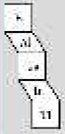
CONCEPT MAP
THE *p*-BLOCK ELEMENTS (Group 13)



Group 13 is the first group to span the dividing line between metals and non-metals and its chemistry is more diverse than that of groups 1 and 2.

GROUP 13 : THE BORON FAMILY

Atomic and Physical Properties

- Elements : B, Al, Ga, In, Tl
- Electronic configuration : [Noble gas] $ns^2 np^1$
- Oxidation States : +1 and +3
- Metallic Character : B non-metal; Al, Ga, In, Tl metals
- Atomic radii, ionic radii, density and stability of +1 oxidation state : Generally increase down the group however, the atomic radius of Ga is lower than that of Al.
- Boiling points and stability of +3 oxidation state : Decrease down the group.
- Electronegativity : First decreases from B to Al then increases from Al to Tl and then decreases marginally down the group.
- Melting points : Decrease from B to Ga and then increase.
- Ionisation energy : B > Tl > Ga > Al > In
- Lewis acids : BCl_3, $AlCl_3$ etc. behave as Lewis acids due to incomplete octet.
- Complex formation : Due to small size, high charge density and availability of vacant d-orbitals.

Chemical Properties

- Reactivity towards air :
  - $4E + 3O_2 \xrightarrow{\Delta} 2E_2O_3$ (E = Group 13 elements) [illegible]
  - B_2O_3 acidic, Al_2O_3, Ga_2O_3 amphoteric, In_2O_3, Tl_2O_3 basic
  - $2E + N_2 \xrightarrow{\Delta} 2EN$ (E = B, Al, Ga, In, Tl)
- Reactivity towards acids :
  - B does not react with non-oxidising acids even at high temperature.
  - $B + 3HNO_3 \xrightarrow{conc.\ HNO_3} H_3BO_3 + 3NO_2$
  - All other elements react with both non-oxidising and oxidising acids liberating H_2 gas.
  - Al becomes passive with conc. HNO_3 due to the formation of a thin protective layer of its oxide (Al_2O_3) on the surface of the metal which prevents it from further action.
- Reactivity towards alkalies :
  - $2B + 6KOH \xrightarrow{fused} 2K_3BO_3 + 3H_2$
  - $2E + 2NaOH + 6H_2O \rightarrow 2Na^+[E(OH)_4]^- + 3H_2$ (E = Al, Ga)
- Reactivity towards halogens :
  - $2E + 3X_2 \rightarrow 2EX_3$ (except TlI$_3$) (X = F, Cl, Br, I)

Anomalous Behaviour of Boron

- Difference in behaviour of B is due to small size, high ionisation enthalpy and absence of d-orbitals.
- B is extremely hard having high melting point.
- B shows maximum covalency of 4 while rest of the elements show maximum covalency of 6.
- Exhibits allotropy.
- B forms only covalent compounds.

Important Compounds of Boron

Borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$)

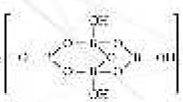
- Preparation :
  - $Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$
  - $4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$
- Properties :
  - White crystalline solid.
  - $Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$
  - $Na_2B_4O_7\cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ (Sodium metaborate; Boric anhydride) — glassy bead

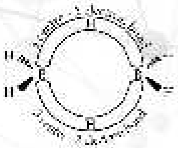
Diborane (B_2H_6)

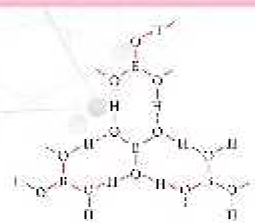
- Preparation :
  - Laboratory method :
  - $2NaBH_4 + I_2 \xrightarrow{diglyme} B_2H_6 + 2NaI + H_2$
  - Industrial method :
  - $2BF_3 + 6NaH \xrightarrow{450\,K} B_2H_6 + 6NaF$
- Properties :
  - Colourless, highly toxic gas.
  - $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$
  - $B_2H_6 + 6H_2O \rightarrow 2B(OH)_3 + 6H_2$
  - $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$ (Borazine)
- Structure :
  - Four terminal 2 centre-2 electron bonds.
  - Two bridge bonds, 3 centre-2 electron bonds (banana bonds).

Orthoboric acid (H_3BO_3)

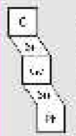
- Preparation :
  - $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$
- Properties :
  - White crystalline solid with soapy touch.
  - Planar BO_3^{3-} units joined by H-bonds to form layer structure, weak acid.
  - Monobasic acid :
  - $B(OH)_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$
  - $H_3BO_3 \xrightarrow{370\,K} HBO_2 + H_2O$ (Metaboric acid)
  - $4HBO_2 \xrightarrow[-H_2O]{410\,K} H_2B_4O_7 \xrightarrow{Red\ hot} 2B_2O_3 + H_2O$ (Tetraboric acid; Boron trioxide)







CONCEPT MAP
THE *p*-BLOCK ELEMENTS (Group 14)



Group 14 elements show a pronounced discontinuity in their general properties between the first and second row elements followed by a gradual transition towards more metallic character.

GROUP 14 : THE CARBON FAMILY

Atomic and Physical Properties

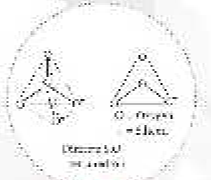
- Elements : C, Si, Ge, Sn, Pb
- Electronic configuration : [Noble gas] $ns^2 np^2$
- Oxidation states : +2 and +4
- Atomic radii, metallic character and stability of +2 O.S. : Generally increase down the group.
- Ionisation enthalpy, melting point, boiling point, reducing character and stability of +4 O.S. : Generally decrease down the group.
- IE of Pb is slightly higher than Sn due to lanthanoid contraction.
- IE_1 and IE_2 are higher and lower than the corresponding group 13 elements respectively.
- Catenation : Tendency of catenation decreases down the group.
- Allotropy : Except Pb, all others show allotropy.
- Complex formation : Except C, all other form complexes due to presence of vacant d-orbitals.

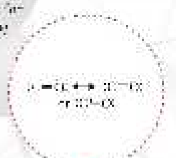
Chemical Properties

- Reactivity towards air :
  - They form oxides of the formula MO and MO_2 on heating in air.
  - Acidic strength of the oxides decreases down the group :
  - CO_2, SiO_2 (Acidic); GeO_2 (Less acidic); SnO_2, PbO_2 (Amphoteric)
- Reactivity towards water :
  - Only Sn can decompose steam.
  - $Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$
  - Pb is unaffected by water due to formation of protective oxide film.
- Reactivity towards halogens :
  - They form halides of the formula MX_2 and MX_4.
  - Except C, all react directly with halogens.
  - Except C and Si, all form dihalides.

Anomalous Behaviour of C

- The anomalous behaviour of C is due to small size, high ionisation energy and absence of d-orbitals.
- C is harder, has the highest m.pt. and b.pt. amongst the elements of group 14.
- C shows maximum covalency of 4 while rest show maximum covalency of 6.
- C has maximum tendency for catenation and multiple bonding ($p\pi$-$p\pi$) and shows allotropy.





Important Compounds of C and Si

Silicates

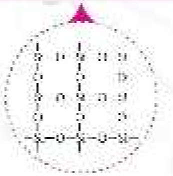
- Basic unit is SiO_4^{4-}.
- They exist either as discrete unit or joined together by sharing 1, 2, 3 or 4 oxygen atoms per silicate unit to form different structures like chain, ring, sheet or 3D network.
- Zeolites are 3D network in which some of the Si atoms are replaced by Al^{3+} ions and to balance the negative charge some cations like Na^+, K^+ or Ca^{2+} are incorporated. They are used in water softening.

Carbon Monoxide (CO)

- Preparation :
  - $C + H_2O \rightarrow CO + H_2$ (Water gas)
  - $2C + O_2 + 4N_2 \xrightarrow{1273\,K} 2CO + 4N_2$ (Producer gas)
- Highly poisonous due to the formation of a complex with haemoglobin (Hb) which is 300 times more stable than O_2-Hb complex. This prevents Hb in the RBCs from carrying O_2 round the body.

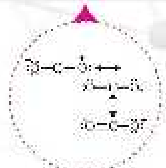
Silicon Dioxide (SiO_2)

- Covalent, three dimensional network solid.
- Almost non-reactive due to high Si – O bond enthalpy.



Carbon Dioxide (CO_2)

- Preparation :
  - $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$
- It is converted during photosynthesis :
  - $6CO_2 + 12H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$



Silicones

- Synthetic organosilicon polymers containing repeated R_2SiO units held by Si – O – Si linkage.
- They are water repelling due to non polar alkyl groups.