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A right Choice for the Real Aspirant

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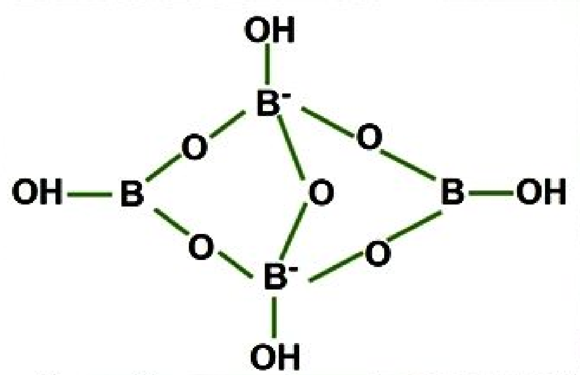
Concept – P-BLOCK ELEMENTS 13TH GROUP

- The general electronic configuration 13th group elements is ns^2np^1
- Boron (B), Aluminum (Al), Gallium (Ga), Indium (In), Thalium (Tl) and Nihonium(Nh) are 13th group elements
- In 13th group elements Boron is non metal and the remaining are metals
- Boron mainly occurs as
  a. Orthoboric Acid - H_3BO_3
  b. Borax - $Na_2B_4O_7.10H_2O$ (Sodium tetra borate deca hydrate)
  c. Kernite - $Na_2B_4O_7,4H_2O$ (Sodium tetra borate tetra hydrate)
- Isotopes of Boron are $^{10}B(19\%)\,^{11}B(81\%)$
- Third most abundant element and most abundant metal in the earth's crust is Aluminium (8.3 % by Mass)
- Minerals of Aluminium
- Bauxite $-Al_2O_3.2H_2O$
- Cryolite $-Na_3AlF_6$
- Atomic radii order : $B > Ga > Al > In > Tl$
- 1st Ionization enthalpy order : $In < Al < Ga < Tl < B$
- 2nd Ionization enthalpy order : $Al < In < Tl < Ga < B$
- 3rd Ionization enthalpy order : $In < Al < Tl < Ga < B$
- Electronegativity order : $B < Tl < In < Ga < Al$
- Density order : Boron to Thallium increases
- Melting point order : $Ga < In < Ti < Al < B$
- Boiling point oder : $Tl < In < Ga < Al < B$
- Highest liquid range metal is Ga (303 K to 2676 K)
- Positive SRP among $\left(M^{3+}/M\right) Al, Ga, In$ and Tl is - Tl
- Stability of +1 oxidation state : $Al < Ga < In < Tl$ (due to inert pair effect)
- $AlCl_3$ achieves stability by forming a dimer
- In dimer of $AlCl_3\left(Al_2Cl_6\right) Al-Cl$ terminal bond length is less than $Al-Cl$ bridge bond length.
- Hybridization of 'B' in $\left[B(OH)_4\right]$ is : sp^3
- Hybridization of 'Al' in $\left[Al\left(H_2O\right)_6\right]^{3+}$ is : sp^3d^2
- Aluminum is more electropositive than thallium
- In solution state Tl^{3+} is power full oxidizing agent

- Boron is unreactive in Crystaline form
- Amorphous boron on heating in air forms B_2O_3 and BN (at high temp)
- Aluminum on heating in air forms Al_2O_3 and AlN (at high temp)
- B_2O_3 is Acidic oxide
- B_2O_3 react with basic metallic oxides form metal borates
- Al_2O_3 and Ga_2O_3 are Amphoteric oxides
- Indium and thallium oxides are Basic
- At moderate temperature Boron does not react with acids and alkalies
- Aluminum dissolves in mineral acids and aqueous alkalies due to its amphoteric character
- Aluminum is passive to concentrated nitric acid due to the formation of protective oxide layer on the surface of Al
- 13th group elements form EX_3 type trihalides except Tl.
- Trihalides of this group elements act as Lewis acids
- BCl_3 has planar structure where as $BCl_3 \leftarrow NH_3$ has Tetrahedral structure
- White fumes appear around the bottle of anhydrous aluminium chloride due to partial hydrolysis with atmospheric moisture to liberate HCl gas
- 13th group Tri-chlorides, bromides and Iodides covalent in nature
- Formation of $F_3B \leftarrow NH_3$ from BF_3 and NH_3 change in hybridization of boron from to is sp^2 to sp^3
- The correct formula of borax is $Na_2\left[B_4O_5(OH)_4\right].8H_2O$
- In $\left[B_4O_5(OH)_4\right]^{2-}$



Number of tetravalent boron atoms 2, Trivalent Boron atoms = 2

1) No. of sp^2 'B' atoms 2

2) No. of sp^3 'B' atoms 2

3) No. of six membered ring = 2

4) No. of $B-O-B$ bonds = 5

5) No. of $B-OH$ bonds = 4

- Aqueous solution of Borax is Alkaline

- Borax on heating gives opaque mass $(Na_2B_4O_7)$ which on further heating gives transparent glassy bead $(NaBO_2 + B_2O_3)$
- Colour of $CO(BO_2)_2$ bead is Blue
- Orthoboric acid sparingly soluble in water but highly soluble Hot water
- H_3BO_3 is mono basic Lewis acid, but not protonic acid
- H_3BO_3 does not donate protons but accept OH^- ions
- $H_3BO_3 \xrightarrow{>370K} X \xrightarrow{StrongHeating} Y(X = HBO_2, Y = B_2O_3)$
- Diborane is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether
  $4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 2LiF + 3AlF_3$
- Oxidation of sodium borohydride with iodine gives Diborane
  $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$
- Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride
  $2BF_3 + 6NaH \xrightarrow{450k} B_2H_6 + 6NaF$
- Diborane is a colourless, highly toxic gas with B.P. of 180 K
- Diborane catches fire spontaneously upin expo sure to air
  $B_2H_4 + 3O_2 \rightarrow B_2O_3 + 3H_2O \qquad \Delta H^0 = -ve$
- Boranes are readily hydrolysis by water to give – Boric acid
- Diborane react with ammonia gives initially $B_2H_6.2NH_3$
- $B_2H_6.2NH_3$ exist as cation and anion complex, then are $[BH_2(NH_3)_2]^+[BH_4]^-$
- Further heating of $[BH_2(NH_3)_2]^+[BH_4]^-$ gives Borazine or Borazole $(B_3N_3H_6)$ which is called Inorgnaic benzene.
- In Borazole the hybridization of both B and N is sp^2

$$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^-$$
$$\downarrow$$
$$2B_3N_3H_6 + 12H_2$$

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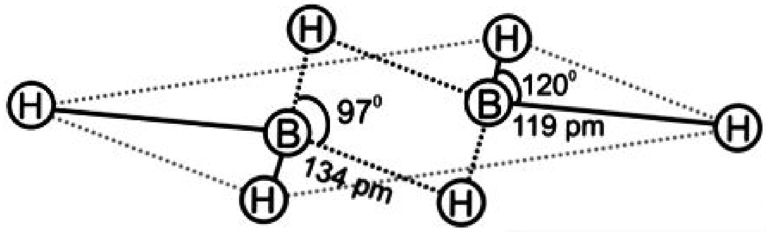
- Diborane readily burns with oxygen to produce B_2O_3
  $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$
- Diborane when reacts with Lewis bases undergoes symmetrical cleaves and forms adducts.

Diborane structure :



- Number of BH_2 groups in the same plane $\Rightarrow 2$
- Number of atoms in the same plane $\Rightarrow 6$
- Number of Bridge / Tau / Banana / 3 centre – 2 electron (B – H – B) Bonds in B_2H_6 is $\Rightarrow 2$
- Number of 2 centre – 2 electron bonds in $B_2H_6 - 4$
- In B_2H_6 Hybridization at Boron atoms $\rightarrow sp^3$
- In B_2H_6 $B-H_T$ Bond length less than $B-H_b$ bonds (H_T - Terminal Hydrogen, H_B - Bridged Hydrogen)
- In organic synthesis $NaBH_4$ and $LiBH_4$ used as reducing agents

Uses of Boron and Aluminum

- Boron fibers are used in making bullet-proof vest and high composite material for air craft
- Metal borides are used in nuclear industry as control rods
- In the manufacture of pyrex glass (Heat resistant borax glass – wool and fiber glass) boric acid is used
- For soldering metals Borax is uses as Flux
- Borax is used for heat, scratch and stain resistant glazed coating to earthenware and medicinal soaps.
- An aqueous solution of orthoboric acid is generally used as a mild antiseptic
- Aluminum form alloy with Cu, Mn, Mg , Si and Zn
- Aluminum foils used for packers
- The use of Aluminum and its compounds for domestic purposes is now reduced due to its toxic nature.

Concept – P-BLOCK ELEMENTS 14TH GROUP

- 14th group elements are : Carbon (C), Silicon (Si), Germanium (Ge), Tin(Sn), Lead (Pb) and Flerovium (Fl).
- 17th most abundant element by mass in earth's crust is : carbon
- Carbon in widely distributed in nature in free as well as in the combined state.
- Natural occurring carbon contains two stable isotopes C^{12} and C^{13}.
- Radioactive isotope of carbon is C^{14}, which is used in radio carbon dating.
- Silicon is the second most abundant element in the earth's crust (27.7% by mass) in the form of silica and silicates.

- Tin occurs mainly as Cassiterite or Tin stone - SnO_2
- Lead occurs as Galena – PbS, Anglesite - $PbSO_4$, Cerussite - $PbCO_3$
- Flerovium is synthetically prepared radioactive element
- Ultra-pure form of germanium and silicon are used to make transistors and semiconductor devices
- The order of covalent radius $\rightarrow$ $C < Si < Ge < Sn < Pb$
- The order of Electronegativity : $C > Pb > Si = Ge = Sn$
- Density of silicon less than diamond but more than graphite
- The order of density increases down the group
- BP order : $Si > Ge > Sn > Pb$
- MP order : $C > Si > Ge > Pb > Sn$
- In 14th group carbon and silicon : non-metals
- Germanium : metalloid
- Tin and lead : metals
- The common oxidiation states of 14th group elements are +2, +4
- Carbon show negative oxidation state also (Ex : CH_4)
- For Lead + 2 oxidation state is stable due to inert pair effect
- Sn^{2+} act as reducing agent
- The maximum covalency of carbon is four
- In $SiF_6^{2-}, [GeCl_6]^{2-}, [Sn(OH)_6]^{2-}$ central atom hybridization is : sp^3d^2
- CO_2, SiO_2, GeO_2 oxides are in acidic in nature, SnO_2, PbO_2 are amphoteric in nature.
- CO is neutral nature, SnO and PbO are amphoteric nature.
- Carbon, silicon lead and germanium are not affected by water.
- Tin reacts with steam to liberate dihydrogen.

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

- 14th group elements from MX_2 and MX_4 halides
- MX_4 halides of 14th group are covalent in nature (except SnF_4, PbF_4)
- PbI_4 does not exist
- Ge and Pb from MX_2 halides
- GeX_4 more stable than GeX_2
- PbX_2 more stable than PbX_4
- Except CCl_4 other tetra chlorides are easily hydrolysed.
- Silicon tetrachloride undergoes hydrolysis gives Silicic acid (H_4SiO_4)
- $[SiF_6]^{2-}$ is known where as $[SiCl_6]^{2-}$ is not due to large size of chlorine atoms
- The order of catenation ability : $C > Si > Ge \cong Sn$
- The 14th group element which does not exhibit catenation ability : Lead (Pb)

- The crystalline allotropes of carbon are : diamond, graphite and fullerene
- Hybridisation of carbon in diamond is sp^3 and C – C bond length in diamond: 154 pm
- The natural hardest material on the earth : diamond
- Diamond does not conduct electricity.
- Graphite possesses 2D layers structure in which layers are held by vander Waals forces.
- The distance between layers of graphite : 340 pm
- The size of planer ring in graphite is : hexagonal
- C – C bond length in graphite : 141.5 pm
- Hybridisation of carbon in graphite : sp^2
- The type of electrons delocalized in between layers of graphite : π electrons
- The soft and slippery nature of graphite is due to weak Vander Waals forces between the layers.
- Graphite is a good conductor of electricity which conducts electricity along the sheet
- Graphite is used as : dry lubricant, in making electrodes
- Fullerenes are made by heating of graphite in an electric arc in the presence of inert gas.
- C_{60} fullerene is known as: Buckminister fullerene
- The structure of fullerene is : cage like
- Fullerene appears as : soccer ball
- Allotrope of carbon without dangling bond : fullerene
- Number of five membered rings in C_{60} fullerene : 12
- Number of six membered rings in C_{60} fullerene : 20
- Five membered rings in C_{60} fullerene is fused with six membered rings only
- Six membered rings in C_{60} fullerene is fused with both five membered and six membered rings.
- The aromatic allotrope of Carbon : fullerene
- C – C single bond and C=C double bond length in C_{60} fullerene : 143.5 pm and 138.3 pm
- Order of thermodynamic stability of crystalline allotropes of carbons : graphite > diamond > fullerene
- Amorphous allotropes of carbon : coal, coke, carbon black, charcoal, gas carbon, petroleum coke
- Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- Coke is used as a fuel and reducing agent in metallurgy.
- Carbon forms carbon monoxide (CO) and carbon dioxide (CO_2)
- Carbon monoxide can be prepared from

$$2C(s)+O_2(g)\xrightarrow{\Delta}2CO(g)$$

$$HCOOH \xrightarrow[conc.\ H_2SO_4]{373K} H_2O + CO\ (small\ scale)$$

$$C(s) + H_2O(g) \xrightarrow{473-1273K} CO(g) + H_2(g)$$ (on commercial scale)

- The mixture of CO and H_2 is known as water gas or synthesis gas
- The mixture of CO and N_2 is known as producer gas, prepared by

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

- CO acting as a powerful reducing agent and used in the extraction of many metals from their oxides
- Alkali and alkaline earth metal oxides, aluminium oxide is not reduced by CO
- In CO molecule, there are one sigma and two π bonds between carbon and oxygen atoms.
- CO binds with haemoglobin. This is a reason for the death of human beings.
- CO having lone pair of electrons on C forms metal carbonyls.
- CO_2 is acidic in nature, it forms H_2CO_3 which is a weak dibasic acid
- Increased content of CO_2 in atmosphere causes "Greenhouse effect".
- Biologically CO_2 is important in photo synthesis
- Solid CO_2 is called dry ice.
- Dry ice is used as a refrigerant for frozen food and ice creams.
- CO_2 is used as fire extinguisher.
- In CO_2 molecule C undergoes sp hybridization.
- The shape of CO_2 molecule is linear, and dipole moment is zero.
- Silicon dioxide, commonly known as silica.
- It is widely found in nature as Quartz.
- Silicon dioxide is covalent.
- Crystalline form of silica are : Quartz, Cristoballite, Tridymite
- Kieselghur, an amorphous form of Silica is used in filtration plants.
- Each Si atom is surrounded by 4 oxygen atoms and each oxygen atom is bonded to 2 silicon atoms.
- In Silica, hybridization of Si atom : sp^3
- Fluorine when reacted with SiO_2 it produces SiF_4 and O_2.
- SiO_2 reacts with HF to produce H_2SiF_6 (Hexa fluoro silicic acid)
- Quartz is extensively used as a Piezoelectric material.
- Silicones, they are a group of organosilicon polymers, which have (R_2SiO) as a repeating unit.
- Silicones can be obtained from alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$.
- Hydrolysis of dimethyl dichlorosilane, CH_3SiCl_2 followed by condensation

polymerization yields straight chain polymers

- Silicones have low thermal conductivity and chemical reactivity.
- Silicones have high thermal stability and dielectric strength.
- Silicones can repel water.
- Silicones are used as sealant, greases, electrical insulator and for water proofing of fabrics.
- Silicones are used in surgical and cosmetic plants.
- The basic structural units of silicates is SiO_4^{4-}
- Feldspar, Zeolites, mica and asbestos are examples of silicates
- In silicates silicon atom is bounded to four oxygen atoms in tetrahedron fashion.
- The SiO_4^{4-} tetrahedral may exist as discrete units or may polymerise into large units by sharing corners with oxygen atoms.
- The important man-made silicates are glass and cement.
- Zeolite are alumino-silicates
- Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation.
- The zerolite catalyst (ZSM – 5) converts alcohols to gasonline.
- Hydrate zeolites are used as ion exchanger in softening of hard water.

Concept – P-BLOCK ELEMENTS 15TH GROUP

- Group 15 includes nitrogen, phosphorus, arsenic, antimony, bismuth and moscovium.
- Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal.
- Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ and potassium nitrate KNO_3.
  Chile saltpetre - $NaNO_3$; Indian saltpetre - KNO_3
- It is found in the form of proteins in plants and animals.
- Phosphorus occurs in minerals of the apatite family, $Ca_9(PO_4)_6$.
  $CaX_2(X = F, Cl \text{ or } OH)$ and fluorapatite $Ca_9(PO_4)_6 . CaF_2$
- The stability of +5 oxidation state decreases down the group due to inert pair effect.
- The only well characterized Bi(V) compound is BiF_5.
- Nitrogen does not form compounds in + 5 oxidation state with halogens as nitrogen does not have d-orbitals.
- In the case of nitrogen, all oxidation states from + 1 to + 4 tend to disproportionate in acid solution.
  For example. $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$
- In case of phosphorus nearly all intermediate oxidation states disproportionate into + 5 and – 3 both in alkali and acid