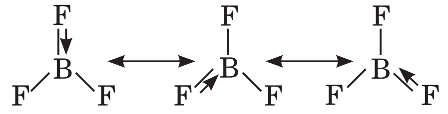
(a) 20 pentagons and 12 hexagons
(b) 12 pentagons and 20 hexagons
(c) 30 pentagons and 30 hexagons
(d) 24 pentagons and 36 hexagons.

7. Al and Ga have nearly the same covalent radii because of

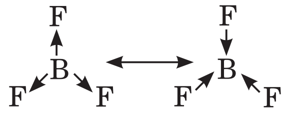
(a) greater shielding effect of *s*-electrons of Ga atom
(b) poor shielding effect of *s*-electrons of Ga atom
(c) poor shielding effect of *d*-electrons of Ga atom
(d) greater shielding effect of *d*-electrons of Ga atom.

8. Which of the following structures correctly represents the boron trifluoride molecule?

(a)



(b)



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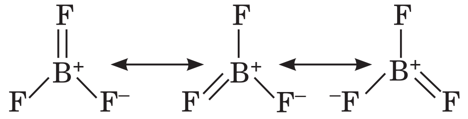
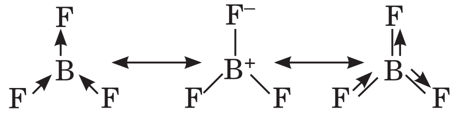


(d)



9. Boron is unable to form BF_6^{3-} because of

(a) high electronegativity of boron
(b) high electronegativity of fluorine
(c) lack of *d*-orbitals in boron
(d) less difference in electronegativity between B and F.

10. Which of the following bonds has the most polar character?

(a) C – O (b) C – Br
(c) C – S (d) C – F

11. In graphite, electrons are

(a) localised on every third C-atom
(b) present in anti-bonding orbital
(c) localised in each C-atom
(d) spread out between the structure.

12. Amongst the halides

(1) BCl_3 (2) $AlCl_3$
(3) $GaCl_3$ (4) $InCl_3$

the order of decreasing Lewis acid character is

(a) 1, 2, 3, 4 (b) 4, 3, 2, 1
(c) 3, 4, 2, 1 (d) 2, 3, 4, 1

13. The +1 oxidation state of thallium is more stable than its +3 oxidation state because of

(a) its atomic size
(b) its ionisation potential
(c) inert pair effect
(d) diagonal relationship.

14. Ionisation enthalpy ($\Delta_i H_1$ kJ mol^{-1}) for the elements of Group 13 follows the order

(a) $B > Al > Ga > In > Tl$
(b) $B < Al < Ga < In < Tl$
(c) $B < Al > Ga < In > Tl$
(d) $B > Al < Ga > In < Tl$

15. Which of the following conceivable structures for CCl_4 will have a zero dipole moment?

(a) Square planar
(b) Square pyramid (carbon at apex)
(c) Irregular tetrahedron
(d) Regular tetrahedron

16. The wrong statement about fullerene is

(a) it has 5-membered carbon ring
(b) it has 6-membered carbon ring
(c) it has sp^2 hybridization
(d) it has 5-membered rings more than 6-membered rings.

17. Fluorine is more electronegative than either boron or phosphorus. What conclusion can be drawn from the fact that BF_3 has no dipole moment but PF_3 does?

(a) BF_3 is not spherically symmetrical, but PF_3 is.
(b) BF_3 molecule must be linear.
(c) The atomic radius of P is larger than the atomic radius of B.
(d) The BF_3 molecule must be planar triangular.

18. Which of the following statements is correct?

(a) Graphite is thermodynamically more stable than diamond.
(b) Diamond is thermodynamically more stable than graphite.
(c) Graphite has such a high thermodynamical stability that diamond spontaneously changes into graphite in ordinary conditions.
(d) Graphite and diamond have equal thermodynamic stability.

19. In the carbon family, the elements other than carbon do not form $p\pi$-$p\pi$ bonds because the atomic orbitals are too

(a) small and diffused to undergo effective lateral overlap
(b) large and diffused to undergo effective lateral overlap
(c) large and far, too less diffused to overlap linearly
(d) small to overlap both laterally and linearly.

20. Which among CH_4, SiH_4, GeH_4 and SnH_4 is most volatile?

(a) CH_4 (b) SiH_4
(c) GeH_4 (d) SnH_4

21. Which of the following does not have a tetrahedral structure?

(a) BH_3 (b) NH_4^+
(c) BH_4^- (d) CH_4

22. Which is least stable compound?

(a) BCl_3 (b) $GaCl_3$
(c) $InCl_3$ (d) $TlCl_3$

23. Which of the following acts as an oxidising agent?

(a) B^{3+} (b) Al^{3+}
(c) Tl^{3+} (d) None of these

24. Match the species given in Column I with the properties mentioned in Column II.

Column I	**Column II**
(i) BF_4^-	(A) Oxidation state of central atom is +4
(ii) $AlCl_3$	(B) Strong oxidising agent
(iii) SnO	(C) Lewis acid
(iv) PbO_2	(D) Can be further oxidised
	(E) Tetrahedral shape

(a) (i) → (E), (ii) → (B), (iii) → (D), (iv) → (A, C)
(b) (i) → (E), (ii) → (C), (iii) → (D), (iv) → (A, B)
(c) (i) → (B), (ii) → (E), (iii) → (D), (iv) → (A, C)
(d) (i) → (D), (ii) → (E), (iii) → (B), (iv) → (A, C)

25. Which element does not exhibit allotropy?
(a) C (b) Sn
(c) Si (d) Pb

26. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-}?
(a) B (b) Al
(c) Ga (d) In

27. Aluminium vessels should not be washed with materials containing washing soda since
(a) washing soda is expensive
(b) washing soda is easily decomposed
(c) washing soda reacts with Al to form insoluble aluminium oxide
(d) washing soda reacts with Al to form insoluble aluminate.

28. Carbon forms a large number of compounds because it has
(a) fixed valency
(b) non-metallic nature
(c) high ionization potential
(d) property of catenation.

29. Thallium shows different oxidation states because
(a) of its high reactivity
(b) of inert pair of electrons
(c) of its amphoteric nature
(d) it is a transition metal.

30. Aluminium is more reactive than iron but aluminium is less easily corroded than iron because
(a) aluminium is a noble metal
(b) iron undergoes reaction easily with water
(c) aluminium with oxygen forms a protective oxide layer
(d) iron forms mono and divalent ions.

31. The shape and hybridisation of $Si(CH_3)_4$ is
(a) bent, *sp* (b) trigonal, sp^2
(c) tetrahedral, sp^3 (d) octahedral, sp^3d^2

32. The element with smallest atomic radius and lowest melting point out of the following is
(a) Al (b) Ga
(c) In (d) Tl

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 33 to 38.

The heavier members of 13 and 14 groups besides the group oxidation state also show another oxidation state which is two units less than the group oxidation state. Down the group (↓), the stability of higher oxidation state decreases and that of lower oxidation state increases. This concept which is commonly called inert pair effect has been used to explain many physical and chemical properties of the element of these groups.

33. Heavier members of groups 13 exhibit oxidation state
(a) +3 only (b) +1 only
(c) +1 and +3 both (d) +1, +2, +3

34. Which among the following is the strongest oxidising agent?
(a) SiO_2 (b) GeO_2
(c) SnO_2 (d) PbO_2

35. Which among the following is the strongest reducing agent?
(a) GaCl (b) InCl
(c) BCl_3 (d) TlCl

36. The strongest reductant among the following is
(a) $SnCl_2$ (b) $SnCl_4$
(c) $PbCl_2$ (d) $GeCl_2$

37. Which of the following statement is wrong?
(a) Tl(III) salt undergo disproportionation.
(b) CO is used as a reducing agent.
(c) CO_2 is a greenhouse gas.
(d) SiO_2 is a covalent solid.

38. Which of the following act as the strongest acid?
(a) Tl_2O_3 (b) SnO_2
(c) PbO_2 (d) CO_2

Case II : Read the passage given below and answer the following questions from 39 to 43.

Allotropy : The phenomenon of existence of the same substance (element or compound) in two or more forms, in the same physical state, having different properties. Different forms are called allotropes or allotropic modifications.

Except lead, all other elements of group 14 show allotropy.

Element	Allotropic form
C	Crystalline : graphite and diamond Amorphous : coal, coke and charcoal
Si	Crystalline and amorphous
Ge	Two crystalline forms
Sn	Three forms : grey tin, white tin, rhombic tin

39. Wood charcoal is used in gas masks because it

(a) is poisonous

(b) liquefies gases

(c) is porous

(d) adsorbs poisonous gases.

40. Which of the following is not sp^2 hybridised?

(a) Graphite (b) Graphene

(c) Fullerene (d) Dry ice

41. Fullerene with formula C_{60} has a structure where every carbon atom is

(a) sp-hybridized (b) sp^2-hybridized

(c) sp^3-hybridized (d) not hybridized.

42. Thermodynamically the most stable form of carbon is

(a) diamond (b) graphite

(c) fullerene (d) coal.

43. The element that does not show catenation among the following p-block elements is

(a) carbon (b) silicon

(c) germanium (d) lead.

Case III : Read the passage given below and answer the following questions from 44 to 47.

The high charge and small size of Al^{3+} ion gives it a high charge density which is responsible for its tendency to show

(a) covalency in its compounds in the gaseous state

(b) high hydration enthalpy which stabilizes its compounds in solution, and

(c) high lattice enthalpy of its compounds in the solid state.

Hence, aluminium can form both covalent and ionic bond. Like halides of boron, halides of aluminium do not show backbonding because of increase in size of aluminium. In fact, aluminium atoms complete their octets by forming dimers. Thus, chloride and bromide of aluminium exist as dimers. Thus, chloride and bromide of aluminium exist as dimers, both in the vapor state and in polar solvents like benzene, while the corresponding boron halides exist as monomer. In boron trihalides, the extent of back bonding decreases with increase in size of halogens and thus Lewis acid character increases. All BX_3 are hydrolysed by water but BF_3 shows as different behavior.

44. Which of the following statements about anhydrous aluminium chloride is correct?

(a) It exists as Al_2Cl_6 dimer in vapour form.

(b) It is not easily hydrolysed.

(c) It sublimes at 100°C under vacuum.

(d) It is a strong Lewis base.

45. Which one of the following statements is correct?

(a) All boron trihalides form back bonding.

(b) Anhydrous aluminium chloride is an ionic compound.

(c) Aluminium bromide make up the electron deficiency by bridging with other aluminium bromide.

(d) None of these.

46. The dimeric structure of aluminium chloride disappear when

(a) it dissolves in water

(b) it reacts with donor molecules like R_3N

(c) it dissolves in benzene

(d) both (a) and (b).

47. Which of the following reaction is incorrect?

(a) $BF_{3(g)} + F^-_{(aq)} \longrightarrow BF_4^-$

(b) $BF_{3(g)} + 2H_2O \longrightarrow [BF_3OH]^- + H_3O^+$

(c) $BCl_{3(g)} + 3C_2H_5OH_{(l)} \longrightarrow B(OC_2H_5)_{3(l)} + 3HCl$

(d) $BCl_{3(g)} + 2C_5H_5N_{(l)} \longrightarrow Cl_3B(C_5H_5N)_{2(s)}$

Assertion & Reasoning Based MCQs

For question numbers 48-55, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

48. Assertion : Compounds formed by non-metals with metals are covalent in nature.

Reason : Compounds formed between non-metals themselves are largely covalent.

49. Assertion : Anhydrous $AlCl_3$ is covalent but hydrated $AlCl_3$ is ionic.

Reason : In water, Al_2Cl_6 dissociates into hydrated Al^{3+} and Cl^- ions due to high heat of hydration of these ions.

50. Assertion : The tetrahalides of carbon are not hydrolysed by water under normal conditions.

Reason : Carbon cannot expand its coordination number beyond 4 because of the absence of *d*-orbitals.

51. Assertion : All the trihalides of boron act as Lewis acids.

Reason : The relative strength of boron trihalides is of the order

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

52. Assertion : Al forms $[AlF_6]^{3-}$ but B does not form $[BF_6]^{3-}$.

Reason : B does not react with F_2.

53. Assertion : The tendency for catenation decreases in the order C > Si > Ge > Sn.

Reason : The catenation depends on the strength of the element-element bond.

54. Assertion : Boron differs from aluminium and other members of group 13 in a number of properties.

Reason : Boron shows anomalous behaviour.

55. Assertion : In carbon dioxide, the carbon is sp^3 hybridized.

Reason : CO is a linear monomeric covalent compound.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. Why does graphite act as a good lubricant?

2. What is inert pair effect?

3. Write reactions to justify amphoteric nature of aluminium.

4. Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

5. How would you explain the lower atomic radius of Ga as compared to Al?

6. Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon?

7. Suggest reasons why the B—F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

8. What are electron deficient compounds? Are BCl_3 and $SiCl_4$ electron deficient species? Explain.

9. What are fullerenes? How are they prepared?

10. If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

Short Answer Type Questions (SA-I)

11. What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

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

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

(i) BCl_3 (ii) $AlCl_3$

14. Describe the general trends in the metallic character of the elements in groups 13 and 14.

15. The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

16. What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

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

18. Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than BCl_3. Comment.

19. Explain, why CO_2 is a gas whereas SiO_2 is a solid?

20. Give reason why CCl_4 is immiscible in water, whereas $SiCl_4$ is easily hydrolysed.

Short Answer Type Questions (SA-II)

21. (a) Classify following oxides as neutral, acidic, basic or amphoteric:

$CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3$

(b) Write suitable chemical equations to show their nature.

22. Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known. Explain.

23. Arrange the following in increasing order of the property indicated :

(a) $SiCl_2, GeCl_2, SnCl_2$ and $PbCl_2$ (stability)
(b) CO, SiO, SnO, GeO, PbO (basicity)
(c) $SiF_4, SiCl_4, SiI_4, SiBr_4$ (stability)

24. Explain the difference in properties of diamond and graphite on the basis of their structures.

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

(i) Oxidation states
(ii) Atomic size
(iii) Nature of halide

26. Explain the following :

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

(ii) Discuss the Lewis acid nature of boron halides.

27. How does $AlCl_3$ act as a Lewis acid?

28. Explain the following :

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

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

29. BCl_3 exists as monomer whereas $AlCl_3$ is dimerised through halogen bridging. Give reason. Explain the structure of the dimer of $AlCl_3$ also.

30. Complete the following chemical equations and identify X, Y and Z.

$$Z + 3\,LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3$$

$$X + 6H_2O \longrightarrow Y + 6H_2$$

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

Long Answer Type Questions (LA)

31. (a) Boron fluoride exists as BF_3 but boron hydride doesn't exist as BH_3. Give reason. In which form does it exist? Explain its structure.

(b) A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element and write formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

32. Explain the following :

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

(b) Lead does not form PbI_4.

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

33. Explain the following:

(i) Why PbO_2 is a stronger oxidising agent than SnO_2?

(ii) Why ionisation enthalpy of Ga is higher than that of Al?

(iii) Thallous compounds (Tl^+) are more stable than thallic (Tl^{3+}) compounds. Why?

34. Three pairs of compounds are given below. Identify that compound in each of the pairs which has group 13 element in more stable oxidation state. Give reason for your choice. State the nature of bonding also.

(i) $TlCl_3$, TlCl (ii) $AlCl_3$, AlCl

(iii) $InCl_3$, InCl

35. Describe the general trends in the following properties of the elements of groups 13.

(i) Atomic size

(ii) Ionisation enthalpy

(iii) Metallic character

(iv) Oxidation states

(v) Nature of halides.

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (a) : In group 13 elements, stability of +3 oxidation state decreases down the group while that of +1 oxidation state increases due to inert pair effect.

Hence, stability of +1 oxidation state increases in the sequence : Al < Ga < In < Tl.

2. (b) : There is a large size difference between B and Al.

3. (d)

4. (b) : In BCl_3, B is sp^2 hybridised.

5. (b) : General electronic configuration of Group-14 elements is ns^2np^2. Thus, they can exhibit +2 oxidation state by losing 2*p*-electron or +4 oxidation state by losing all 4 valence electrons.

6. (b) : C-60 contains 12 pentagons and 20-hexagons folded into a sphere.

7. (c) : Due to poor shielding effect of *d*-electrons of Ga, the outer electrons experience more attraction by the nucleus.

8. (a) : BF_3 molecule involves extensive back bonding from fluorine to boron.

9. (c)

10. (d) : C – F bond has maximum electronegativity difference, hence most polar.

11. (d) : In graphite, electrons are spread out between the structure.

12. (a) : Lewis acid strength of group 13 halides follows the order :

$BCl_3 > AlCl_3 > GaCl_3 > InCl_3$

13. (c)

14. (d) : *I.E.* has the order B > Al < Ga > In < Tl

Decrease from B to Al is associated with increase in size. Discontinuity between Al and Ga and between In and Tl are due to poor shielding of *d* and *f* electrons.

15. (d) : CCl_4 has regular tetrahedral structure where dipole moment of all four C–Cl bonds are cancelled out by each other and CCl_4 as a molecule remains non-polar.

16. (d) : Fullerene consists of 12 five-membered rings and 20 six-membered rings. So, it has five-membered rings less than six-membered rings.

17. (d) : In BF_3, B is sp^2 hybridised and compound is planar triangular so that BF_3 is non-polar.

18. (a) : Graphite is thermodynamically more stable than diamond.

19. (b) : In carbon family, elements other than carbon do not form $p\pi$-$p\pi$ bonds because the atomic orbitals are too large and diffused to undergo effective lateral overlap.

20. (a) : CH_4 is most volatile due to lower molecular mass.

21. (a) : BH_3 is trigonal planar where B is sp^2 hybridised.

22. (d) : All the given compounds belong to group 13 of the periodic table. In this group, the +3 oxidation state becomes less stable on moving down the group due to inert pair effect. Hence, BCl_3 is most stable and $TlCl_3$ is least stable.

23. (c) : Due to inert pair effect Tl^{3+} is unstable and is reduced to more stable Tl^{+} thus behaving as an oxidising agent.

24. (b) : (i) → (E), (ii) → (C), (iii) → (D), (iv) → (A, B)

25. (d) : Lead (Pb) does not show allotropy.

26. (a) : Boron can not expand its coordination number from 4 due to absence of *d*-orbitals.

27. (d) : Aluminium vessel has an upper layer of aluminium oxide. When this vessel is washed with material containing washing soda then insoluble sodium metaaluminate is formed.

$$Al_2O_3 + Na_2CO_3 \rightarrow \underset{\text{Sodium metaaluminate}}{2NaAlO_2} + CO_2$$

28. (d) : Carbon has high tendency to catenate thus forms large number of compounds.

29. (b) : Tl^{+} ions are more stable than Tl^{3+} due to inert pair effect which results in reluctance of *s*-electrons to unpair to show higher oxidation state.

30. (c) : Al forms a protective oxide layer, on reaction with oxygen which is hard and impervious.

31. (c)

32. (b) : Element with smallest atomic radius (135 pm) and lowest melting point (303 K) is Ga.

33. (c) : In heavier members due to inert pair effect both +1, +3 oxidation state are possible.

34. (d)

35. (c) : +1, +3 oxidation state are possible in Ga.
Ga^{3+} is more stable than Ga^{1+} hence. GaCl act as reducing agent.

36. (d) : $GeCl_2$ is the strongest reductant because Ge in +4 oxidation state is more stable than Ge in +2 oxidation state.

37. (a) : Tl(III) salt doesn't undergo disproportionation reaction because +3 oxidation state of Tl is more stable due to inert pair effect.

38. (d) : CO_2 is most acidic as acidic character of oxide decrease down the group.

39. (d) : Wood charcoal adsorbs large volume of poisonous gases from atmosphere.

40. (d) : Solid CO_2 is dry ice in which carbon atom undergoes *sp*-hybridisation.

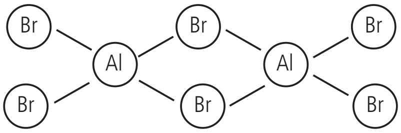
41. (b) : In fullerene with formula C_{60}, all the carbon atoms are equal and they undergo sp^2 hybridisation.

42. (b)

43. (d)

44. (a) : Anhydrous $AlCl_3$ dimerise to form Al_2Cl_6 in vapour form.

45. (c) : AlX_3 (X = Cl, Br, I) make up the electron deficiency by forming the dimer Al_2X_6



46. (a) : $AlCl_3 + H_2O \rightarrow Al(OH)_3$

47. (b) : $BF_3 + H_2O \rightarrow BF_4^-$

48. (d) : Compounds formed by non-metals with metals are generally ionic in view of larger differences in their electronegativities. Compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities.

49. (a)

50. (a)

51. (b) : BF_3 is weakest Lewis acid.

52. (c) : B does not have vacant *d*-orbitals as for B, second shell is the outermost shell.

53. (a) : As we move down the group 14, the element-element bond energies decrease rapidly, *viz*. C–C (355 kJ mol^{-1}), Si–Si (222 kJ mol^{-1}), Ge–Ge (167 kJ mol^{-1}) and Sn–Sn (155 kJ mol^{-1}), so the tendency for catenation decreases in the order C > Si > Ge > Sn.

54. (b) : This is due to small atomic size, high electronegativity, high ionization energy and absence of *d*-orbital of B.

55. (d) : In CO_2, C is *sp* hybridized. It forms two σ bonds with two oxygen atoms and two $p\pi$-$p\pi$ multiple bonds. So CO_2 is a linear, monomeric and covalent compound.

SUBJECTIVE TYPE QUESTIONS

1. Graphite has sheet like structure and it is slippery so, it can act as lubricant.

2. The tendency of *s*-electrons of the valence shell to participate in bond formation decreases down the group. This reluctance of the *s*-electrons to participate in bond formation is called inert pair effect.

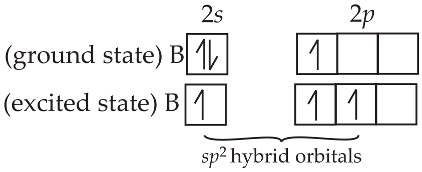
3. Amphoteric substances are those that can react with both acids and bases. Aluminium reacts with HCl to liberate H_2 gas as :

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_{2(g)}$$

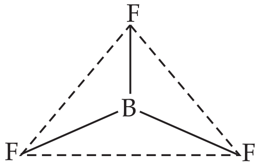
Aluminium can react with aqueous alkali and liberate hydrogen gas.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow \underbrace{2Na^{+}[Al(OH)_4]^{-}_{(aq)}}_{\text{Sodium tetrahydroxoaluminate (III)}} + 3H_2\uparrow$$

4. BF_3 has a planar triangular structure which arises from the sp^2 hybrid orbitals.

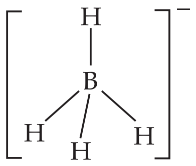


These three sp^2 hybrid orbitals are directed towards the corners of triangle and BF_3 has a trigonal structure.



Trigonal planar structure of BF_3

BH_4^- may be assumed to be made of a central B atom, 3H atoms and one hydride ion H^-.



In order to accommodate the 3H atoms and one H^- ion, B undergoes sp^3 hybridisation yielding four orbitals, 3 of which contain one e^- each and one is empty. The fourth, empty orbital accomodates the H^- ion. Thus, the structure of BH_4^- is tetrahedral.

5. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect for the outer electron from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

6. Large decrease in ionisation potential from C to Si is due to increase in size of the atom and shielding effect.

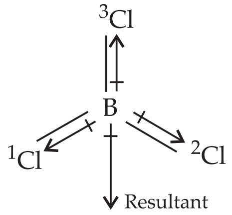
7. The bond length in any compound is dependent on the hybridisation of the central atom. Boron in BF_3 is sp^2 hybridised which means that the *s*-character is 33% and therefore, the bond length is shorter. Also due to similar size of both atoms and vacant *p*-orbital of B, a $p\pi$-$p\pi$ back bonding from F to B occurs causes partial double bond character. This further decreases the bond length of B — F. In BF_4^-, the hybridisation of B is sp^3 which means that the *s*-character is 25% and therefore, a longer bond length.

8. Electron deficient compounds are those where the central atom has less than 8 electrons in its outermost shell. Out of BCl_3 and $SiCl_4$, the former is an electron deficient compound since it has only 6 electrons in the outermost shell. $SiCl_4$ is not an electron deficient compound.

However, it can accept electrons by expanding its octet due to presence of empty *d*-orbitals. Thus, it may form species like $SiCl_6^{2-}$.

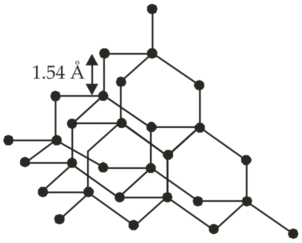
9. Fullerenes are the purest form of carbon, consisting of mainly C_{60} units. C_{60} unit has a shape of football, called Buckminsterfullerene. Fullerenes are prepared by heating graphite in an electric arc in the presence of inert gas such as helium or argon.

10. The dipole moment of any molecule is the vector sum total of each of the dipole moments. In BCl_3 molecule, although the B–Cl bonds individually are polar, the resultant dipole moment becomes zero.

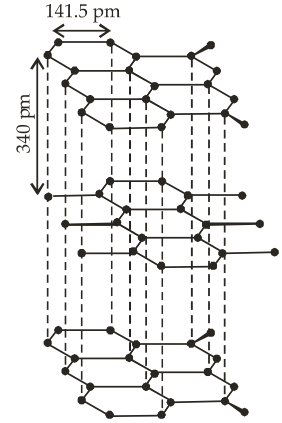


We can see that the dipole moments of B–^{1}Cl and B–^{2}Cl produce a resultant which is equal in magnitude but opposite in direction to B–^{3}Cl and hence cancels it out. That is why the net dipole moment of BCl_3 is zero.

11. The property due to which an element exists in two or more forms which differ in their physical and some of the chemical properties is known as allotropy and the various forms are called allotropes or allotropic modifications. Carbon exists in two allotropic forms crystalline and amorphous. The crystalline forms are diamond and graphite.



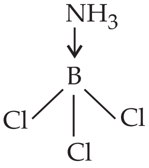
Structure of diamond



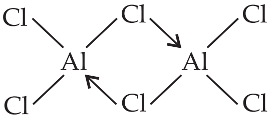
Structure of graphite

Diamond due to extended covalent bonding is the hardest natural substance on the earth. Graphite has layer of sheets which are held by weak van der Waals' forces thus, it can be cleaved easily between layers which makes it soft and slippery.

12.

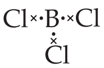


$BCl_3 \cdot NH_3$



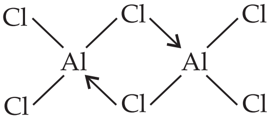
$AlCl_3$ (dimer)

13. (i) BCl_3 – Boron has 6 electrons in its outermost orbital and has a vacant *p*-orbital. Thus, it is an electron deficient compound hence acts as Lewis acid and accepts a lone pair of electrons.



$$\underset{\overset{\times\cdot}{Cl}}{Cl \times\cdot B \cdot\times Cl}$$

(ii) $AlCl_3$ is also an electron deficient compound and acts as Lewis acid. It generally forms a dimer to achieve stability.



$AlCl_3$ (dimer)

14. Metallic character : Metallic character increases from boron to aluminium then decreases down the group for group 13 elements. Due to smaller size group 14 elements are less metallic. Metallic character increases gradually down the group. C (non-metal), Si,Ge (metalloid) Sn, Pb (metals).

15. In group 13 and 14, as we move down the group, the tendency of *s*-electrons of the valence shell to participate in bond formation decreases. This is due to ineffective shielding of ns^1 and ns^2 electrons of the valence shell by intervening *d*- and *f*-electrons. This is called inert pair effect.

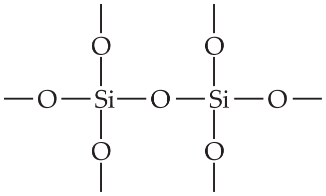
Due to this, ns^1 and ns^2 electrons of valence shell of group 13 and 14 are unable to participate in bonding. Hence, +1 and +2 oxidation states become more stable with increasing atomic number.

16. (a) Inert pair effect : The reluctance of ns^2 pair in *p*-block elements having higher atomic number to take part in bond formation is called inert pair effect.

(b) Allotropy : The existence of an element in more than one form having different physical properties but same or slightly different chemical properties is called allotropy.

(c) Catenation : The property by virtue of which a large number of atoms of the same element get linked together through covalent bonds resulting in the formation of long chains, branched chains and rings of different sizes is called catenation.

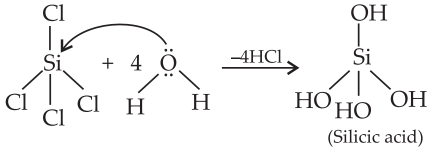
17. Due to absence of *d*-orbitals multiple $p\pi$-$p\pi$ bonding is present in carbon dioxide hence CO_2 is linear ($O{=}C{=}O$) with *sp* hybridisation. SiO_2 has discrete single bonded structure in a tetrahedral manner.



18. Due to back bonding in B — F, electron deficiency is compensated which makes it a weaker Lewis acid than BCl_3. However, in B-Cl, back bonding is not significant due to much bigger size of 3*p*-orbital of Cl than vacant 2*p*-orbital of B.

19. Silicon dioxide is a covalent three dimensional network solid due to absence of $p\pi$-$p\pi$ bonding in SiO_2 and very high Si — O bond enthalpy but in CO_2 due to $p\pi$-$p\pi$ bonding gives discrete molecules unlike SiO_2. Thus, CO_2 is a gas.

20. CCl_4 cannot be hydrolysed by water because carbon atom can not accommodate lone pair of electrons from oxygen atom of water due to absence of *d*-orbital. $SiCl_4$ can be hydrolysed to give $Si(OH)_4$ due to presence of *d*-orbitals.



21. (a) Neutral oxides : CO

Acidic oxides : B_2O_3, SiO_2, CO_2

Basic oxides : Tl_2O_3

Amphoteric oxides : Al_2O_3, PbO_2

(b) (i) CO Neutral to litmus [Neutral]

(ii) B_2O_3 reacts with basic (metallic) oxides forming meta-borates.

$B_2O_3 + CuO \longrightarrow Cu(BO_2)_2$ [Acidic]

(iii) $SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$ [Acidic]

(iv) $CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$ [Acidic]

(v) $Tl_2O_3 + 3H_2SO_4 \longrightarrow Tl_2(SO_4)_3 + 3H_2O$ [Basic]

(vi) $\left.\begin{array}{l} Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O \\ Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O \end{array}\right\}$ [Amphoteric]

(vii) $\left.\begin{array}{l} PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O \\ PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O \end{array}\right\}$ [Amphoteric]

22. SiF_6^{2-} ion exists because of presence of *d*-orbitals. Silicon expands its octet to give sp^3d^2 hybridisation and forms complexes or ions by accepting electron pairs from donor species like SiF_6^{2-}. Carbon cannot exceed its covalency more than 4. Thus, CF_6^{2-} is not known.

23. (a) The stability of dihalides increases down the group because divalent state becomes more and more stable as we move down the group.

$SiCl_2 < GeCl_2 < SnCl_2 < PbCl_2$

(b) Basicity of oxides increases down the group as metallic character increases.

$CO < SiO < GeO < SnO < PbO$

(c) Si—*X* bond strength decreases as the size of the halogen increases. The correct order is

$SiI_4 < SiBr_4 < SiCl_4 < SiF_4$

24.

Criterion	**Diamond**	**Graphite**
Hybridisation	sp^3	sp^2
Structure	Tetrahedral carbon which gives rise to a 3-dimensional structure.	Planar trigonal which gives rise to a 2-dimensional sheet like structure of carbon.
C — C	154 pm	141.5 pm
Hardness	Due to 3-D structure, diamond is the hardest natural element on the earth.	It is made up of 2-D sheets of carbon which slip over each other. This gives graphite a slippery surface.
Electrical Conductivity	Diamond is an insulator.	Graphite is a good conductor of electricity due to presence of delocalised π-electrons.

25. (i) Oxidation states : For group 13 both +1 and +3 oxidation state are observed. +1 oxidation state becomes more stable as we move down the group due to inert pair effect. Boron does not show +3 oxidation state.

For group 14 common oxidation state are +4 and +2. Tendency to show +2 oxidation state increases down the group.

(ii) Atomic size : Atomic radii of group13 elements increases down the group with exception Ga < Al due to presence of 10 *d*-electrons which offer poor screening effect. In group 14, there is a considerable increase in radius from C to Si, thereafter from Si → Pb a small increase is seen due to presence of completely filled *d* and *f*-orbitals.

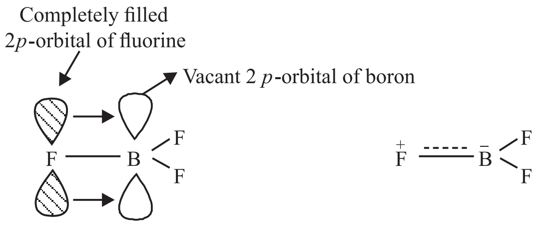
(iii) Nature of halides : Group 13 elements form trihalides (except TlI_3). Due to electron deficient nature BCl_3 accepts electrons and forms adducts. $AlCl_3$ achieves stability by forming a dimer. Group 14 elements form halides with formula MX_2 and MX_4. Except CCl_4 other halides are easily hydrolysed. Stability of dihalides increases down the group.

26. (i) Due to small size of boron, the sum of its first three ionisation enthalpies is very high, hence, it does not exist in +3 form.

(ii) The Lewis acid character of boron trihalides follows the order :

$BI_3 > BBr_3 > BCl_3 > BF_3$.

The above order is just the reverse of the expected order on the basis of relative electronegativities of the halogens. This can be explained on the basis of the tendency of the halogen atom to back-donate its electrons to the boron atoms resulting in the formation of an additional $p\pi–p\pi$ bond. This type of bond formation is known as dative or back bonding.



Formation of back bonding between boron and fluorine in BF_3 molecule.

As a result of back donation of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and therefore, the Lewis acid character of BF_3 decreases.

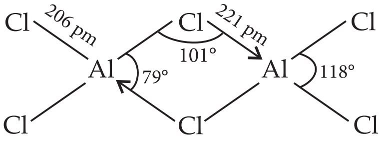
The tendency to form $p\pi–p\pi$ bond is maximum in the case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3

27. $AlCl_3$ is a Lewis acid since it is an electron deficient halide. It has only six electrons in its outermost shell therefore, to complete its octet it accepts a lone pair of electrons and acts as a Lewis acid.

28. (a) Due to small size of fluorine there is inter-electronic repulsion which reduces its tendency to accepts electron.

(b) Pb^{4+} acts as oxidising agent because it has a tendency to exist in Pb^{2+} form which is more stable. Sn^{2+} is a reducing agent due to tendency to form Sn^{4+} compounds.

29. Due to absence of *d*-orbitals in boron, it exists as an electron deficient monomer and achieves stability through accepting electrons from a base like NH_3. It cannot exists as dimer due to small size of B which cannot accomodate bigger size 4 Cl atoms around it. $AlCl_3$ achieves stability by forming a dimer.



Tetrahedral dimer

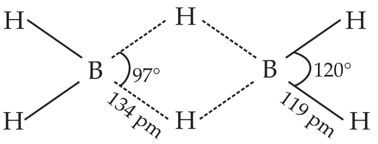
30. $$\underset{(Z)}{4BF_3} + 3LiAlH_4 \longrightarrow \underset{(X)}{2B_2H_6} + 3LiF + 3AlF_3$$

$$\underset{(X)}{B_2H_6} + 6H_2O \longrightarrow \underset{(Y)}{2H_3BO_3} + 6H_2$$

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

31. (a) Due to non-availability of *d*-orbitals, boron is unable to expand its octet hence, it exists as BF_3 and is electron deficient compound. Due to back bonding, electron deficiency of BF_3 is compensated. But in boron hydride, hydrogen atoms does not have lone pairs for back bonding thus, to compensate electron deficiency it exists in the form of diborane.

In the structure of diborane, four terminal hydrogen atoms and two boron atoms are in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B — H bonds are regular two centre two electron bonds while the two bridge B — H — B bonds are different and are three centre – two electron bonds.



(b) The tetravalent element is carbon which forms CO and CO_2. When heated in air it forms producer gas.

$$\underbrace{2C + O_2 + 4N_2}_{\text{(From air)}} \xrightarrow{1273\ K} \underbrace{2CO + 4N_2}_{\text{Producer gas}}$$

CO is a powerful reducing agent and reduces ferric oxide to iron.

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$$

32. (a) Property of catenation is maximum in carbon because C — C bonds are very strong due to smaller size. The tendency of catenation decreases down the group due to increase in size and decrease in electronegativity.

(b) $Pb + 2I_2 \not\longrightarrow PbI_4$

I^- is a good reducing agent and therefore, reduces Pb (IV) to Pb (II) easily. That is why, PbI_4 does not exist.

(c) Pb^{4+} acts as an oxidising agent because it has a tendency to exist in Pb^{2+} form which is more stable. Sn^{2+} is a reducing agent due to tendency to form Sn^{4+} compounds.

33. (i) Lead compounds in +2 oxidation state are more stable than +4 oxidation state hence are stronger oxidising agents. Due to stronger inert pair effect Pb^{2+} is more stable than Sn^{2+}.

(ii) As we move from Al to Ga, due to poor shielding of the nucleus by 3*d*-electrons, the effective nuclear charge acting on Ga is slightly higher than that on Al. As a result, ionisation enthalpy of Ga is higher than that of Al.

(ii) TlCl is more stable than $TlCl_3$ due to inert pair effect.

34. (i) $TlCl_3$, TlCl – TlCl is in more stable oxidation state (+1 O.S. more stable). It is ionic in nature.

(ii) $AlCl_3$, AlCl – $AlCl_3$ is more stable (+3 oxidation state). It is covalent in nature.

(iii) $InCl_3$, InCl – $InCl_3$ is relatively more stable than InCl due to higher stability of +3 oxidation state. It is covalent in nature.

35. (i) Atomic size : Atomic radii of group 13 elements increase down the group with the exception that atomic radius of Ga is less than that of Al due to the presence of 10 d-electrons which offer poor screening effect for the outer electrons from the increased nuclear charge in Ga.

(ii) Ionisation enthalpy : For group 13 elements, the trend of ionisation enthalpy is

B > Al < Ga > In < Tl. This is due to increase in size and low screening effect of d- and f- electrons.

(iii) Metallic character : Metallic character increases from boron to aluminium then decreases down the group.

(iv) Oxidation states : For group 13 elements, both +1 and +3 oxidation states are observed. The +1 oxidation state becomes more stable as we move down the group due to inert pair effect. Boron does not show +3 oxidation state.

(v) Nature of halides : Group 13 elements form trihalides (except TlI_3). Due to electron deficient nature, BCl_3 accepts electrons and forms adducts. $AlCl_3$ achieves stability by forming a dimer.

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