(iv) **Gypsum** $(CaSO_4.2H_2O)$: On partially dehydrates to produce plaster of paris.

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} \xrightarrow{120\,^{o}C} \underset{\text{Plaster of paris}}{CaSO_4.\frac{1}{2}H_2O} + 1\frac{1}{2}H_2O$$

Plaster of paris : $\underset{\text{Plaster of paris}}{CaSO_4.\frac{1}{2}H_2O} \xrightarrow[\text{Setting}]{H_2O} \underset{\text{orthorhombic}}{CaSO_4.2H_2O} \xrightarrow{\text{Hardening}} \underset{\text{Monoclinic (gypsum)}}{CaSO_4.2H_2O}$

$$\text{Gypsum} \xrightarrow{200^{o}C} \underset{\text{(dead burnt plaster)}}{CaSO_4\,\text{(anhydrous)}}$$

Gypsum when heated to about $200^{o}C$ is converted into anhydrous calcium sulphate. The anhydrous form (anhydrite) is known as dead burnt plaster because it does not set like plaster of paris when moistened with water.

(v) **Calcium Hydroxide** $Ca(OH)_2$ (slaked lime)

$$CaO + H_2O \rightarrow Ca(OH)_2; \quad Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + Ca(HCO_3)_2$$

Suspension of $Ca(OH)_2$ in water is called milk of lime.

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

Boron Family.

Group 13 of long form of periodic table (previously reported as group III A according to Mendeleefs periodic table) includes boron (B) ; aluminium (Al) , gallium (Ga), indium (In) and thallium (T*l*) Boron is the first member of group 13 of the periodic table and is the only non-metal of this group. The all other members are metals. The non-metallic nature of boron is due its small size and high ionisation energy. The members of this family are collectively known as boron family and sometimes as aluminium family.

Electronic configuration

Element	**Electronic configuration** ($ns^2\ np^1$)
$_5B$	$1s^2,2s^22p^1$ **or** $[He]2s^22p^1$
$_{13}Al$	$1s^2,2s^22p^6,3s^23p^1$ **or** $[Ne]3s^23p^1$
$_{31}Ga$	$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^1$ **or** $[Ar]3d^{10}4s^24p^1$
$_{49}In$	$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^64d^{10},5s^25p^1$ **or** $[Kr]4d^{10}5s^25p^1$
$_{81}Tl$	$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^64d^{10}4f^{14},5s^25p^65d^{10},6s^26p^1$ **or** $[Xe]4f^{14}5d^{10}6s^26p^1$

Physical properties

(1) A regular increasing trend in density down the group is due to increase in size.

(2) Melting points do not vary regularly and decrease from B to Ga and then increase.

(3) Boron has very high m.pt because it exist as giant covalent polymer in both solid and liquid state.

(4) Low m.pt of Ga (29.8^0C) is due to the fact that consists of only Ga_2 molecule; it exist as liquid upto 2000^0C and hence used in high temperature thermometry.

(5) Boiling point of these elements however show a regular decrease down the group.

(6)The abrupt increase in the atomic radius of Al is due to greater screening effect in Al (it has 8 electrons in its penultimate shell) than in B (it has 2 electrons in its penultimate shell)

(7)The atomic radii of group 13 elements are smaller than the corresponding s-block elements. This is due to the fact that when we move along the period, the new incoming electron occupy the same shell whereas the nuclear charge increases regularly showing more effective pull of nucleus towards shell electrons. This ultimately reduces the atomic size.

(8) The atomic radius of Ga is slightly lesser than of Al because in going from Al to Ga, the electrons have already occupied 3d sub shell in Ga. The screening effect of these intervening electrons being poor and has less influence to decrease the effective nuclear charge, therefore the electrons in Ga experience more forces of attractions towards nucleus to result in lower size of Ga than A*l*

(9) Oxidation state

(i) All exhibit +3 oxidation state and thus complete their octet either by covalent or ionic union.

(ii) Boron being smaller in size cannot lose its valence electrons to form B^{3+} ion and it usually show +3 covalence. The tendency to show +3 covalence however decreases down the group Even Al shows +3 covalence in most of its compounds.

(iii) Lower elements also show +1 ionic state e.g Tl^{+}, Ga^{+}. This is due to inert pair effect. The phenomenon in which outer shell 's' electrons (ns^2) penetrate to (n-1) d electrons and thus become closer to nucleus and are more effectively pulled the nucleus. This results in less availability of ns^2 electrons pair for bonding or ns^2 electron pair becomes inert. The inert pair effect begins after $n \geq 4$ and increases with increasing value of n.

(iv) The tendency to form M^{+} ion increases down the gp. $Ga^{+1} < Tl^{+1}$

(10) Hydrated ions : All metal ions exist in hydrated state.

(11) Ionisation energy

(i) Inspite of the more charge in nucleus and small size, the first ionisation energies of this group elements are lesser than the corresponding elements of s block. This is due to the fact that removal of electron from a p-orbitals (being far away from nucleus and thus less effectively held than s-orbitals) is relatively easier than s-orbitals.

(ii) The ionisation energy of this group element decrease down the group due to increases in size like other group elements.

(iii) However, ionisation energy of Ga are higher (table) than that of Al because of smaller atomic size of Ga due to less effective shielding of 3d electrons in Ga. Thus valence shell exert more effective nuclear charge in Ga to show higher ionisation energies.

(12) Electropositive character

(i) Electropositive character increases from B to T*l*.

(ii) Boron is semi metal, more closer to non-metallic nature whereas rest all members are pure metals.

(iii) Furthermore, these elements are less electropositive than s-block elements because of smaller size and higher ionisation energies.

(13) Oxidation potential

(i) The standard oxidation potentials of these element are quite high and are given below,

	B	Al	Ga	In	Tl
E^0op for $M \rightarrow M^{3+} + 3e$	–	+1.66	+0.56	+0.34	+1.26
E^0op for $M \rightarrow M^{+} + e$	–	+0.55	–	+0.18	+0.34

(ii) However Boron does not form positive ions in aqueous solution and has very low oxidation potential.

(iii) The higher values of standard oxidation potentials are due to higher heats of hydration on account of smaller size of trivalent cations.

(iv) Aluminium is a strong reducing agent and can reduce oxides which are not reduced even by carbon. This is due to lower ionisation energy of aluminium than carbon. The reducing character of these elements is *Al* > Ga > In > T*l*.

(14) Complex formation : On account of their smaller size and more effective nuclear charge as well as vacant orbitals to accept elements, these elements have more tendency to form complexes than-s block elements.

Chemical properties

(1) Occurrence : The important of this group elements are given below,

Boron : Borax (Tincal) ($Na_2B_4O_7.10H_2O$), Colemanite ($Ca_2B_6O_{11}5H_2O$)
Boracite ($2Mg_3B_8O_{15}.MgCl_2$), Boronatro calcite ($CaB_4O_7.NaBO_2.8H_2O$),
Kernite ($Na_2B_4O_7.4H_2O$), Boric acid (H_3BO_3)

Aluminium **:** Corundum (Al_2O_3), Diaspore ($Al_2O_3.H_2O$), Bauxite ($Al_2O_3.2H_2O$), and Cryolite (Na_3AlF_6).

(2) Hydrides

(i) Elements of gp 13 do not react directly with hydrogen but a number of polymeric hydrides are known to exist.

(ii) Boron forms a large no. of volatile covalent hydrides, known as boranes e.g. $B_2H_6, B_4H_{10}, B_5H_{11}, B_6H_{10}$ Two series of borones with general formula B_nH_{n+4} and B_nH_{n+6} are more important.

(iii) Boranes are electron deficient compounds. It is important to note that although BX_3 are well known, BH_3 is not known. This is due of the fact that hydrogen atoms in BH_3 have no free electrons to form pπ-pπ back bonding and thus boron has incomplete octet and hence BH_3 molecules dimerise to form B_6H_6 having covalent and three centre bonds.

(iv) Al forms only one polymeric hydride $(AlH_3)_n$ commonly known as alane It contains A1…..H……Al bridges.

(v) Al and Ga forms anionic hydrides e.g. $LiAlH_4$ and Li Ga H_4 , $4LiH + AlCl_3 \xrightarrow{ether} Li[AlH_4] + 3LiCl$

(3) Reactivity towards air

(i) Pure boron is almost unreactive at ordinary temperature. It reacts with air to form B_2O_3 when heated It does react with water. Al burns in air with evolution of heat give Al_2O_3.

(ii) Ga and In are not effected by air even when heated whereas Tl is little more reactive and also form an oxide film at surface. In moist air , a layer of Tl (OH) is formed.

(iii) Al decomposes H_2O and reacts readily in air at ordinary temperature to form a protective film of its oxides which protects it from further action.

(4) Oxides and hydroxides

(i) The members of boron family form oxide and hydroxides of the general formula M_2O_3 and $M(OH)_3$ respectively.

(ii) The acidic nature of oxides and hydroxides changes from acidic to basic through amphoteric from B to Tl.

$$\underset{\text{(acidic)}}{B_2O_3 \text{ and } B(OH)_3} > \underset{\text{(amphoteric)}}{Al_2O_3 \text{ and } Al(OH)_3} > \underset{\text{(amphoteric)}}{Ga_2O_3 \text{ and } Ga(OH)_3} > \underset{\text{(basic)}}{In_2O_3\, In(OH)_3} > \underset{\text{(strong basic)}}{Tl_2O_3\; Tl(OH)_3}$$

Note : ✹ $B(OH)_3$ or H_3BO_3 is weak monobasic Lewis acid.

(iii) Boric acid, $B(OH)_3$ is soluble in water as it accepts as it accepts lone pair of electron to act as Lewis acid. Rest all hydroxides of group 13 are insoluble in water and form a gelatinous precipitate.

$$B(OH)_3 + H_2O \rightarrow B(OH)_4^{1-} + H^+$$

(iv) Al_2O_3 being amphoteric dissolves in acid and alkalies both.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \quad ; \quad Al_2O_3 + 2NaOH \xrightarrow{fuse} \underset{\text{Sodium meta aluminate}}{2NaAlO_3} + H_2O$$

(v) One of the crystalline form of alumina (Al_2O_3) is called corrundum. It is very hard and used as abrasive. It is prepared by heating amorphous form of Al_2O_3 to 2000 K.

(5) Action of Acids

(i) Boron does not react with non oxidizing acids, however, it dissolves in nitric acid to form boric acids.

(ii) Al, Ga and In dissolve in acids forming their trivalent cations; however, Al and Ga become passive due to the formation of protective film of oxides.

(iii) Thallium dissolves in acids forming univalent cation and becomes passive in HCl due to the formation of water insoluble TICl.

(6) Action of Alkalies

(i) Boron dissolves only in fused alkalis, $2B + 6NaOH\text{ (fused)} \rightarrow 2Na_3BO_3 + 3H_2$

(ii) Al and Ga dissolves in fused as well as in aqueous alkalis, $2Al + 2\,NaOH + 2H_2O \rightarrow 2NAlO_2 + 3H_2$

(iii) Indium remains unaffected in alkalies even on heating.

(7) Halides

(i) All the group 13 elements from the trihalides, MX_3 on directly combining with halogens.

$$M + X_2 \rightarrow MX_3$$

(ii) All the trihalides of group 13 elements are known except Tl (III) iodide.

(iii) Due to small size and high electronegativity of boron, all boron halides are covalent and Lewis acids. These exist as monomeric molecules having plane triangular geometry (sp^2 hybridization).

(iv) All Boron trihalides except BF_3 are hydrolysed to boric acid.

$$BX_3 + 3H_2O \rightarrow B(OH)_3 + 3HX; \qquad [X = Cl, Br, I]$$

However, BF_3 forms as addition product with water, $BF_3 + H_2O \rightarrow H^+[BF_3OH]^- \xrightleftharpoons{H_2O} H_3O^+[BF_3OH]^-$.

BF_3 having less tendency for hydrolysis as well as Lewis acid nature, is extensively used as a catalyst in organic reactions e.g. Friedel- Crafts reaction.

(v) Boron atom, in BX_3, has six electrons in the outermost orbit and thus it can accept a pair of electrons form a donor molecule like NH_3 to complete its octet. Hence boron halides act as very efficient Lewis acids. The relative Lewis acid character of boron trihalides is found to obey the order ; $BI_3 > BBr_3 > BCl_3 > BF_3$.

However, the above order is just the reverse of normally expected order on the basis relative electronegativities of the halogens. Fluorine, being the most electronegative, should create the greatest electron deficiency on boron and thus B in BF_3 should accept electron pair from a donor very rapidly than in other boron trihalides. But this is not true.

This anomalous behaviour has been explained on the basis of the relative tendency of the halogen atom to back-donate its unutilised electrons to the vacant p orbitals of boron atom. In boron trifluoride, each fluorine has completely filled unutilised 2p orbitals while boron has a vacant 2p orbital. Now since both of these orbitals belong to same energy level (2p) they can overlap effectively as a result of which fluorine electrons are transferred into the vacant 2p orbital of boron resulting in the formation of an additional $p\pi - p\pi$ bond. This type of bond formation is known as ***back bonding*** or ***back donation***. Thus the B- F bond has some double bond character. Back bonding may take place between boron and of the three fluorine atoms and thus boron trifluoride is regarded as a resonance hybrid of some structures.

Resonance in boron trifluoride is also evidenced by the fact that the three boron-fluorine bonds are indentical and are shorter than the usual single boron-fluorine bond As a result of back bonding, the electron deficiency of boron is reduced and hence Lewis acid nature is decreased. The tendency for the formation of back bonding ($p\pi$- $p\pi$ bond) is maximum in BF_3 and decreases very rapidly from BF_3 to BI_3 This is probably due to the fact that overlapping of the vacant 2p orbitals of boron cannot take place easily with the p-orbitals of high energy levels (3p in Cl, 4p in Br and 5p in iodine). Thus BI_3 Br_3 and BCl_3 are stronger Lewis acids than the BF_3.

(vi) Lewis acid character of halides of the group 13 elements decreases in the order,B > Al > Ga > In

(vii) Boron halides form complex halides of the type, $[BF_4^-]$, in which boron atom extends its coordination number to four by utilising empty p-orbital. It cannot extend its coordination number beyond four due to non availability of d-orbitals. However, the other trihalides of this group form complex halides of the type $(AlF_6)^{3-}$, $(GaCl_6)^{3-}$ and $(InCl_6)^{3-}$, etc where the central atom extends its coordination number to 6 by the use of d-orbitals.

(viii) The fluorides of Al, Ga In and Tl are ionic and have high melting points. The high melting points of metal fluorides can be explained on the basis that their cations are sufficiently large and have vacant d-orbitals for attaining a coordination number of six towards the relatively small fluorine atom.

(ix) Other halides of Al, Ga, In and Tl are largely covalent in anhydrous state and possess low m.pt. These halides do not show backbonding because of increases in the size of the element. However, the make use of vacant p-orbitals by co-ordinate bond i.e. metal atoms complete their octet by forming dimers. Thus aluminium chloride, aluminium bromide and indium iodide exist as dimers, both in the vapour state and in non-polar solvents.

The dimer structure for Al_2Cl_6 is evidenced by the following facts,

(a) Vapour density of aluminium chloride measured at 400^0C corresponds to the formula $Al_2\ Cl_6$.

(b) Bond distance between aluminium chlorine bond forming bridge is greater ($2.21A^0$) than the distance between aluminum-chlorine bond present in the end ($2.06\ A^0$). The dimeric structure disappears when the halides are dissolved in water This is due to high heat of hydration which split the dimeric structure into $[M(H_2O)_6]^{3+}$ and $3X^-$ ions and the solution becomes good conductor of electricity.

$Al_2Cl_6 + 2H_2O \rightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$; Therefore Al_2Cl_6 is ionic in water.

The dimeric structure may also split by reaction with donor molecules e.g. R_3N. This is due to the formation of complexes of the type R_3NAlCl_3 The dimeric structure of Al_2Cl_6 exist in vapour state below 473 K and at higher temperature it dissociates to trigonal planar $AlCl_3$ molecule.

Note : ✸ Boron halides do not exist as dimer due to small size of boron atom which makes it unable to co-ordinate four large-sized halide ions.

(x) BF_3 and $AlCl_3$ acts as catalyst and Lewis acid in many of the industrial process.

Anomalous Behaviour of Boron

Like Li and Be, Boron – the first member of group 13 also shows anomalous behaviour due to extremely low size and high nuclear charge/size ratio, high electronegativity and non-availability of d electrons. The main point of differences are,

(1) Boron is a typical non- metal whereas other members are metals.

(2) Boron is a bad conductor of electricity whereas other metals are good conductors.

(3) Boron shows allotropy and exists in two forms – crystalline and amorphous. Aluminium is a soft metal and does not exist in different forms.

(4) Like other non-metals, the melting point and boiling point of boron are much higher than those of other elements of group 13.

(5) Boron forms only covalent compounds whereas aluminium and other elements of group 13 form even some ionic compounds.

(6) The hydroxides and oxides of boron are acidic in nature whereas those of others are amphoteric and basic.

(7) The trihalides of boron (BX_3) exist as monomers On the other hand, aluminium halides exist as dimers (Al_2X_6).

(8) The hydrides of boron i.e. boranes are quite stable while those of aluminium are unstable.

(9) Dilute acids have no action on boron Others liberate H_2 from them.

(10) Borates are more stable than aluminates.

(11) Boron exhibit maximum covalency of four e.g., BH^-_4 ion while other members exhibit a maximum covalency of six e.g., $[Al(OH)_6]^{3-}$.

(12) Boron does not decompose steam while other members do so.

(13) Boron combines with metals to give borides e.g. Mg_3B_2. Other members form simply alloys.

(14) Concentrated nitric acid oxidises boron to boric acid but no such action is noticed other group members.

$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO_2$

Diagonal relationship between Boron and Silicon

Due to its small size and similar charge/mass ratio, boron differs from other group 13 members, but it resembles closely with silicon, the second element of group 14 to exhibit diagonal relationship. Some important similarities between boron and silicon are given below,

(1) Both boron and silicon are typical non-metals, having high m.pt. b.pt nearly same densities (B=2.35g ml $^{-1}$ S=2.34 g//ml). low atomic volumes and bad conductor of current. However both are used as semiconductors.

(2) Both of them do not form cation and form only covalent compounds.

(3) Both exists in amorphous and crystalline state and exhibit allotropy.

(4) Both possess closer electronegativity values (B=2.0;Si=1.8).

(5) Both form numerous volatile hydrides which spontaneously catch fire on exposure to air and are easily hydrolysed.

(6) The chlorides of both are liquid, fume in most air and readily hydrolysed by water.

$$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl \;;\; SiCl_4 + H_2O \rightarrow Si(OH)_4 + 4HCl$$

(7) Both form weak acids like H_3BO_3 and H_2SiO_3.

(8) Both form binary compounds with several metals to give borides and silicide. These borides and silicide react with H_3PO_4 to give mixture of boranes and silanes.

$$3Mg + 2B \rightarrow \underset{\text{(Magnesium boride)}}{Mg_3B_2} \;;\; Mg_3B_2 + H_3PO_4 \rightarrow \text{Mixture of boranes}$$

$$2Mg + Si \rightarrow Mg_2Si \;;\; \underset{\text{(magnesium silicide)}}{Mg_2Si} + H_3PO_4 \rightarrow \text{Mixture of silanes}$$

(9) The carbides of both Boron and silicon (B_4C and SiC) are very hard and used as abrasive.

(10) Oxides of both are acidic and can be reduced by limited amount of Mg In excess of Mg boride and silicide are formed.

$$B_2O_3 + 3Mg \rightarrow 3MgO + 2B \;;\; SiO_2 + 2Mg \rightarrow 2MgO + Si$$

(11) Both the metals and their oxides are readily soluble in alkalies.

$$2B + 6NaOH \rightarrow \underset{\text{(borate)}}{2Na_3BO_3} + 3H_2\uparrow \;;\; Si + 2NaOH + H_2O \rightarrow \underset{\text{(silicate)}}{Na_2SiO_3} + 2H_2\uparrow$$

$$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2O \;;\; SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

Both borates and silicates have tetrahedral structural units BO_4^{n-} and SiO_4^{n-} respectively. Boro silicates are known in which boron replaces silicon in the three dimensional lattice. Boron can however form planar BO_3 units.

(12) Acids of both these elements form volatile esters on heating with alcohol in presence of conc. H_2SO_4.

$$B(OH)_3 + 3ROH \rightarrow B(OR)_3 + 3H_2O \;;\; Si(OH)_4 + 4ROH \rightarrow Si(OR)_4 + 4H_2O$$

Boron and its compounds

Boron is the first member of group –13 (IIIA) of the periodic table. Boron is a non- metal . It has a small size and high ionization energy due to which it can not lose its valence electrons to form B^{+3} ion. Its compounds especially the hydrides and halides are electron deficient and behave as Lewis acid.

(1) Ores of boron

(i) ***Borax or tincal*** : $Na_2B_4O_7 . 10H_2O$

(ii) ***Kernit or Rasorite :*** $Na_2B_4O_7 . 10H_2O$

(iii) ***Colemanite :*** $Ca_2B_6O_{11} . 5H_2O$

(iv) ***Orthoboric acid :*** H_3BO_3 (It occurs in the jets of steam called soffioni escaping from ground in the volcanic region of the ***Tuscany***). Boron is present to a very small extent (0.001%) in earth's crust.

(2) Isolation : Elemental boron in the form of dark brown powder is obtained either by reduction of boric oxide with highly electropositive metals like *K*, *Mg*, *Al*, *Na*, etc. in the absence of air and boron halides with hydrogen at high temperature eg. $B_2O_3 + 6K \xrightarrow{Heat} 2B + 3K_2O$; $2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$.

By thermal decomposition of boron tri-iodide over red hot tungsten filament and boron hydrides for example,

$$2BI_3 \xrightarrow{W, heat} 2B + 3I_2 \; ; \; B_2H_6 \xrightarrow{Heat} 2B + 3H_2$$

(3) Properties : It exists in mainly two allotropic forms i.e. amorphous dark brown powder and crystalline black very hard solid. It occurs in two isotopic forms, *i.e.*, ${}_5B^{10}$ (20% abundance) and ${}_5B^{11}$ (80% abundance). With air, boron forms B_2O_3 and BN at 973*K*, with halogens, trihalides (BX_3) are fromed with metals, borides are formed. eg. $4B + 3O_2 \xrightarrow{Heat} \underset{\text{Boron trioxide}}{2B_2O_3}$; $2B + N_2 \xrightarrow{Heat} \underset{\text{Boron nitride}}{2BN}$;

$$2B + 3X_2 \longrightarrow \underset{\text{Boron trihalide}}{2BX_3} \; ; \quad 3Mg + 2B \xrightarrow{Heat} \underset{\text{Magnesium boride}}{Mg_3B_2}$$

Water, steam and *HCl* have no action on *B*. oxidising acids (HNO_3, H_2SO_4) convert boron to H_3BO_3.

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2 \; ; \; 2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

Fused alkalies (NaOH , KOH) dissolve boron forming borates, liberating hydrogen.

$$2B + 6KOH \xrightarrow{Fused} 2K_3BO_3 + 3H_2$$

(4) Uses of Boron : Boron is used in atomic reactors as protective shields and control rods, as a semiconductors for making electronic devices in steel industry for increasing the hardness of steel and in making light composite materials for air crafts.

(5) Compounds of Boron

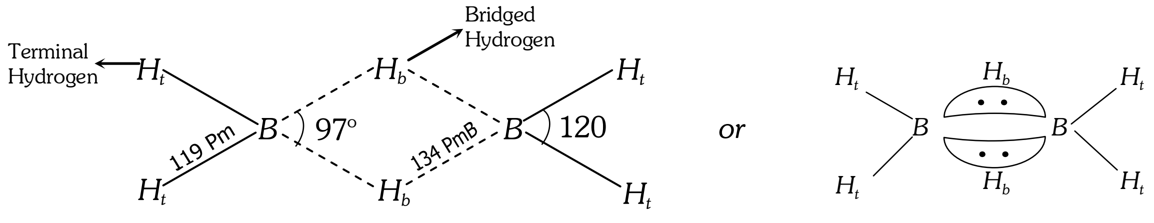
Boron Hydrides

Boron forms hydrides of the types B_nH_{n+4} and B_nH_{n+6} called boranes. Diborane is the simplest boron hydride which is a dimer of BH_3.

Structure of diborane : B_2H_6 has a three centre electon pair bond also called a banana shape bond.

(i) $B - H_t$: It is a normal covalent bond (two centre electron pair bond i.e., $2c - 2e$).

(ii) $B - H_b$: This is a bond between three atoms, $B - H_b - B$, (three centre electron pair bond i.e., $3c - 2e$).



Structure of diborane (B_2H_6)

The other boron hydrides are $B_5H_9, B_4H_{10}, B_5H_{11}$ etc.

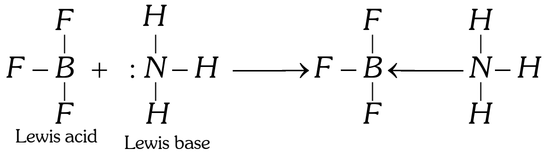
Boron Halides

Boron reacts with halogens on strong heating to form boron halides .

$$2B + 3X_2 \xrightarrow{Heat} 2BX_3 (X = F, Cl, Br, I)$$

BF_3 and BCl_3 are gases, BBr_3 is a volatile liquid while BI_3 is a solid.

In these halides, the central boron atom has three shared pairs of electrons with the halogen atoms. Therefore, these have two electrons less than the octet and are electron deficient compounds. They acts as Lewis acids.



$$\underset{\text{Lewis acid}}{F-\overset{F}{\underset{F}{B}}} + \underset{\text{Lewis base}}{:\overset{H}{\underset{H}{N}}-H} \longrightarrow F-\overset{F}{\underset{F}{B}} \longleftarrow \overset{H}{\underset{H}{N}}-H$$

The relative acidic strength of boron trihalides decreases as : $BI_3 > BBr_3 > BCl_3 > BF_3$.

Borax ($Na_2B_4O_7.10H_2O$)

It occurs naturally as **tincal** (Suhaga) which contains about 50% borax in certain land, lakes. It is also obtained from the mineral colemanite by boiling it with a solution of Na_2CO_3.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7} + 2CaCO_3 + 2NaBO_2$$

Properties : (i) Its aqueous solution is alkaline due to hydrolysis,

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3.$$

(ii) On heating borax loses its water of crystallization and swells up to form a fluffy mass. On further heating, it melts to give a clear liquid which solidifies to a transparent glassy bead consisting of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3), $Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Borax bead}}{2NaBO_2 + B_2O_3}$.

Borax bead is used for the detection of coloured basic radicals under the name borax bead test.

(iii) When heated with C_2H_5OH and conc. H_2SO_4 it gives volatile vapours of triethyl borate which burns with a green edged flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3 ; \quad H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{Triethyl borate}}{B(OC_2H_5)_3} + 3H_2O$$

This reaction is used as a test for borate radical in qualitative analysis.

Uses : (1) In making optical and hard glasses. (2) In the laboratory for borax bead test. (3) In softening of water. (4) In the preparation of medicinal soaps due to its antiseptic character.

Borax bead test **:** Borax bead is a mixture of $NaBO_2$ and B_2O_3. B_2O_3 on heating combines readily with a number of coloured transition metal oxides such as Co, Ni, Cr, Cu, Mn, etc. to form the corresponding metaborates which possess characteristic colours, $CoSO_4 \xrightarrow{\Delta} CoO + SO_3$; $CoO + B_2O_3 \longrightarrow \underset{\substack{\text{Cobalt meta borate} \\ \text{(Blue)}}}{Co(BO_2)_2}$

Colours of some important metaborates are: Cupric metaborate, $Cu(BO_2)_2$ is dark blue, chromium metaborate, $Cr(BO_2)_2$ is green, nickel metaborate, $Ni(BO_2)_2$ is brown and manganese metaborate, $Mn(BO_2)_2$ is pink violet.

Boric acid or orthoboric acid (H_3BO_3)

It is obtained from borax by treating with dil. HCl or dil. H_2SO_4,

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

It can also be obtained from the mineral colemanite by passing SO_2 through a mixture of powdered mineral in boiling water, $Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

Properties : (i) It is a very weak monobasic acid, does not act as a proton doner but behaves as a Lewis acid i.e. it accepts a pair of electrons from OH^- ion of H_2O, $H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$

It acts as a strong acid in presence of polyhydroxy compounds such as glycerol, mannitol etc. and can be titrated against strong alkali .

(ii) With $NaOH$ it forms, sodium metaborate, $H_3BO_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$

(iii) With C_2H_5OH and conc. H_2SO_4, it gives triethyl borate

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{Conc.\,H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

(iv) ***Action of heat*** **:** The complete action of heat on boric acid may be written as,

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{373K} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{433K} \underset{\text{Tetra boric acid}}{H_2B_4O_7} \xrightarrow{\text{Red hot}} \underset{\text{Boron oxide}}{B_2O_3}$$

Structure : In boric acid, planar BO_3^{-3} units are joined by hydrogen bonds to give a layer structure.

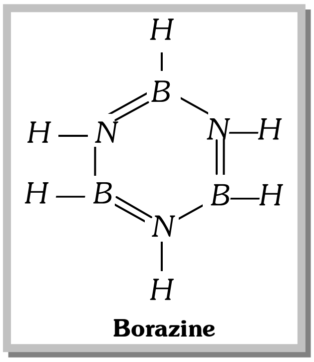
Uses : (i) As a food preservative. (ii) As a mild antiseptic for eye wash under the name boric lotion. (iii) For the preparation of glazes and enamels in pottery.

Borazine or Borasole or Triborine triamine ($B_3N_3H_6$)

It is a compound of *B*, *N* and *H*. It is a colourless liquid and is also called inorganic benzene.

$$2B_2H_6 + 6NH_3 \xrightarrow{180^\circ C} 2B_3N_3H_6 + 12H_2.$$

It has a six membered ring of alternating *B* and *N* atoms, each is further linked to a *H*- atom.



Borazine

Boron nitride (*BN*)

It is prepared by treating BCl_3 with an excess of NH_3 and pyrolysing the resulting mixture in an atmosphere of NH_3 at $750^\circ C$,

$$BCl_3 + NH_3 \longrightarrow [H_3N \longrightarrow BCl_3] \xrightarrow[\text{Excess } NH_3]{750^\circ C} BN + 3HCl.$$

It is a colourless, good insulator, diamagnetic and almost unreactive solid

Aluminium and its compounds

(1) **Ores of Aluminium :** Bauxite $(Al_2O_3.2H_2O)$, Cryolite $(Na_3AlF_6$, Felspar $(KAlSi_3O_8)$, Kaolinite $(Al_2O_3.2SiO_2.2H_2O)$, Mica $(K_2O.3Al_2O_3.6SiO_2.2H_2O)$, Corundum (Al_2O_3), Diaspore $(Al_2O_3.H_2O)$, Alunite or alum stone $[K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3]$.

(2) **Extraction :** Aluminium is obtained by the electrolysis of the oxide (alumina) dissolved in fused cryolite. This involves following steps,

Purification of ore

(i) ***Baeyer's process***

$$\underset{\substack{\text{Finely powdered}\\ \text{(red)}}}{\text{Bauxite}} \xrightarrow[FeO \to Fe_2O_3]{\text{Roasted}} \text{Roasted ore} \xrightarrow[\substack{\text{High pressure}\,(150^\circ \text{C, 80 atm})\\ \text{filtered, } Fe_2O_3 \text{ as residue}}]{+\text{ Caustic soda solution}} \underset{\text{(Sod. Aluminate)}}{Filtrate} \xrightarrow[CO_2]{Filtered} Pure\ Al_2O_3 \xrightarrow{Heat} Al(OH)_3$$

(ii) ***Hall's process***

$$\underset{\substack{\text{(Finely powdered)}\\ \text{(red)}}}{\text{Bauxite}} \xrightarrow[\substack{\text{Fused, extracted with}\\ \text{water. Residue } Fe_2O_3}]{+Na_2CO_3} \text{Solution} \xrightarrow[\substack{50\text{-}60^\circ \text{C and filtered.}\\ \text{Filtrate } (Na_2CO_3)}]{CO_2} \text{Precipitate } Al(OH)_3 \xrightarrow{Heat} Pure\ Al_2O_3$$

(iii) ***Serpek's process***

$$\underset{\substack{\text{(Finely powdered)}\\ \text{(white)}}}{\text{Bauxite}} \xrightarrow[\substack{\text{Heated to}\\ 1800^\circ \text{C}}]{+Coke+N_2} \substack{\text{Silica reduced to}\\ \text{Si which volatalises}} + \substack{\text{Alumina form}\\ \text{aluminium nitride}} \ AlN \xrightarrow{Hydrolysis} Pure\ Al_2O_3 \xrightarrow{Heated} Al(OH)_3$$

(iv) ***Hall and Heroult process*** : It is used for extraction of aluminium. In this process a fused mixture of alumina (20%), cryolite (60%) and fluorspar (20%) is electrolysed using carbon electrodes. Whereas cryolite makes Al_2O_3 conducting fluorspar decreases the m.pt. of alumina.

Note : ✹ Aluminium is refined by Hoope's electrolytic process.

(3) Compounds of Aluminium

(i) ***Aluminium oxide or Alumina*** (Al_2O_3) **:** It occurs in nature as colourless corundum and several coloured minerals like ruby (red), topaz (yellow), Sapphire (blue), amethyst (violet) and emerald (green). These minerals are used as ***precious stones*** (gems).

(ii) ***Aluminium chloride*** (Al_2Cl_6) **:** It is prepared by passing dry chlorine over aluminium powder.

$$Al_2O_3 + 3C + 3Cl_2 \to \underset{\text{(anhydrous)}}{2AlCl_3} + 3CO(g)$$

It exists as dimer Al_2Cl_6, in inert organic solvents and in vapour state. It sublimes at $100\,^\circ C$ under vacuum. Dimeric structure disappears when $AlCl_3$ is dissolved in water. It is hygroscopic in nature and absorbs moisture when exposed to air.

(iii) ***Thermite*** **:** A mixture of aluminium powder and Fe_2O_3 in the ratio 1:3. It is used for welding of iron. The reaction between Al and Fe_2O_3 is highly exothermic, $Al + Fe_2O_3 \to Al_2O_3 + Fe + \text{Heat}$

(iv) ***Aluminium sulphate*** $[Al_2(SO_4)_3]$ **:** It is used for the preparation of alums e.g., potash alum $Al_2(SO_4)_3.K_2SO_4.24H_2O$. It is also used for making fire proof clothes.

Carbon Family.

Carbon is the first member of group 14 or IVA of the periodic table. It consists of five elements carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Carbon and silicon are nonmetals, germanium is metalloid and tin and lead are metals.

Electronic configuration

Elements	***Electronic configuration*** $(ns^2\ np^2)$
$_6C$	$1s^2, 2s^2 2p^2$ **or** $[He]2s^2 2p^2$
$_{14}Si$	$1s^2, 2s^2 2p^6, 3s^2 3p^2$ **or** $[Ne]3s^2 3p^2$

$_{32}Ge$	$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^2$	**or**	$[Ar]3d^{10}4s^24p^2$
$_{50}Sn$	$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^64d^{10},5s^25p^2$	**or**	$[Kr]4d^{10}5s^25p^2$
$_{82}Pb$	$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^64d^{10}4f^{14},5s^25p^65d^{10},6s^26p^2$	**or**	$[Xe]4f^{14}5d^{10}6s^26p^2$

Physical properties

(1) **Non-metallic nature :** The non-metallic nature decreases along the group.

C	Si	Ge	Sn	Pb
Non-metal		metalloid or semi metal	metal	metal

(2) **Abundance :** Carbon and silicon are most abundant elements in earth's crust whereas germanium occurs only as traces. Tin and lead also occur in small amounts. Only carbon occurs in free state as coal, diamond and graphite and in combined state as carbonates, CO_2 petroleum and natural gas Silicon is the second most abundant element after oxygen in earth's crust in form of silicates and silica. Germanium found in traces in coal and in certain deposits. It important constituent for making conductors and transistors The important ore of tin is tin stone (SnO_2) or cassiterite. Lead is found is form of galena (PbS) anglesite ($PbSO_4$) and cerussite ($PbCO_3$) The abundance ratio in earth's crust is given below,

Element	C	Si	Gs	Sn	Pb
Abundance in earth's crust (ppm)	320	277200	7	40	16

(3) **Density :** The density of these elements increases down the group as reported below

Element	C	Si	Ge	Sn	Pb
Density (g/ml)	3.51 (for diamond) 2.22 (for graphite)	2.34	5.32	7.26	11.34

(4) **Melting point and boiling points**

(i) The m.pt and b.pt. of this group members decrease down the group.

Element	C	Si	Ge	Sn	Pb
m.pt(K)	4373	1693	1218	505	600
b.pt.(K)	–	3550	3123	2896	2024

(ii) The m.pt and b.pt of group 14 elements are however, higher than their corresponding group 13 elements. This is due to the formation of four covalent bonds on account of four electrons in their valence shells which results in strong binding forces in between their atoms in solid as well as in liquid state.

(5) **Atomic radii and atomic volume**

(i) Both atomic radii and atomic volume increases gradually on moving down the group due to the effect of extra shell being added from member to member.

	C	Si	Ge	Sn	Pb
Atomic radius (pm)	0.77	111	122	141	144
Atomic volume (ml)	3.4	11.4	13.6	16.3	18.27

(ii) The atomic radii of group 14 elements are than their corresponding group 13 elements due to increase in nuclear charge in the same period.

(iii) Some of the ionic radii involving six co-ordination of these group elements are given below,

	C	Si	Ge	Sn	Pb
Ionic radius (M^{2+}) in pm	–	–	73	118	119
Ionic radius (M^{++}) in pm	–	40	53	69	78

(6) Electronegativity : The electronegativity decreases from C to Si and then becomes constant.

	C	Si	Ge	Sn	Pb
Electronegativity on pauling scale	2.5	1.8	1.8	1.7	1.6

The electronegativity from silicon onwards is almost is almost constant or shows a comparatively smaller decreases due to screening effects of d^{10} electrons in elements from Ge onwards.

(7) Ionisation energy

(i) The ionisation energy decreases regularly down the group; Pb however shows a higher value than Sn due to poor shielding of inner f-orbitals as a result of which effective nuclear charge experienced by outer shell electrons becomes more in Pb.

Ionisation energy (kJ mol^{-1})	C	Si	Ge	Sn	Pb
IE_1	1086	786	761	708	715
IE_2	2352	1577	1537	1411	1450
IE_3	4620	3284	3300	2942	3081
IE_4	6220	4354	4409	3929	4082

(ii) The first ionisation energies of group 14 elements are higher than their corresponding group 13 elements because of smaller size.

(iii) The electropositive character of these elements increases down the group because of decreases in ionisation energy.

(8) Oxidation state

(i) Presence of four electrons in outermost shell of these elements reveals that the members of this family can gain four electrons forming M^{4+} or M^{4-} ions to show ionic nature or exhibit tetravalent covalent nature by sharing of four electron pairs in order to attain stable configuration.

(ii) The formation of M^{4+} or M^{4-} ions require huge amount of energy which is normally not available during normal course of reactions, therefore, these elements usually do not form M^{4+} or M^{4-} ions, but they usually form compounds with covalence of four.

(iii) Ge, Sn and Pb also exhibit +2+ oxidation state due to inert pair effect.

(iv) Sn^{2+} and Pb^{2+} show ionic nature.

(v) The tendency to form +2 ionic state increases on moving down the group due to inert pair effect.

(9) Catenation

(i) The tendency of formation of long open or closed atom chains by the combination of same atoms in themselves is known as catenation.

(ii) The catenation is maximum in carbon and decreases down the group.

(iii) This is due to high bond energy of catenation.

Bond	Bond energy in kJ mol^{-1}
C-C	348
Si-Si	180
Ge-Ge	167
Sn-Sn	155
Pb-Pb	No catenation

(iv) Only carbon atoms also form double or triple bonds involving pπ-pπ multiple bond within itself.

$> C = C<; - C \equiv C -$

(v) Carbon also possesses the tendency to form closed chain compounds with O,S and N atoms as well as forming pπ-pπ multiple bonds with other elements particularly nitrogen and oxygen e.g. $C=O$; $C=N$; $C\equiv N$; $C=S$ are the functional groups present in numerous molecules due to this reason.

(vi) Carbon can form chain containing any number of carbon atoms Si and Ge cannot extend the chain beyond 6 atoms, while Sn and Pb do not form chains containing more than one or two atoms.

(vii) The reason for greater tendency of carbon for catenation than other elements in the group may further be explained by the fact that the C-C bond energy is approximately of the same magnitude as the energies of the bond between C and other elements. On the other hand, the Si-Si bond is weaker than the bond between silicon and other elements.

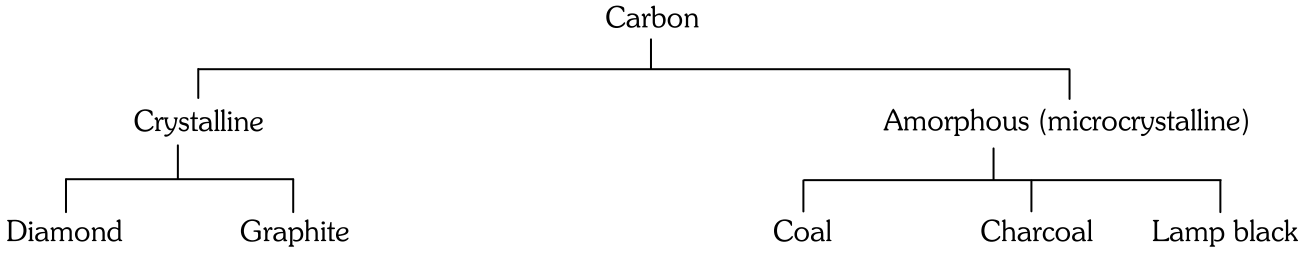
Bond	Bond energy (k J/mol)	Bond	Bond energy (kJ/mol)
C-C	348	Si-Si	180
C-O	315	Si-O	372
C-H	414	Si-H	339
C-Cl	326	Si-Cl	360
C-F	439	Si-F	536

(10) Allotropy

(i) The phenomenon of existence of a chemical element in two or more forms differing in physical properties but having almost same chemical nature is known as allotropy. If an element or compound exists in two or more forms, it is also known as polymorphism e.g. zinc blende and wurtzite are polymorphs of ZnS. This phenomenon is due to the difference either in the number of atoms in the molecules [as in the case of oxygen (O_2) and ozone (O_3)] or arrangement of atoms in the molecules in crystal structure (as in the case of various forms of carbon).

(ii) All the elements of group 14 except lead exhibit allotropy.

(iii) Crystalline carbon occurs mainly into two allotropic forms (i) graphite and (ii) diamond (a third allotropic form called fullerenes e.g. C_{60} and C_{70} were recently discovered by Prof. Richard E. Smalley and his coworkes), amorphous carbon exists in different forms viz coal, coke, carbon black, lamp black, bone charcoal. Amorphous carbon is usually considered to contain microcrystals of graphite.



(iv) ***Diamond and Graphite*** **:** The two allotropic forms of crystalline carbon. Diamond is the purest and hardest form of carbon. Its structure involves a giant molecular form where each carbon atom is surrounded by four other carbon atoms (sp^3 hybridization) In doing so, each carbon atom is located in the centre of a regular tetrahedron with its four valencies directed towards the four corners which are linked with four other carbon atoms ($C-C-C$ angle = 109^0 28'C-C=154 pm = 1.54 Å). The hardness of diamond result due to the uniformity of the C-C covalent bonds. Since the C-C bond length is very small, it has very high density (3.51 g cm^{-3}) and has more compact structure than graphite (density, 2.25 g cm^{-3}) It does not melt (vapourises at 3773K) has very high refractive index (2.45) and is insoluble in all ordinary solvents. It does not conduct electricity as all the four valence electrons are used up in forming covalent bonds with other carbon atoms Diamond, because of its hardness is used in cutting, grinding instruments such as glass and drilling equipments Its ability to reflect and refract light makes diamond an important jewellery material.

Difference between diamond and graphite

Diamond	*Graphite*
Crystalline, transparent with extra brilliance.	**Crystalline, opaque and shiny substance**
Hardest form	**Soft having soapy touch**
Bad conductor of electricity	**Good conductor of electricity**
High Density (3.51 g /cm^3) heavy	**Low Density (2.25 g/cm^3), lighter than diamond**
Colourless	**Greyish white**
Tetrahedral shaped	**Two dhnensional layer structure having regular hexagonal sheets.**
sp^3 hybridisation	**sp^2 hybridization**
Less stable, more energy	**More stable, less energy**
$C_D \rightarrow C_G$; $\Delta H = -0.5$ k.cal	**$C_G \rightarrow C_D$ at high temperature and high P**
Used in cutting glass and jewellery; an abrasive	**Used as lubricating agent, electrodes, in pencils, crucibles (due to high m.pt)**

Carbon also exists in three common microcrystalline or amorphous forms (charcoal, carbon black and cocke) Carbon black is formed when hydrocarbons, petroleum, turpentine oil or substances rich in carbon contents are heated in limited supply of oxygen, $CH_{4(g)} + O_{2\,(g)} \rightarrow C_{(s)} + 2H_2O_{(g)}$

These substances yield a large amount of smoke which is passed into chambers having wet blankets. The soot collected on these blankets is lamp black or carbon black or soot. It is almost pure carbon having as high as 98%to 99% carbon content with small amount of impurities It is a soft black power and is used as a pigment in black inks; large amounts are also used in making automobile tyres.

Charcoal is formed when wood cellulose or other substances containing carbonaceous matter are heated strongly in the absence of air Charcoal has highly open structure, giving it an enormous surface area per unit mass. Charcoal is of various forms such as wood charcoal, sugar charcoal, coconut charcoal, animal charcoal etc. These forms contain varying amount of carbon content. A very pure form of carbon is obtained from sugar. Activated charcoal, a pulverised form whose surface is cleaned. by heating with steam. is widely used to adsorb molecules. It is used in filters to remove offensive odours from air and coloured, foul smelling, bad tasting and toxic chemical as impurities from water.

Coke is an impure form of carbon and is produced when coal is heated strongly in the absence of air (as residue in the destructive distillation of coal) It is widely used as a reducing agent in metallurgical operations.

(v) Silicon also exists in crystalline and amorphous allotropic forms Germanium exists in two crystalline allotropic forms Tin has three allotropic forms as grey tin , white tin and rhombic tin.

Graphite occurs in Nature and can also obtained from coke, In graphite, out of four valence electrons, only three form covalent bonds (sp^2 hybridization) with three other carbon atoms. This forms hexagonal rings as sheets of on atom thickness. These sheets are held together by weak attractive forces One electron of each carbon atom is free and this enables these thin sheets slide over one another. For this reason graphite is a soft material with lubricating properties.

Graphite is a dark, opaque and soft material (density = 2250 kg/m^3) Although graphite is non-metallic still it possesses a metallic lustre. It is insoluble in ordinary solvents. Graphite is a good conductor of heat and electricity because of the present of one free electron on each carbon atom. Graphite is used as a dry lubricant in making electrodes in electric furnaces. It is chiefly used in lead pencils.

Chemical properties

(1) **Hydrides :** All the elements of group 14 combine with hydrogen directly or indirectly to form the covalent hydrides, MH_4 (M = C, Si, Ge, Sn or Pb). The number of hydrides and the ease of preparation decrease on going from carbon to lead.

The hydrides of silicon are called *silanes* having the general formula Si_nH_{2n+2}. The hydrides of germanium are called *germanes* while those of tin are called the *stannanes*. Only lead forms an unstable hydride of the formula, PbH_4 called the *plumbane*.

Three hydrides of germanium, i.e., GeH_4, Ge_2H_6 and Ge_3H_8 and only two hydrides of tin i.e., SnH_4 and Sn_2H_6 are well known.

(2) **Oxides :** *Carbon forms five oxides* CO, CO_2, C_3O_2 (carbon suboxide), C_5O_2 and $C_{12}O_9$, C_3O_2 is the anhydride of malonic acid and CO_2 is the anhydride of H_2CO_3 (carbonic acid) CO_2 *is a non-polar linear molecule due to maximum tendency of C to form* $p\pi\text{–}p\pi$ *multiple bond with oxygen.* *Si* forms SiO_2. *Pb* forms a number of oxides. *PbO* can be obtained by heating $Pb(NO_3)_2$, $2Pb(NO_3)_2 \xrightarrow{\text{Heat}} 2PbO + 4NO_2 + O_2$. The red form of PbO is called ***litharge*** and the yellow form is ***massicot***. Pb_3O_4 (Red lead, or Sindur) is prepared by heating litharge in air at 470°C, $6PbO + O_2 \xrightarrow{470^\circ C} 2Pb_3O_4$, Pb_3O_4 is a mixed oxide of $PbO_2.2PbO.Pb_2O_3$ is called lead sesquioxide. GeO_2, SnO_2 etc. are also network solids.

Note : ✹ SiO_2, GeO_2, SnO_2 and PbO_2 are all solids.

- CO_2 and SiO_2 is acidic, GeO_2 is weakly acidic while SnO_2 and PbO_2 are amphoteric in nature.
- All the elements of group 14 except silicon from monoxides e.g., CO, GeO, SnO and PbO. Out of these monoxides only CO is neutral, while all other monoxides are basic.

(3) **Halides :** Elements of group 14 react with halogens directly to form tetrahedral and covalent halides except C where its halide is produced by the action of halogens on hydrocarbons. $PbBr_4$ and PbI_4 do not exist because Pb^{4+} is a strong oxidant and Br^- and I^- are strong reductants. Hence Pb^{4+} ion is difficult to survive in presence of strong reductants Br^- and I^- and is immediately reduced to Pb^{2+}.

Anomalous behaviour of Carbon

Carbon is found to differ in many properties from the rest of the members of group 14. This is because of the following : (i) Its smallest size (ii) Its high electronegativity (iii) Its property to catenate (iv) Absence of *d*-orbitals in it.

Some of the properties in which it differs from other members are,

(1) The melting and boiling points of carbon are very high as compared to the rest to the members of the family.

(2) Carbon in its diamond form is one of the hardest substance known.

(3) It has maximum tendency to show catenation.

(4) Carbon has high tendency to form $P\pi - P\pi$ multiple bonds with other elements like nitrogen, oxygen, sulphur etc. Other members of the family form $P\pi - d\pi$ bonds and that also to a lesser extent.

(5) CO_2 is a gas while the dioxides of all other members are solids.

(6) Carbon shows a maximum covalency of four while other members of the family may expand their covalency to six e.g., $[SiCl_6]^{2-}, [PbCl_6]^{2-}$ etc.

(7) Carbon is not affected by alkalies whereas other members react on fusion. For example, silicon form silicates, $Si + 2NaOH + 1/2O_2 \rightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2$.

Silicon and its compounds

Silicon, being a second member of group – 14, has a much larger size and lower electronegativity than hat of carbon. As a result silicon does not form double bond with itself or with oxygen. Thus *SiO* bonds are much stronger than *Si – Si* and *Si –H* bonds. Silicon has vacant 3*d*-orbitals in its valence shell due to which it can extend its covalency from four to five and six.

(1) **Occurrence :** Silicon is the second most abundant element (27.7%) in earth's crust next to oxygen .It does not occur in free state. It occurs mainly in the form of Silica and silicates. Silicates are formed in rocks and clay as silicates of *Mg*, *Al*, *K* or *Fe*. e.g. Feldspar ; $K_2Al_2O_3.6SiO_2$, Kaolinite; $Al_2O_3.2SiO_2.2H_2O$.

(2) **Preparation :** Elemental silicon is obtained by reduction of silica with high purity coke in an electric furnace using excess of silica e.g. $SiO_2 + 2C \longrightarrow Si + 2CO$

Very high purity silicon required for making semiconductors is obtained by reduction of highly purified $SiCl_4$ form ($SiHCl_3$) with hydrogen followed by purification by zone refining eg.

$$SiCl_4 + 2H_2 \longrightarrow Si + 4HCl \text{ ; } SiHCl_3 + H_2 \longrightarrow Si + 3HCl$$

(3) **Properties :** Silicon exists in three isotopes $_{14}Si^{29}$ (most common), $_{14}Si^{30}$ with air at high temperature SiO_2 form, $Si + O_2 \longrightarrow SiO_2$.

With steam, Si reacts when heated to redness to liberate hydrogen, $Si + 2H_2O \xrightarrow{\text{Redness}} SiO_2 + 2H_2$.

With halogens, Si reacts at elevated temperature forming SiX_4 except fluorine which reacts at room temperature.

Silicon combines with C at 2500K forming Silicon Carbide (SiC) known as carborundum (an extremely hard substance), $Si + C \xrightarrow{2500K} SiC$.

It reacts with metals like Ca, Mg etc in an electric arc furnace to form Silicides (Ca_2Si, Mg_2Si etc.)

Silicon dissolves in hot aqueous alkalies liberating hydrogen, $Si + 4NaOH \xrightarrow{Heat} Na_4SiO_4 + 2H_2 \uparrow$

It also dissolves in fused Na_2CO_3 displacing carbon $Na_2SiO_3 + C$.

(4) **Uses of silicon :** It is added to steel as ferrosilicon (an alloy of Fe and Si) to make it acid resistant. It is used in the pure form as a starting material for production of silicon polymers (Silicones).

(5) Compounds of silicon

Silica or silicon dioxide (SiO_2)

It occurs in nature in various forms such as sand, quartz and flint .It is also a constituent of various rocks. It is solid at room temperature. It is insoluble in water.

Silica has a three dimensional network structure in which each Si is bonded to four oxygen atoms which are tetrahedrally disposed around silicon atom. Each O atom is shared by two Si atoms. It may be noted that CO_2 is a gas, while SiO_2 is hard solid with very high melting point.

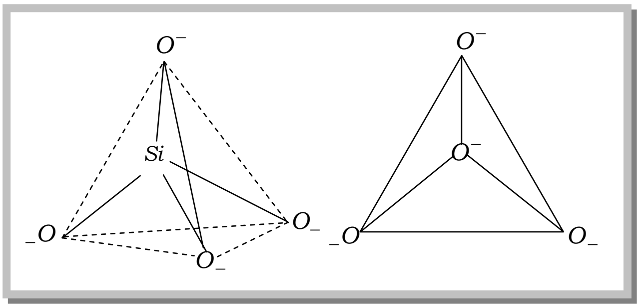
$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O ; SiF_4 + 2HF \longrightarrow \underset{\text{(Hydro flouro silicic acid)}}{H_2SiF_6}$$

HF readily dissolves Silica, therefore HF can not be store in glass bottles which contain Silica.

It is used in large amount to form mortar which is a building material. It is also used in the manufacture of glass and lenses.

Silicates

Almost all rocks and their products (Soil, clay and sand) are made up of silicate minerals and Silica. The basic unit of all silicates is tetrahedral SiO_4^{-4} ion. Some of the important silicates are quartz, mica, asbestos, felspar and zeolites.



Silica gel

When a mineral acid (Such as HCl) is added to a concentrated solution of a silicate, gelatinous white ppt. of hydrated silica (silicic acid) separate out.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + SiO_2.xH_2O$$

The white ppt. thus obtained is heated to lose water. When the water content is very low, the solid product is called silica gel. It possesses excellent absorptive properties due to its porous nature and is used for absorbing moisture and an adsorbent in chromatography.

Glass

Glass is an amorphous and transparent solid which is obtained by solidification of various silicates and borates of potassium and calcium.

(1) **Preparation :** Ordinary glass is a mixture of sodium and calcium silicates and is produced by fusing together a mixture of sodium carbonate, calcium oxide and silicon dioxide (Silica) in a furnace at about 1700K

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow ; \quad CaO + SiO_2 \longrightarrow CaSiO_3$$

On continuously heating the entire amount of CO_2 is driven out and clear viscous fused mass is obtained. It is poured into moulds to get different types of articles, which are allowed to cool gradually.

This typed of glass is called soda glass or soft glass which has the approximate composition, $Na_2SiO_3, CaSiO_3, 4SiO_2$.

(2) **Various varieties of glass :** The different varieties of glasses and their special constituents are given below,

Type of glass	*Constituents*	*Special use*
Soft glass	$Na_2CO_3, CaCO_3, SiO_2$	**Ordinary glass for window panes, test tubes, bottles, etc.**
Hard glass	$K_2CO_3, CaCO_3, SiO_2$	**For combustion tubes and chemical glassware**
High refractive index glass	**Lead oxide,** K_2CO_3	**For making lenses cut glasses**
Pyrex glass	Na_2CO_3, Al_2O_3, B_2O_3 **or borax, sand**	**For high quality glass apparatus cooking utensils**
Crook's glass	$K_2CO_2, PbCO_3$, CeO_2, **sand**	**Absorbs ultra violet rays, for making lenses**

(3) **Coloured glass :** Addition of transition metal compounds to glass give coloured glasses . Small amounts of Cr(III), Mn(IV), Co(II) and Fe(III) compounds impart green, violet blue or brown colour respectively

Compound added – Colour imparted	*Compound added – Colour imparted*
Cobalt axide (CoO) – Blue	**Chromium oxide (** Cr_2O_3 **) – Green**
Cuprous oxide (Cu_2O **) – Red**	**Auric chloride** $(AuCl_3)$ **– Ruby**
Cadmium sulphide (CdS) – Lemon yellow	**Manganese dioxide (** MnO_2**) – Purple**

Nitrogen Family.

Nitrogen is the first member of group 15 or VA of the periodic table. It consists of five elements nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). The elements of this group are collectively called

pnicogens and their compounds as pniconides. The name is derived from Greek word "Pniomigs" meaning suffocation. Pniconide contain M^{3-} species.

Electronic configuration

Elements	***Electronic configuration*** $(ns^2\ np^3)$
$_7N$	$1s^2, 2s^2 2p^3$ **or** $[He]2s^2 2p^3$
$_{15}P$	$1s^2, 2s^2 2p^6, 3s^2 3p^3$ **or** $[Ne]3s^2 3p^3$
$_{33}As$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^3$ **or** $[Ar]3d^{10} 4s^2 4p^3$
$_{51}Sb$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^3$ **or** $[Kr]4d^{10} 5s^2 5p^3$
$_{83}Bi$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^3$ **or** $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

Physical properties

(1) **Physical state :** Nitrogen– (gas), phosphorus – (solid) (vaporises easily), *As*, *Sb*, *Bi*–solids.

Note : ✹ Nitrogen is the most abundant gas in the atmosphere. It constitutes about 78% by volume of the atmosphere. Phosphorus is the most reactive element in this group and its yellow form is always kept under water.

(2) **Atomic radii :** Atomic radii increases with atomic number down the group i.e., from *N* to *Bi* due to addition of extra principal shell in each succeding elements.

(3) **Ionisation energy :** The ionisation values of the elements of this group decreases down the group due to gradual increases in atomic size.

(4) **Electronegativity :** Generally the elements of nitrogen family have high value of electronegativity. This value shows a decreasing trend in moving down the group from nitrogen to bismuth.

(5) **Non-metallic and metallic character :** Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids (semi-metal) and bismuth a typical metal.

(6) **Molecular state :** Nitrogen readily forms triple bond (two $p\pi - p\pi$ bonds) and exists as discrete diatomic gaseous molecule $(N \equiv N)$ at room temperature. Phosphorus, arsenic and antimony exist in the form of discrete tetra atomic molecules such as P_4, As_4, Sb_4 in which the atoms are linked to each other by single bonds.

(7) **Melting and boiling points :** The melting points and boiling points of group 15 elements do not show a regular trend.

Note : ✹ M.pt. first increases from *N* to As and then decreases from *As* to *Bi*. Boiling point first increases from *N* to Sb. Boiling point of *Bi* is less than *Sb*.

(8) **Allotropy :** All the members of group 15 except *Bi* exhibit the phenomenon of allotropy.

(i) Nitrogen exists in two solid and one gaseous allotropic forms.

(ii) Phosphorus exists in several allotropic forms such as white, red, scarlet, violet and black form.

(a) *White or yellow phosphorus* : White phosphorus is prepared from rock phosphate $Ca_3(PO_4)_2, SiO_2$ and coke which are electrically heated in a furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{\Delta} 6CaSiO_3 + P_4O_{10};\ P_4O_{10} + 10C \xrightarrow{\Delta} P_4 + 10CO$$

When exposed to light, it acquires a yellow colour.

(b) *Red phosphorus* : It is obtained by heating yellow phosphorus, between 240 –250°C in the presence of an inert gas. Yellow phosphorus can be separated from red phosphorus by reaction with $NaOH$ (*aq*) or KOH (*aq*) when the former reacts and the latter remains unreacted.

(iii) Arsenic exists in three allotropic forms namely grey, yellow and black. Antimony also exists in three forms, viz., metallic, yellow and explosive.

(9) **Oxidation state :** The members of the group 15 exhibit a number of positive and negative oxidation states.

(i) ***Positive oxidation states* :** The electronic configuration (ns^2np^3) for the valence shell of these elements shows that these elements can have +3 and +5 oxidation states. In moving down this group, the stability of +3 oxidation state increases. It may be pointed out here that nitrogen does not exhibit an oxidation state of +5, because it fails to expand its octet due to nonavailability of vacant *d*-orbitals.

(ii) ***Negative oxidation states* :** For example oxidation state of nitrogen is –3. The tendency of the elements to show –3 oxidation state decreases on moving down the group from *N* to *Bi*.

(10) **Catenation** (self linkage) **:** Elements of group 15 also show some tendency to exhibit catenation. This tendency goes on decreasing in moving down the group due to gradual decrease in their bond (*M–M*) energies.

Note : ✸ Out of the various allotropic forms of phosphorus, black phosphorus is a good conductor of electricity (similarity with graphite).

✸ Proteins, the building blocks of our body contain 16% of nitrogen in them.

✸ Radioactive phosphorus (P^{32}) is used in the treatment of leukemia (*blood cancer*).

✸ The disease caused by the constant touch with white phosphorus is called Phossy Jaw.

Chemical properties

(1) **Hydrides :** All the members form volatile hydrides of the type AH_3. All hydrides are pyramidal in shape. The bond angle decreases on moving down the group due to decrease in bond pair–bond pair repulsion.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107°	94°	92°	91°	90°

The decreasing order of basic strength of hydrides is as follows : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

The increasing order of boiling points is as follows : $PH_3 < AsH_3 < NH_3 < SbH_3$.

NH_3 is thermally most stable and BiH_3 is least stable. This is because in NH_3, $N-H$ covalent bond is the strongest due to small size of N atom. Hence, the *decomposition temperature of* NH_3 *will be the highest.* The increasing order of reducing character is as follows, $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.

Note : ✸ Diphosphine (P_2H_4) and hydrazine (N_2H_4) are other two important hydrides. Hydrazine a strong reducing agent, is used in organic synthesis and rocket fuels and is prepared as follows,

$$2NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O$$

✸ Phosphine is poisonous and does not form any complexes.

✸ Phosphine forms vortex rings of P_2O_5 in the form of white smoke when it comes in contact with air due to combustion. This is due to impurities of diphosphine (P_2H_4).

✸ Phosphine is used to prepare smoke screens in warfare. Calcium phosphide reacts with water to form phosphine which burns to give clouds of P_2O_5 which acts as smoke screens.

✸ Liquor ammonia is a concentrated solution of NH_3 in water.

✸ Ammonia will not burn in air, but burns in pure O_2 with a yellowish flame to produce N_2 and H_2O.

(2) **Halides :** The members of the family form trihalides (MX_3) and pentahalids (MX_5). The trihalides are sp^3-hybridized with distorted tetrahedral geometry and pyramidal shape while pentahalides are sp^3d-hybridized and are trigonal *bi*pyramidal in shape. The trihalides are hydrolysed by water and ease of hydrolysis decreases when we move down the group. Hence, NCl_3 is easily hydrolysed but $SbCl_3$ and $BiCl_3$ are partly and reversibly hydrolysed. NF_3 is not hydrolysed due to lack of vacant d-orbital with nitrogen. PF_3 and PF_5 are also not hydrolyzed because the P – F bond is stronger than P – O covalent bond. The hydrolysis products of the other halides are as follows : $NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$; $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$2AsCl_3 + 3H_2O \rightarrow As_2O_3 + 6HCl$; $SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$; $BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$

Their basic character follows this decreasing order as $NI_3 > NBr_3 > NCl_3 > NF_3$. Except NF_3, the trihalides of nitrogen are unstable and decompose with explosive violence. NF_3 is stable and inert. NCl_3 is highly explosive. Trifluorides and trichlorides of phosphorus and antimony act as Lewis acid. The acid strength decreases down the group. For example, acid strength of tri-chlorides is in the order ; $PCl_3 > AsCl_3 > SbCl_3$.

Nitrogen does not form pentahalides due to non-availability of vacant *d*-orbitals. The pentachloride of phosphorus is not very stable because axial bonds are longer (and hence weaker) than equitorial bond. Hence, PCl_5 decomposes to give PCl_3 and Cl_2; $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

The unstability of PCl_5 makes it a very good chlorinating agent. All pentahalides act as lewis acids since they can accept a lone pair of electron from halide ion.

Note : ✸ *Solid* PCl_5 *is an ionic compound consisting of* $[PCl_4]^+ [PCl_6]^-$, $[PCl_4]^+$ has a tetrahedral structure, while $[PCl_6]^-$ has an octahedral structure.

- ✸ *Since,* PCl_5 reacts readily with moisture it is kept in well stoppered bottles.
- ✸ PI_5 does not exist due to large size of *I* atoms and lesser electronegativity difference between phosphorus and iodine.
- ✸ Down the group, the tendency to form pentahalides decreases due to inert pair effect. e.g., BiF_5 *does not exist.*

(3) **Oxides :** These elements form oxides of the type X_2O_3, X_2O_4 and X_2O_5.

(i) ***Oxides of Nitrogen*** **:** Nitrogen forms two more oxides i.e., N_2O and NO and both are neutral. Nitrous oxide (N_2O) has a sweet taste and its main use is as anaesthetic. When inhaled in mild quantities it causes hysterical laughter so it is also called Laughing gas. Nitric oxide (*NO*) can be obtained by treating a mixture of sodium nitrite and ferrous sulphate with dil. H_2SO_4. Other oxides of nitrogen are : NO_2, N_2O_3, N_2O_5.

The acidic strength of oxides : $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$.

(ii) ***Oxides of phosphorus*** **:** P_4O_6 (Phosphorus trioxide), P_4O_{10} (Phosphorus pentaoxide).

(iii) ***Oxides of other elements*** **:** The decreasing order of stability of oxides of group 15 follows as,

$P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$

Except P_2O_5, all pentaoxides show oxidising properties. Also P_2O_5 is acidic in nature. N_2O_5 is the strongest oxidising agent. The nature of oxides of group 15 elements is as follows,

N_2O_3 and P_2O_3 (acidic) ; As_2O_3 and Sb_2O_3 (amphoteric) ; Bi_2O_3 (basic)

(4) **Oxyacids :** Oxyacids of nitrogen are $HNO_2, HNO_3, \underset{\text{(Nitroxylic acid)}}{H_4N_2O_4}$ and $\underset{\text{(Pernitric acid)}}{HNO_4}$, which are explosive.

Note : ✹ HNO_3 is called aqua fortis and prepared from air (Birkel and Eyde process) and NH_3 (Ostwald process). It acts as a strong oxidising agent.

Oxyacids of phosphorus are,

(i) H_3PO_2 (Hypophosphorus acid) : Reducing agent and monobasic.

(ii) H_3PO_3 (Orthophosphorus acid) : Reducing agent and dibasic.

(iii) H_3PO_4 (Orthophosphoric acid) : Weak tribasic acid.

(iv) $H_4P_2P_7$ (Pyrophosphoric acid) : It is obtained by heating H_3PO_4 to 220°C. It is tetrabasic.

(v) HPO_3 (Metaphosphoric acid) : It is formed by the dehydration of H_3PO_4 at 316°C. Also exists as a trimer and is monobasic.

(vi) $H_4P_2O_6$ (Hypophosphoric acid) : Tetrabasic

(vii) $H_4P_2O_5$ (Pyrophosphoric acid) : Dibasic acid

Anamalous behaviour of Nitrogen

Nitrogen is known to differ form other members of the family because of the following facts,

(i) Its small size (ii) Its high electronegativity (iii) Its high ionisation energy (iv) non-availability of *d*-orbital in the valence shell. (v) Its capacity to form $p\pi$-$p\pi$ multiple bonds.

The main points of difference are,

(1) Nitrogen is a gas (N_2) while other members are solids.

(2) Nitrogen is diatomic while other elements like phosphorus and arsenic form tetra-atomic molecules (P_4, As_4).

(3) Nitrogen form five oxides $(N_2O, NO, N_2O_3, N_2O_4$ and $N_2O_5)$ while other members of the family form two oxides (tri and pentaoxides).

(4) Hydrides of nitrogen show H-bonding while those of other elements do not.

(5) Nitrogen does not show pentacovalency because of absence of *d*-orbitals while all other elements show pentacovalency.

(6) Nitrogen dos not form complexes because of absence of d-orbitals while other elements show complex formation e.g., $[PCl_6]^-, [AsCl_6]^-$ etc.

(7) The hydride of nitrogen (NH_3) is highly basic in nature while the hydrides of other elements are slightly basic.

(8) Except for NF_3, other halides of nitrogen e.g., NCl_3, NBr_3 and NI_3 are unstable while the halides of other elements are fairly stable.

Nitrogen and its compounds

N_2 was discovered by ***Daniel Rutherford***. It is the first member of group 15 in the periodic table.

(1) **Occurrence :** N_2, occurs both in the free state as well as in the combined state. N_2 occurs in atmosphere to the extent of 78% by volume in free state. N_2 is present in many compounds such as potassium nitrate (nitre). Sodium nitrate (Chile salt peter) and many ammonium compounds. N_2 is an important constituent of proteins in plants and animals in combined state.

(2) **Preparation :** It is prepared by the following methods,

(i) ***Laboratory method*** : In the laboratory N_2 is prepared by heating an aqueous solution containing an equivalent amounts of NH_4Cl and $NaNO_2$.

$$NH_4Cl\,(aq.) + NaNO_2\,(aq.) \xrightarrow{\text{Heat}} N_2\,(g) + 2H_2O(l) + NaCl$$

(ii) ***Commercial preparation*** **:** Commercially N_2 is prepared by the fractional distillation of liquid air.

(3) **Physical properties :** N_2 is a colourless, odourless and tasteless gas. It is a non-toxic gas. It's vapour denstiy is 14. It has very low solubility in water.

(4) **Chemical properties**

(i) N_2 is neutral towards litmus. It is chemically unreactive at ordinary temp. It is neither combustible nor it supports combustion.

(ii) The N – N bond in N_2 molecule is a triple bond $(N \equiv N)$ with a bond distance of 109.8 *pm* and bond dissociation energy of 946 *kJ mol*$^{-1}$

(iii) ***Combination with compounds*** **:** N_2 combines with certain compounds on strong heating . eg

$$\underset{\text{Calsium carbide}}{CaC_2} + N_2 \xrightarrow{1300K} \underset{\text{Calsium cyanamide}}{CaCN_2 + C}\ ;\quad \underset{\text{Aluminium oxide}}{Al_2O_3} + N_2 + 3C \xrightarrow{2100K} \underset{\text{Al. nitride}}{2AlN} + 3CO$$

Both these compounds are hydrolysed on boiling with water to give ammonia.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3;\quad AlN + 3H_2O \longrightarrow Al\,(OH)_3 + NH_3$$

Therefore, calcium cyanamide is used as a fetilizer under the name nitrolim $(CaCN_2 + C)$

(5) **Uses of nitrogen :** N_2 is mainly used in the manufacture of compounds like $NH_3, HNO_3, CaCN_2$ etc.

(6) **Compounds of nitrogen**

(i) ***Hydrides of nitrogen***

Ammonia

Ammonia is the most important compound of nitrogen. It can be manufactured by Haber's process. In this process, a mixture of N_2 and H_2 in the ratio of 1 : 3 is passed over heated *Fe* at 650 –800*K* as catalyst and *Mo* as promotor, $N_2 + 3H_2 \rightleftharpoons 2NH_3,\ \Delta H = -93.6\,kJ\,mol^{-1}$ This is a reversible exothermic reaction.

Ammonia is prepared in the laboratory by heating ammonium salt (NH_4Cl) with a strong alkali like *NaOH*

$NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$ Ammonia can be dried by passing over quick lime (*CaO*). How ever, it can not be dried with dehydrating agents such as conc. H_2SO_4, P_2O_5 and anhydrous $CaCl_2$ because ammonia reacts with these compounds.

NH_3 is a colourless gas with a characteristic pungent smell called ammonical smell. It is highly soluble in water and its solution is basic in nature, $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

NH_3 is expected to have a tetrahedral geometry, but the lone pair distorts its geometry and the molecule has pyramidal geometry with N – H bond length of 101.7 *pm* and a bond angle of 107.5°. Liquid ammonia is widely used as a refrigerant due to its high heat of vaporization.

Hydrazine, (NH_2 – NH_2)

Hydrazine is prepared commercially by boiling aqueous ammonia or urea with sodium hypochloride in the presence of glue or gelatin.

$$2NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O$$

The resulting solution is concentrated and anhydrous hydrazine may be obtained by further distillation over barium oxide. Alternatively, the hydrazine present in the resulting solution is precipitated as sparingly soluble crystalline hydrazine sulphate on treatment with sulphuric acid, $NH_2NH_2 + H_2SO_4 \rightarrow N_2H_4.H_2SO_4$.

The precipitate is removed and treated with an alkali when hydrazine hydroxide $H_2N.NH_3OH$ is obtained. This is distilled under reduced pressure, over barium oxide to liberate free hydrazine.

$$H_2N.NH_3OH + BaO \xrightarrow{distil} NH_2NH_2 + Ba(OH)_2$$

Physical properties : Anhydrous hydrazine is a colourless fuming liquid (m.p. 2^0C and b.p. 114^0C) soluble in water in all proportions. It is also soluble in alcohol. It is strongly hygroscopic.

Chemical properties **:** It behaves as a diacid base, Thus with hydrochlorides it forms hydrazine monochloride $H_2N.NH_3Cl$ and hydrazine dichloride $ClH_3N.NH_3Cl$.

(i) Hydrazine burns in air with the evolution of heat. $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$ $\Delta H = -622$ kJ

The alkyl derivative of hydrazine are used as rocket fuels.

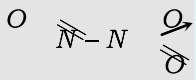
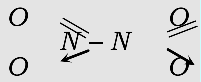
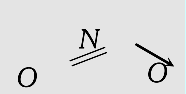
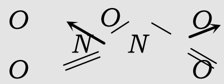
(ii) It reduces Fehling's solution to red cuprous oxide and iodates to iodides.

$$4Cu^{2+} + NH_2NH_4 \rightarrow 4Cu^{+} + 4H^{+} + N_2 \,;\, 2IO_3^{-} + 3NH_2NH_2 \rightarrow 2I^{-} + 6H_2O + 3N_2$$

Uses **:** Hydrazine is used as a rocket fuel. It is also used as a reagent in organic chemistry.

(ii) ***Oxides of nitrogen*** **:** Nitrogen combines with O_2 under different conditions to form a number of binary oxides which differ with respect to the oxidation state of the nitrogen atom. The important oxides are $N_2O, NO, N_2O_3, NO_2, N_2O_4$ and N_2O_5.

Oxides of Nitrogen

Oxide	Oxidation State of N	Physical appearance	Structure
Nitrous oxide (N_2O)	**+1**	**Colourless gas**	$N \equiv N \rightarrow O$
Nitric oxide (NO)	**+2**	**Colourless**	**N = O**
Dinitrogen trioxide (N_2O_3)	**+3**	**Blue solid**	
Dinitrogen tetraoxide (N_2O_4)	**+4**	**Colourless liquid**	
Nitrogen dioxide (NO_2)	**+4**	**Brown gas**	
Dinitrogen pentoxide (N_2O_5)	**+5**	**Colourless gas**	

Oxide of Nitrogen	Preparation
Nitrous Oxide (N_2O)	**By heating ammonium nitrate upto 240^0C** $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ **Collected over hot water.**
Nitrous oxide (NO)	**(a) By the action of cold dil. HNO_3 on copper turnings (Laboratory method)** $3Cu + 8$ dil. $HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ **(b) By the action of H_2SO_4 on a mixture of $FeSO_4$ and KNO_3 (4:1)**

$2KNO_3 + 5H_2SO_4 + 6FeSO_4 \rightarrow 2KHSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

(c) **By catalytic oxidation of ammonia.**

$$4NH_3 + 5O_2 \xrightarrow[850^0C]{Pt} 4NO + 6H_2O$$

Dinitrogen trioxide(N_2O_3) (a) **By the action of 50% HNO_3 on arsenious oxide.**

$$2HNO_3 + As_2O_3 + 2H_2O \rightarrow NO + NO_2 + 2H_3AsO_4$$
$$\downarrow 250\ K$$
$$N_2O_3$$

Nitrogen dioxide (NO_2) (a) **By heating nitrates of heavy metals, e.g., lead nitrate.**

$$2Pb(NO_3)_2 \xrightarrow{673\,K} 4NO_2 + 2PbO + 2O$$

(b) **By heating copper turnings with conc. HNO_3.**

$$Cu + 4\ \text{conc.}\ HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Dinitrogen pentoxide(N_2O5) (a) **By dehydrating HNO_3 with phosphorus pentoxide**

$$4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4\ HPO_3$$

(iii) **Oxyacids of nitrogen**

Oxyacids of nitrogen

Name of oxoacid	*M. F.*	*Structure*	*Oxidation State of N*	*Basicity*	*pK_a*	*Nature*
Hyponitrous acid	**$H_2N_2O_2$**		**+1**	**2(dibasic)**	**Very weak**	**Highly explosive**
Nitrous acid	**HNO_2**	$H-\underset{\underset{O}{\downarrow}}{N}=O$	**+3**	**1 (monobasic)**	**3.3**	**Unstable Weak acid**
Nitric acid	**HNO_3**	$H-O-\underset{\underset{O}{\downarrow}}{N}=O$	**+5**	**1 (monobasic)**	**-3.0**	**Stable, Strong acid**
Pernitric acid	**HNO_4**	$O=\underset{\underset{O}{\downarrow}}{N}-O-O-H$	**+5**	**1 (monobasic)**		**Unstable and explosive**

Phosphorus and its compounds

It is the second member of group 15 (VA) of the Periodic table. Due to larger size of P, it can not form stable $P\pi$ - $P\pi$ bonds with other phosphorous atoms where as nitrogen can form $P\pi$ - $P\pi$ bonds .

(1) **Occurence :** Phosphorous occurs mainly in the form of phosphate minerals in the crust of earth. Some of these are : (i) Phosphorite $Ca_3(PO_4)_2$, (ii) Fluorapatite $Ca_5(PO_4)_3F$, (iii) Chlorapatite $3Ca_3(PO_4)_2.CaCl_2$, (iv) Hydroxyapatite; $Ca_5(PO_4)_3OH$. Phosphates are essential constituents of plants and animals . It is mainly present in bones, which contains about 58% calcium phosphate.

(2) **Isolation :** Elemental phosphorus is isolated by heating the phosphorite rock with coke and sand in an electric furnace at about 1770*K*, $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow \underset{\text{Calicum silicate}}{6CaSiO_3} + P_4O_{10}$; $P_4O_{10} + 10C \longrightarrow P_4 + 10CO$

(3) **Allotropic forms of phosphorus** : Phosphorus exists in three main allotropic forms,

(i) White phosphorus, (ii) Red phosphorus, (iii) Black phosphorus

Some physical properties of three forms of phosphorus

Properties	*White phosphorus*	*Red phosphorus*	*Black phosphorus*
Colour	**White but turns yellow on exposure**	**Dark red**	**Black**

State	**Waxy solid**	**Brittle powder**	**Crystalline**
Density	**1.84g cm^{-3}**	**2.1 g cm^{-3}**	**2.69 g cm^{-3}**
Ignition temperature	**307 K**	**533 K**	**673 K**
Stability	**Less stable at ordinary temperature**	**More stable at ordinary temperature**	**Most stable**
Chemical reactivity	**Very reactive**	**Less reactive**	**Least reactive**

Compounds of phosphorus

(1) **Oxides and oxyacids of phosphorus :** Phosphorus is quite reactive and forms number of compounds in oxidation states of –3 , +3 and +5.

(i) ***Oxides* :** Phosphorus forms two common oxides namely, (a) phosphorus trioxide (P_4O_6) and (b) phosphorus penta oxide (P_4O_{10}).

(a) *Phosphorus (III) oxide* (P_4O_6) : It is formed when P is burnt in a limited supply of air, $P_4 + \underset{\text{(limited)}}{3O_2} \rightarrow P_4O_6$.

It is a crystalline solid with garlic odour. It dissolves in cold water to give phosphorous acid,

$P_4O_6 + \underset{\text{cold}}{6H_2O} \rightarrow \underset{\text{Phosphorous acid}}{4H_3PO_3}$, It is therefore, considered as anhydride of phosphorus acid.

With hot water, it gives phosphoric acid and inflammable phosphine, $P_4O_6 + 6H_2O\,(\text{hot}) \rightarrow \underset{\text{Phosphoric acid}}{3H_3PO_4} + PH_3$

It reacts vigorously with Cl_2 to form a mixture of phosphoryl chloride and meta phosphoryl chloride.

$$P_4O_6 + 4Cl_2 \rightarrow \underset{\text{Phosphoryl chloride}}{2POCl_3} + \underset{\text{Metaphosphoryl chloride}}{2PO_2Cl}$$

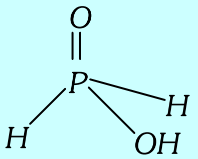
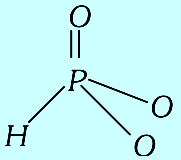
(b) *Phosphorus (V) oxide* (P_4O_{10}): It is prepared by heating white phosphorus in excess of air, $P_4 + 5O_2\,(excess) \rightarrow P_4O_{10}$. It is snowy white solid. It readily dissolves in cold water forming metaphosphoric acid. $P_4O_{10} + \underset{\text{(Cold)}}{2H_2O} \rightarrow \underset{\text{Metaphosphoric acid}}{4HPO_3}$. With hot water, it gives phosphoric acid, $P_4O_{10} + \underset{\text{Het}}{6H_2O} \rightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4}$.

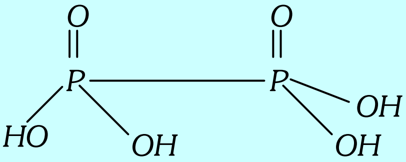
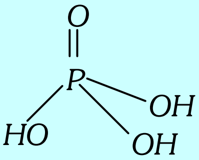
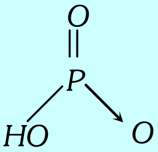
P_4O_{10} is a very strong dehydrating agent. It extracts water from many compounds including H_2SO_4 and HNO_3,

$$H_2SO_4 \xrightarrow[-H_2O]{P_4O_{10}} SO_3\,;\ 2HNO_3 \xrightarrow[-H_2O]{P_4O_{10}} N_2O_5\,;\ \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Methyl cyanide}}{CH_3CN}$$

(ii) ***Oxyacids of phosphorus* :** Phosphorus forms a number of oxyacids which differs in their structure and oxidation state of phosphorus.

Oxyacids of phosphorus

Name	***Formula***	***Oxidation state of P***	***Basicity***	***Structure***
Hypophosphorous acid	H_3PO_2	**+1**	**Monobasic**	
Phosphorous acid	H_3PO_3	**+3**	**Dibasic**	

Hypophosphoric acid	$H_4P_2O_6$	**+4**	**Tetrabasic**	
Orthophosphoric acid	H_3PO_4	**+5**	**Tribasic**	
Metaphosphoric acid	$(HPO_3)_n$	**+5**	**Monobasic**	
Pyrophospric acid **(Diphosphoric acid).**	$H_4P_2O_7$	**+5**	**Tetrabasic**