The *p*-Block Elements

11 Chapter

(1) THE *p*-BLOCK ELEMENTS

- General valence shell electronic configuration of *p*-block elements is ns^2np^{1-6}
- Maximum oxidation states = total number of valence electrons.
- The occurence of oxidation states two unit less than the group oxidation states are sometime attributed to the inert pair effect
- The second period elements of *p*-groups are restricted to a maximum covalence of four (using 2*s* and there 2*p* orbitals)
- Third period elements of *p*-groups can expand their covalence above four due to vacant 3*d* orbitals
- Only first member of group can form $p\pi - p\pi$ multiple bonds to itself. The heavier elements do form π bonds but this involves *d*-orbitals ($d\pi - p\pi$ or $d\pi - d\pi$).

(2) GROUP 13 ELEMENTS : THE BORON FAMILY

- B (non-metal), Al (metal but shows many chemical similarities to B) Ga, In, Tl, Nh (metal)
- Boron mainly occurs as orthoboric acid (H_3BO_3), borax ($Na_2B_4O_7.10H_2O$) and kernite ($Na_2B_4O_7.4H_2O$)
- Boron has two isotopes ^{10}B(19%) and ^{11}B(81%)
- Aluminium is the most abundant metal, Bauxite ($Al_2O_3.2H_2O$) and cryolite (Na_3AlF_6) are important minerals of aluminium.
- **Outer electronic configuration** of boron family is ns^2np^1
- **Atomic Radii**
  - (i) B < Al > Ga < In < Tl
  - (ii) Atomic radius of Ga is less than Al due to poor screening effect of 10d - electrons of Ga.
- **Ionization Enthalpy**
  - (i) The decrease from B to Al is associated with increase in size.
  - (ii) The observed discontinuity between Al and Ga, and between In and Tl are due to inablity of *d*-and *f*-electrons to cause screening effect.
- **Electronegativity** – First decreases from B to Al and then increases marginally.

- **Physical Properties**
  - (i) Boron is hard and black coloured solid, exists in many allotropic forms, high melting point due to strong crystalline lattice.
  - (ii) Rest members are soft metals
  - (iii) Gallium has low melting point (303 K) and high boiling poin (2676 K)
  - (iv) Density increases down the group
- **Chemical Properties**
  - (i) B forms only covalent compounds.
  - (ii) In Ga, In and Tl, both +1 and +3 oxidation states are observed. Relative stability of +1 oxidation state : Al < Ga < In < Tl
  - (iii) For Tl, + 1 is predominant and +3 oxidation state is oxidising
  - (iv) Reactivity towards air

$$4E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$$

B_2O_3(Acidic), Al_2O_3 and Ga_2O_3 (Amphoteric)
In_2O_3 and Tl_2O_3(Basic)

  - (v) Al dissolves in mineral acids and aqueous alkalies thus shows amphoteric character

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$$

  - (vi) Reactivity towards halogen

$$2E(s) + 3X_2(g) \rightarrow 2EX_3(s)\ (X = F, Cl, Br, I)$$

- **Important Trends and Anomalous Properties of Boron**
  - (i) Tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water.
  - (ii) Monomeric trihalides are electron deficient and strong Lewis acids.
  - (iii) Halides other than boron are dimerised through halogen bridging.
- **Some Important Compounds of Boron**
  - **(i) Borax ($Na_2B_4O_7.10H_2O$)**
    - (1) Contains tetranuclear units $[B_4O_5(OH)_4]^{2-}$ therefore the correct formula is $Na_2[B_4O_5(OH)_4].8H_2O$.
    - (2) Borax give alkaline solution in water

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

    - (3) On heating, borax first loses water molecules and swells up. On further heating turns into a transparent liquid with solidifies into glass like borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

    Metaborates of many transition metals have characteristic colour therefore borax bead test is used to detect metals.
  - **(ii) Orthoboric acid**
    - (1) White crystalline solid with soapy touch, sparingly soluble in water but highly soluble in hot water.
    - (2) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$
    - (3) Layer structure in which planar BO_3 units are linked by H-bonds.
    - (4) H_3BO_3 monobasic Lewis acid not protonic acid.

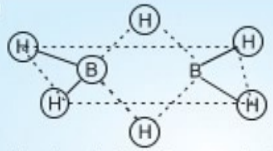
$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

    - (5) $H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$
  - **(iii) Diborane (B_2H_6)**
    - (1) Preparation : $4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$
    - (2) Lab method : $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$
    - (3) Industrial method : $2BF_3 + 6NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$
    - (4) Colourless, highly toxic gas, catches fire spontaneously in air

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$

    - (5) Readily hydrolyse to give boric acid
    - (6) $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$ ($B_3N_3H_6$ inorganic benzene)

(7)



Four terminal B – H are regular two centre-two electron bonds while the two bridge (B – H – B) bonds are three centre-two electron bonds.

(8) Lithium and sodium tetrahydridoborate also known as **borohydrides**

$2MH + B_2H_6 \rightarrow 2M^+[BH_4]^-$ (M = Li or Na)

3 GROUP 14 ELEMENTS : THE CARBON FAMILY

- C, Si, Ge, Sn, Pb and Fl are 14th group elements.
- C has two stable isotopes : ^{12}C and ^{13}C and radioactive isotope ^{14}C
- Ge exists only in traces, Sn as cassiterite (SnO_2), Pb as galena (PbS)
- General valence shell electronic configuration ns^2np^2
- **Physical Properties**
  C and Si (Non-metals), Ge (metalloid), Sn and Pb (Metals)
- **Covalent Radius** : Considerable increase in covalent radius from C to Si, small increase thereatfer due to completely filled *d* and *f* orbitals of heavier members.
- **Electronegativity** values from Si to Pb are almost same
- **Ionization Enthalpy:** In general decreases down the group, small decrease from Si to Ge to Sn and slight increase from Sn to Pb.
- **Anomalous Behaviour of Carbon**
  (i) Maximum covalence = 4
  (ii) Order of catenation C > > Si > Ge ≈ Sn, Pb does not show catenation.
- **Allotropes of Carbon**
  (i) Diamond – sp^3 hybridised, crystalline lattice
  (ii) Graphite – Layered structure (held by van der Waals forces), sp^2 hybridised, conducts electricity
  (iii) Fullerenes
- **Chemical properties**
  (i) Common oxidation states are + 4 and + 2, C also exhibits negative oxidation states.
  (ii) +4 oxidation state are generally covalent in nature Heavier elements show + 2 oxidation state.
  (iii) Halides of group 14 elements except carbon undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species.
  (iv) **Reactivity towards oxygen :** (1) All members form mainly two types of oxides MO and MO_2.
  (2) CO_2, SiO_2, GeO_2 are acidic and SnO_2, PbO_2 are amphoteric
  (v) **Reactivity towards water**
  (1) C, Si and Ge are not affected by water, Tin decomposes steam to form SnO_2 and H_2

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

  (2) Pb is unaffected by H_2O due to protective oxide film formation
  (vi) **Reactivity towards halogen**
  (1) Form halides of formula MX_2 and MX_4.
  (2) Except C all other members react directly with halogen
  (3) Most MX_4 are covalent except SnF_4 and PbF_4
  (4) PbI_4 does not exist as energy released due to bond formation is not sufficient to unpair $6s^2$ electrons.
  (5) GeX_4 is more stable than GeX_2 whereas PbX_2 is more stable than PbX_4
- **Some Important compound of Carbon and Silicon**
  (i) **Carbon Monoxide (CO)**
  (1) Preparation

$$C(s) + H_2O(g) \xrightarrow{473\text{-}1273\ K} CO(g) + H_2(g)$$
(Water gas)

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\ K} 2CO(g) + 4N_2(g)$$
(Producer gas)

  (2) In CO molecule, there is one sigma and two π bonds
  (3) CO is highly poisonous due to its ability to form a complex with haemoglobin
  (ii) **Carbon Dioxide (CO_2)**
  (1) Lab preparation

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

  (2) Colourless, odourless gas, low solubility in H_2O, with water forms carbonic acid H_2CO_3(weak dibasic acid)
  (3) H_2CO_3/HCO^-_3 buffer system helps to maintain pH of blood.
  (4) CO_2 is removed from atmosphere by photosynthesis
  (iii) Silicon Dioxide (SiO_2): It resists the attack of halogens, dihydrogen and most of the acids and metals even at elevated temperature. However it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

  (iv) Silicones
  (1) $+R_2SiO+$ as a repeating unit.
  (2) Preparation

$$2CH_3Cl + Si \xrightarrow[570\ K]{Cu\ Powder} (CH_3)_2SiCl_2$$

$$Silicone \xleftarrow[-H_2O]{Polymerisation} (CH_3)_2Si(OH)_2 \xleftarrow[-2HCl]{+2H_2O} (CH_3)_2SiCl_2$$

The chain length of polymer can be controlled by adding $(CH_3)_3SiCl$

  (v) Silicates :
  (1) Silicates mineral like feldspar, Zeolites, mica etc. exist in nature
  (2) The basic structural unit of silicates is SiO_4^{4-}
  (vi) Zeolites
  (1) If aluminium atoms replace few silicon atoms in three-dimensional network of silicondioxide, overall structure known as aluminosilicate
  (2) A type of zeolite ZSM-5 used to convert alcohols directly into gasoline

Sharpen Your Understanding

1. Correct order of atomic radii is [NCERT Pg. 317]
   (1) B < Al < Ga < In (2) B > Al > Ga > In
   (3) B < Al > Ga < In (4) Al < B < Ga < In
2. +1 oxidation state is predominant in [NCERT Pg. 318]
   (1) B (2) Al
   (3) Ga (4) Tl
3. Hybridisation of Al when $AlCl_3$ dissolved in acidified aqueous solution is [NCERT Pg. 319]
   (1) *sp* (2) sp^2
   (3) sp^3 (4) sp^3d^2
4. Which of the following trihalides is least stable? [NCERT Pg. 320]
   (1) BCl_3
   (2) $AlBr_3$
   (3) TlI_3
   (4) BI_3
5. Select the correct statement(s) [NCERT Pg. 320]
   (1) Boron is unable to form BF_6^{3-}
   (2) Boron is unable to expand its octet
   (3) Maximum covalence of boron is 4
   (4) All of these

NCERT Based MCQs

6. Colour of $Co(BO_2)_2$ bead is [NCERT Pg. 320]
   (1) Red (2) Blue
   (3) Green (4) Orange
7. Number of water of crystallization in Borax is [NCERT Pg. 320]
   (1) 10 (2) 9
   (3) 8 (4) 5
8. $3B_2H_6 + 6NH_3 \longrightarrow X \xrightarrow{\Delta} Y + H_2$, Y is [NCERT Pg. 320]
   (1) $B_3N_3H_6$
   (2) BH_3
   (3) $[BH_2(NH_3)_2]^+ [BH_4]^-$
   (4) BN
9. In B_2H_6, maximum number of coplanar atoms is [NCERT Pg. 322]
   (1) 3
   (2) 4
   (3) 6
   (4) 8
10. Amphoteric oxide among the following is [NCERT Pg. 324]
    (1) CO_2 (2) SiO_2
    (3) GeO_2 (4) SnO_2
11. Ionic tetrahalide among the following is [NCERT Pg. 324]
    (1) SnF_4
    (2) CF_4
    (3) $PbBr_4$
    (4) $SiCl_4$
12. Catenation is not shown by [NCERT Pg. 325]
    (1) Si
    (2) Ge
    (3) Sn
    (4) Pb
13. Buckminsterfullerene contains [NCERT Pg. 326]
    (1) 20 six-membered rings and 12 five-membered rings
    (2) 20 six-membered rings and 20 five-membered rings
    (3) 12 six-membered rings and 20 five membered rings
    (4) 12 six-membered rings and 12 five-membered rings
14. When air is used instead of steam over hot coke, the gas produced is called [NCERT Pg. 328]
    (1) Water gas (2) Hydrogen gas
    (3) Producer gas (4) Carbon dioxide

15. Which of the following is not the resonance structure of CO_2? [NCERT Pg. 329]

(1) $\ddot{\underset{\cdot\cdot}{\overset{-}{O}}}-C\equiv\overset{+}{O}:$

(2) $:\ddot{O}=C=\ddot{O}:$

(3) $\overset{+}{:}O\equiv C-\ddot{\underset{\cdot\cdot}{\overset{-}{O}}}:$

(4) $\overset{+}{\ddot{\underset{\cdot\cdot}{O}}}-C\equiv O:^{-}$

16. The chain length of silicone can be controlled by adding [NCERT Pg. 330]

(1) $SiCl_4$ (2) CH_3SiCl_3

(3) $(CH_3)_2SiCl_2$ (4) $(CH_3)_3SiCl$

17. Silicon dioxide on reaction with hydrogen fluoride gives [NCERT Pg. 329]

(1) Si

(2) SiF_4

(3) SiO

(4) $[SiF_6]^{2-}$

18. Least electronegative element among the following is [NCERT Pg. 319]

(1) B (2) Al

(3) In (4) Tl

19. Maximum number of H-bond formed by one molecule of orthoboric acid is [NCERT Pg. 321]

(1) 1 (2) 3

(3) 4 (4) 6

20. On commercial scale, CO_2 is obtained by [NCERT Pg. 328]

(1) Burning coal

(2) Burning CH_4

(3) Heating Limestone

(4) $CaCO_3$ with HCl

Thinking in Context

1. $SiCl_4$ on hydrolysis gives _____. [NCERT Pg. 325]

2. Silica is attacked by _____ and _____. [NCERT Pg. 329]

3. Group of organosilicon polymer having _____ as a repeating units are known as silicones [NCERT Pg. 329]

4. Hybridisation of B in BH_4^- is _____. [NCERT Pg. 331]

5. _____ catches fire spontaneously upon exposure to air [NCERT Pg. 321]

6. Borax dissolves in water to give an _____ solution. [NCERT Pg. 320]

7. Maximum covalence of boron is _____. [NCERT Pg. 320]

8. In B_2H_6 _____ 3-centre-2-electron bonds are present. [NCERT Pg. 322]

9. _____ isotope of carbon used for radiocarbon dating. [NCERT Pg. 323]

10. Cassiterite is the ore of _____. [NCERT Pg. 323]

11. _____ are only form of pure carbon. [NCERT Pg. 326]

12. Water gas is _____. [NCERT Pg. 327]

13. _____ buffer system helps to maintain the pH of blood between 7.26 to 7.42 [NCERT Pg. 328]

14. _____ Is used to convert alcohols directly into gasoline [NCERT Pg. 330]

15. Boric acid is mono basic _____ [NCERT Pg. 331]

16. B–F bond length in BF_3 is _____ than B–F bond length in BF_4^- [NCERT Pg. 332]

17. CO forms _____ when combine with haemoglobin [NCERT Pg. 332]

18. Graphite is used as _____ due to its layer type structure. [NCERT Pg. 332]

19. CO is a _____ oxide [NCERT Pg. 333]

20. Due to inert pair effect, oxidation state decrease by _____. [NCERT Pg. 333]

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