

Some p -Block Elements - I

5.1 Introduction

- General introduction of p-Block Elements. Group 13 elements- electronic configuration-occurrence, Variation in properties, oxidation states, Trends in chemical reactivities, Anomalous behaviour of first element in the group.

5.2 Boron - physical and chemical properties.

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5.4 Properties of Aluminium, uses and chemical reactions with acids and bases.

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5.1 Introduction

The elements (except He) having outermost valence shell electronic configuration **$ns^2 np^1$ to $ns^2 np^6$** are called p-Block Elements where $n = 2$ to 6 . Since p-orbitals can accommodate maximum six electrons, there are six groups of p-block elements. In periodic table group 13 to 18 are called p-block elements. The p-block elements are situated on the right side to the transitional elements in periodic table. Due to difference in inner core electronic configuration, the elements show variation in physical and chemical properties. The first element of the group shows anomalous behaviour in some properties from the other elements of that group. In this unit, let us study the elements of group 13 (IIIA) and group 14 (IVA). The first element of group 13 and 14 are Boron and Carbon respectively, so these groups are also known as Boron group and Carbon group respectively. Due to catenation properties of carbon, carbon forms number of organic compounds which are included in Organic Chemistry. Now, we shall study the general introduction to p-block elements.

General Introduction to p-Block Elements : Group 13 to 18 means p-block elements show variation in physical and chemical properties. Although their trends in some properties can be indicated as given below.

We shall study in detail some properties of the elements of group 13 and 14 after the general introduction of p-block elements.

Group 13 elements (Boron group) :
Electronic configuration : The group 13 includes elements. Boron (B), Aluminium (Al),

Gallium (Ga), Indium (In) and Thallium (Tl). The valence shell electronic configuration is ns^2, np^1 where $n = 2$ to 6. Hence, there are two electrons in s orbital and one electron in p orbital, therefore, in total three electrons are there. The electronic configurations of elements of group 13 are as shown in table 5.3.

Table 5.3 Electronic Configuration of Elements of Group 13

Element	Atomic No.	Electronic Configuration	
		Complete	With inert gas core
Boron (B)	5	$1s^2 2s^2 2p^1$	[He] $2s^2 2p^1$
Aluminium (Al)	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	[Ne] $3s^2 3p^1$
Gallium (Ga)	31	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	[Ar] $3d^{10} 4s^2 4p^1$
Indium (In)	49	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ $4d^{10} 5s^2 5p^1$	[Kr] $4d^{10} 5s^2 5p^1$
Thallium (Tl)	81	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ $4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$

Occurrence : The abundance of boron in earth's crust is less than 0.0001% by weight. It occurs in ore form. The main important ores of boron are

Borax : $(Na_2B_4O_7 \cdot 10H_2O)$,

Kernite : $(Na_2B_4O_7 \cdot 4H_2O)$,

Colemanite : $(Ca_2B_6O_{11} \cdot 2H_2O)$

Orthoboric acid : (H_3BO_3) .

The boron is found in California (USA) and in Turkey State. While in India it is found as borax in Puga valley of Ladakh region in Kashmir and also in Sambhar lake of Rajasthan. Aluminium is the third most abundant element found in earth's crust, while the first is oxygen (45.5% by weight), the second is silicon (27.7% by weight) and the third is aluminium (8.3% by weight). Some important ores of aluminium are given below :

Bauxite : $Al_2O_3 \cdot xH_2O$

Orthoclase : $KAlSi_3O_8$

Cryolite : Na_3AlF_6

Corundum : Al_2O_3

Beryl : $Be_3Al_2Si_6O_{18}$

Mica : $KAl_2(Si_3AlO_{10})(OH)_2$

The important ores of aluminium are bauxite and cryolite. In India mica is found in Madhya Pradesh, Karnataka, Orissa and Jammu. India is the world's largest supplier of mica. Gallium, Indium and Thallium are less abundant. Gallium (0.1 – 1%) is found in the mineral Germanite which is a complex sulphide of Zn, Cu, Ge and As, while the traces of Indium are found in sulphide ore of zinc.

Variation in properties : Variation in some properties are observed in elements of Boron group which are as shown in Table 5.4.

Table 5.4 Some physical properties of group 13 elements

Physical Property	Elements					
	B	Al	Ga	In	Tl	
Atomic number	5	13	31	49	81	
Atomic mass	10.81	26.98	69.72	114.82	204.38	
Atomic radius (pm)	85	143	135	167	170	
Ionic radius m^{3+} (pm)	27	53.5	62.0	80.0	88.5	
Ionic radius m^{1+} (pm)	—	—	120	140	150	
Ionisation enthalpy (kJmol^{-1}) (I)	800	577	578	558	590	
	(II)	2427	1816	1979	1820	1971
	(III)	3659	2744	2962	2704	2877
	(IV)	25026	11578	6200	5200	—
Electronegativity (Pauling scale)	2.0	1.5	1.6	1.7	1.8	
Density (g cm^{-3})	2.35	2.70	5.90	7.31	11.85	
Melting point (K)	2453	933	303	430	576	
Boiling point (K)	3923	2740	2676	2353	1730	
$E_{(V)}^0$ 298 K $M_{(aq)}^{3+} + 3e^- \rightarrow M_{(s)}$	—	− 1.66	− 0.56	− 0.34	+ 1.26	
$E_{(V)}^0$ 298 K $M_{(aq)}^+ + e^- \rightarrow M_{(s)}$	—	+ 0.55	—	− 0.18	− 0.34	

pm = Picometer = 10^{-12} meter

(i) Atomic radii and ionic radii :

In elements of boron group as the atomic number increases, new electron shell gets added and so the distance between the nucleus and outermost orbital having electron increases; hence the atomic radius increases. Similar trends can be observed in ionic radius. Anyhow, there is exception in atomic radius of Al and Ga. The atomic radius of Al (143 pm) is more than atomic radius Ga (135 pm) because there is no d-orbital in electronic configuration of Al while there is d-orbital in electronic configuration of Ga. As the d-orbitals are large in size, hence the magnitude of screening effect decreases with nucleus by electrons present in them. Now, the nuclear charge of Gallium is high; as a result the attraction towards the nucleus by outermost orbital electron increases. Hence, atomic radius of Ga is less than that of Al. However a regular trend is observed in ionic radii.

(ii) Ionisation enthalpy :

The order of first ionisation enthalpy ($\Delta_i H_1$) for boron group elements is **B > Al < Ga > In < Tl**. The first ionisation enthalpy of Al is less than that of B because in Al the new valence shell is added and so the atomic size of Al increases which in turn increases the screening effect in Al that results in decreasing attractive forces towards the nucleus by the outermost orbital electrons. So first ionisation enthalpy is less than that of B, but the first ionisation enthalpy of Ga is little more (1 kJ mol^{-1}) compared to Al because in Ga the addition of new valence shell and also presence of 3d-orbital, which decreases the screening effect. This means it does not remain more effective so in Ga the attractive forces of electron towards the nucleus increases and hence, the first ionisation enthalpy is little more. In the same way Indium possesses 4d-orbital, which reduces the magnitude of screening effect and

increase in nuclear charge ($49 - 31 = 18$ units) which is overweighing the screening effect towards nucleus by the electron arranged in outermost orbital is less compared to Ga. Hence, the first ionisation enthalpy of Indium is less compared to that of Ga. Now, the first ionisation enthalpy of Tl is higher than that of Indium because in Tl as the nuclear charge increases ($81 - 49 = 32$ units) and also presence of 4f and 5d-orbitals still the decreases in reactivity of screening effect is overweighed by nuclear charge. **As a result force of attraction towards nucleus by the outermost orbital electrons increases.** So, the first ionisation enthalpy increases.

Moreover, the value of second ionisation enthalpy ($\Delta_i H_2$) and third ionisation enthalpy ($\Delta_i H_3$) are very high because when first electron is removed, then the size of ion decreases and the effective nuclear charge increases and so the force of attraction towards the nucleus increases. Moreover, the second and third electrons are removed from s-type orbital which has more attractive forces towards the nucleus, so more energy is required to remove electron from them. Hence the value of $\Delta_i H_2$ and $\Delta_i H_3$ are very high.

(iii) Metallic character : The elements of group 13 show variation in metallic character. The metallic character is higher in Al than that of B. So Al is good conductor of heat and electricity. The reduction potential values go on increasing from Al to Tl, so the values of electropositivity decreases as a result, metallic character decreases. Thus, B is non-metal, while Al is metal and in Indium, Ga and Tl the metallic character decreases successively. So Tl possesses non-metallic character.

(iv) Electronegativity : On moving down the elements of group 13, electronegativity decreases suddenly from B to Al and after that it increases gradually as moving from Al to Tl, because the atomic volume increases as the atomic number increases. As the atomic volume increases, the attractive force for electron towards nucleus decreases.

(v) Melting points and Boiling points :

The elements of group 13 show irregular trends in melting points, viz the melting point of B is the highest, while melting point of Al is low and melting point of Ga is the lowest; the melting point of In is more than that of Ga and Tl has little more. The order of melting points of group 13 elements are in order **B > Al > Ga < In < Tl**. The crystal structure of element is responsible for this. The boiling points of the elements of group 13 on moving down the group show regular trend. As the atomic number goes on increasing the boiling point decreases regularly.

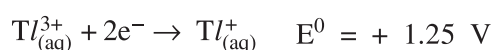
(vi) Density : The density goes on increasing as the atomic number increases for the elements of group 13 because as the atomic number increases the volume increases but the increase in atomic mass is more compared to volume and hence, density increases.

(vii) Characteristic as reducing agent :

The characteristic as reducing agent goes on decreasing on moving down the group, which means moving from Al to Tl, because the values of reduction potential increase from Al to Tl and so the reduction power decreases and the characteristic as reducing agent also decreases.

(viii) Nature of compounds : The elements of group 13 have a decreasing tendency to form covalent bond compounds. The elements of group 13 have increasing tendency to form ionic compounds because the size of B is small and to form B^{3+} ion the sum of three ionisation enthalpy values ($\Delta_i H_1 + \Delta_i H_2 + \Delta_i H_3$) is high, so boron does not form B^{3+} ion easily and hence, it forms covalent bond. Now, as the atomic number goes on increasing the atomic size also increases and total ionisation enthalpy value decreases. So, the tendency to form covalent bond decreases and tendency to form ionic bond increases. Boron forms compounds having covalent bond, while Al forms covalent bond and also to some extent has tendency to form ionic bond. While in Ga, In and Tl as the atomic number increases, the tendency to form compounds having ionic bond becomes prominent.

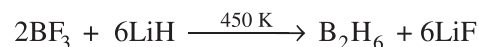
Oxidation state : In the electronic configurations of elements of group 13 they have two electrons in s-type orbital and one electron in p-type orbitals, so total three electrons in outermost orbital, hence it possesses +3 oxidation state. The oxidation state of boron and aluminium is +3 while Ga, In and Tl have both +1 and +3 oxidation states. As the atomic number is increasing the stability of +3 oxidation state decreases and stability of +1 oxidation state increases because on going down the group as the atomic number is increasing the tendency of s-electron to participate in bond formation decreases which means ns^2 electron of Ga, In and Tl remain paired because of intervening of d and f orbitals. The screening effect of ns^2 orbitals becomes poor and inert pair effect becomes more predominant as atomic number increases and so the ns^2 orbital electrons are more strongly attracted towards the nucleus and therefore, it is difficult to remove that electron, so the stability of oxidation state +1 increases and that of +3 oxidation state decreases. The stability of oxidation state is supported by following reaction.



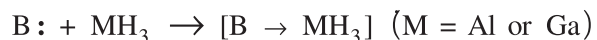
The reaction indicates that the +1 oxidation state is more stable than + 3 because **the reduction potential of this reaction has positive value.**

Trends in Chemical Reactivity : The variation is observed in chemical reactivity of group 13 elements, because in the electronic configuration of B and Al they have $ns^2 np^1$ type electronic configuration after the noble gas electronic configuration. While in electronic configuration of Ga and In, the intervening of d-orbital after the noble gas electronic configuration is followed by $ns^2 np^1$ -type electronic configuration. Now in electronic configuration of Tl there is intervening of both d and f-type orbitals and after that $ns^2 np^1$ type electronic configuration takes place so that chemical reactivity of group 13 elements is as given below :

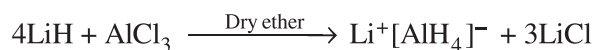
(i) Hydride compounds : Elements of group 13 do not combine directly with dihydrogen but they combine indirectly with dihydrogen to form hydride compounds e.g. Boron hydride is obtained by reaction of BF_3 with LiH.



Boron forms number of hydrides, most of hydrides having molecular formula, $B_n H_{n+4}$ and $B_n H_{n+6}$ which is known as **Borane**. Other hydride elements are polymeric e.g. $(AlH_3)_n$, $(GaH_3)_n$ and $(InH_3)_n$ their structure contains M.....H.....M bridge (M = Al, Ga, In). The stability of hydrides decreases with increasing atomic number and so thallium hydride is quite unstable. These hydrides are Lewis acids which readily combine with strong Lewis base (B :).



In addition to these polymeric hydrides, Al or Ga also form complex tetrahydrides e.g. lithium tetrahydro aluminate (III). This is known as lithium aluminium hydride, which can be obtained by the reaction of LiH and $AlCl_3$ in presence of dry ether.



Particularly in organic reaction $LiAlH_4$ is used as a reducing agent.

(ii) Halide Compounds : Elements of group 13 form MX_3 type trihalides where X = F, Cl, Br and I. TlI_3 is unknown. Due to small size and high ionisation enthalpy boron atom has tendency to form covalent bond by sp^2 hybridisation and form trihalide. The trihalides BX_3 act as Lewis acid and the order of its strength is $BI_3 > BBr_3 > BCl_3 > BF_3$. In vapour form $AlCl_3$ exists in dimer form due to bridging of chlorine atoms and its structure is as shown in Figure 5.1.

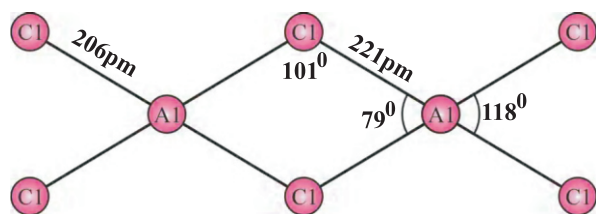


Fig 5.1 Structure of Al_2Cl_6 (dimer) (gaseous state)

AlCl_3 is Lewis acid. **BF_3 and AlCl_3 are strong Lewis acids and therefore used as a catalyst in Friedel and Crafts alkylation reaction and electrophilic aromatic substitution reaction.**

Ga and Tl also form MX type halides where $M = \text{Cl}, \text{Br}, \text{I}$. The stability of MX type halide increases as the atomic number increases, so that TlX is more stable than GaX.

(iii) Oxide and Hydroxide Compounds :

The group 13 elements form oxides having formula M_2O_3 and hydroxide having formula $\text{M}(\text{OH})_3$. As the atomic number of element goes on increasing the acidic character of oxide and the hydroxide decreases, and at the same time the basic character goes on increasing .e.g. oxide and hydroxide of boron are acidic, those of Al and Ga are amphoteric and In are basic while those of Tl are strong base.

(iv) Complex and Double Salt Compounds : In elements of group 13, in the electronic configuration of boron the d-orbital is absent, so it forms only tetrahedral complex like $[\text{BH}_4]^-$, $[\text{BI}_4]^-$, etc. The electronic configuration of Al, Ga, In and Tl have d-orbital (in Al it is in form of $3d^0$), so they form octahedral complexes like $[\text{AlF}_6]^{3-}$, $[\text{GaCl}_6]^{3-}$, $[\text{InCl}_6]^{3-}$, and $[\text{TlCl}_6]^{3-}$, with octahedral aqua ions can be described as $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, (where $M = \text{Al}, \text{Ga}, \text{In}, \text{and Tl}$). Aluminium sulphate reacts with sulphate of NH_4^+ and alkali metal ions and form double salts known as alums with formula $\text{M}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ or $\text{MAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (where $M = \text{Na}^+, \text{K}^+, \text{Rb}^+ \text{ and } \text{NH}_4^+$). The uses of this **double salts are to change hard water to soft water and as a mordant in chemicals of colour dye.**

The anomalous behaviour of the first element (boron) of group 13 : The first element of group 13, boron shows anomalous behaviour. For example,

- Boron is non-metal while other elements except boron show metallic characters.
- Boron trihalide is monomeric while in other elements trihalides exist as a dimer or polymer.
- Boron hydride is monomeric while in other elements hydrides exist as a dimer or polymer.
- Boron does not react with water while other elements react with water and form oxides.
- Oxides and hydroxides of boron are acidic while the oxides and hydroxides of other elements are amphoteric or basic.
- Except boron, trihalides of other elements on hydrolysis result in complex ions.

5.2 Physical and Chemical Properties of Boron (Chemical Reactions)

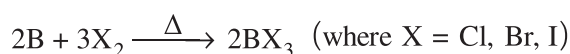
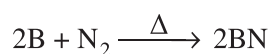
Physical properties of boron :

- Boron is extremely hard substance. In order of hardness, it comes next to diamond.
- The melting point and boiling point of boron are very high.
- Boron is poor conductor of heat and electricity.
- Boron has two isotopes ^{10}B and ^{11}B and its relative abundances is 20% and 80% respectively.
- Boron has two allotropes. The colour of amorphous form is dark brown whereas the crystalline form is found in black metallic luster.

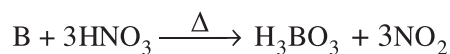
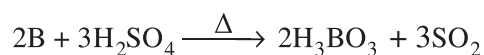
Chemical properties (Chemical reactions) : Boron is chemically less reactive. It is almost inert towards normal chemical

reagents at normal temperature, but however, it reacts with strong oxidising agent and with some typical reagents as given below :

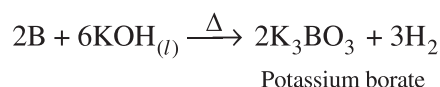
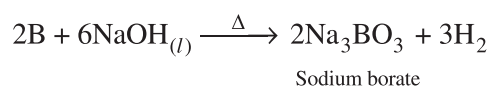
- (i) **Reaction with non-metal :** Non-metal dinitrogen, dioxygen and dihalogen react with boron at high temperature.



- (ii) **Reaction with acid :** Boron does not react with HCl but it reacts with con. HNO_3 and H_2SO_4 and oxidises into boric acid.



- (iii) **Reaction with alkali :** Boron reacts with fused alkalis like NaOH and KOH and converts into corresponding borates and liberates dihydrogen.



- (iv) **Reaction with metal :** Boron reacts with some metals on heating and converts in to borides which are very hard and solid substance having high melting point. e.g.



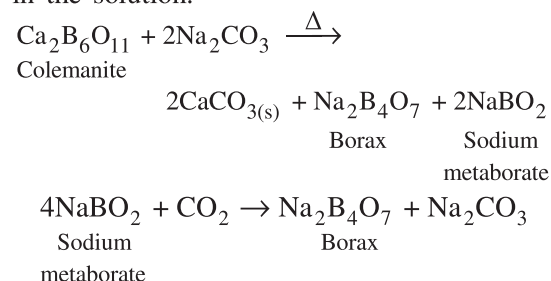
5.3 Some Important Compounds of Boron

(1) **Borax Powder ($Na_2B_4O_7$) :** The important compound of boron is borax or **sodium tetraborate ($Na_2B_4O_7$)**. The impure form of borax is Tincal which contains 55% borax. It is found in certain dried up lakes of India, Tibet, Sri Lanka and California.

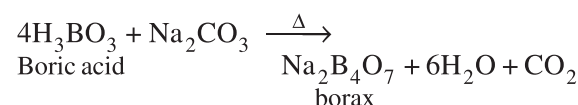
Preparation :

(i) **Borax from Tincal :** Tincal is dissolved in water and boiled. On filtration insoluble impurities like sand, clay etc are removed. While borax remains soluble in solution, the solution is concentrated, and on cooling crystals of borax separates out.

(ii) **Borax from colemanite :** On boiling mineral colemanite with sodium carbonate, the borax, $CaCO_3$ and sodium metaborate are formed. The $CaCO_3$ which is obtained as insoluble so it is in form of precipitates and removed by filtration and solution is obtained. Concentrate the solution and on cooling crystals of borax are obtained. Mother liquor still having sodium metaborate is converted to borax by passing CO_2 in the solution.



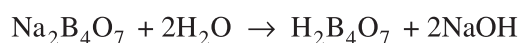
(iii) **Borax from boric acid :** On neutralization of boric acid by Na_2CO_3 borax is obtained.



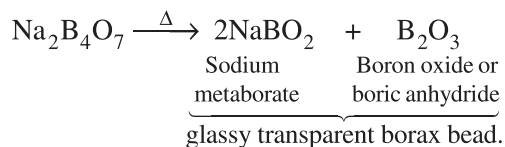
The mixture is heated and on cooling borax separates as crystals.

Properties of Borax :

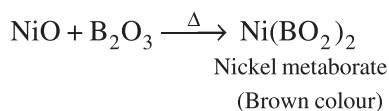
- (1) Borax is found in three forms. (a) **Prismatic $Na_2B_4O_7 \cdot 10H_2O$** (b) **Octahedral $Na_2B_4O_7 \cdot 5H_2O$** (c) **Borax glass $Na_2B_4O_7$**
- (2) Borax is white, crystalline solid substance sparingly soluble in cold water and highly soluble in hot water.
- (3) Aqueous solution of borax is basic due to its hydrolysis.



- (4) On heating borax, due to its decomposition swells and loses water of crystallization and becomes anhydrous; on further heating it melts and forms glassy, transparent bead known as borax bead.



- (5) When the glassy, transparent bead is dipped in coloured ions like Ni^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} and heated, they are converted into their metaborates respectively and they are colored and their colours are brown, blue, green and pink respectively e.g.



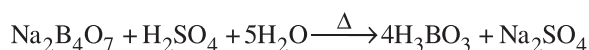
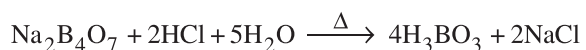
Uses :

- (i) It is used in laboratory to perform borax bead test in qualitative analysis.
- (ii) It is used in manufacturing of enamels and glazing of earthen pots.
- (iii) Used in preparation of candles.
- (iv) Due to its antiseptic properties it is used in preparation of medicinal soap.
- (v) It is used in making optical glass.
- (vi) Used in softening of hard water.

(2) Boric acid (H_3BO_3) : Its trivial name is **orthoboric acid**.

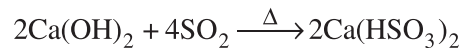
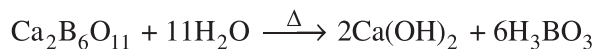
Preparation :

(i) Boric acid from borax : Acidifying the aqueous solution of borax by adding HCl or H_2SO_4 , Boric acid is obtained which on concentration and cooling gives crystals of boric acid.

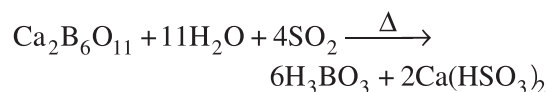


(ii) Boric acid from mineral colemanites : Powder the mineral colemanite, add water and boil it. On passing SO_2 gas boric acid and calcium bisulphite are obtained. Calcium bisulphite is highly soluble in water while

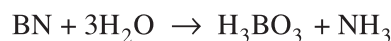
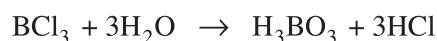
boric acid is sparingly soluble, so on cooling boric acid gets separated.



net reaction :

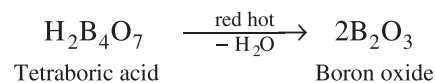
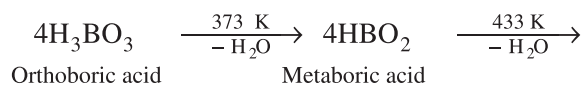


(iii) Boric acid from hydrolysis of boron compounds : On hydrolysis of BCl_3 and BN , they give boric acid.

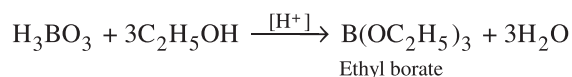


Properties :

- (i) Boric acid is a white crystalline solid substance with a soft soapy touch.
- (ii) It is sparingly soluble in cold water but fairly soluble in hot water.
- (iii) At different temperatures the effects of heat on it are as given below :



- (iv) It is a weak monobasic acid and acts as a Lewis acid.
- (v) In presence of H_2SO_4 it reacts with ethanol and form ethyl borate.



- (vi) The structure of boric acid having H-bond is given in Fig. 5.2.

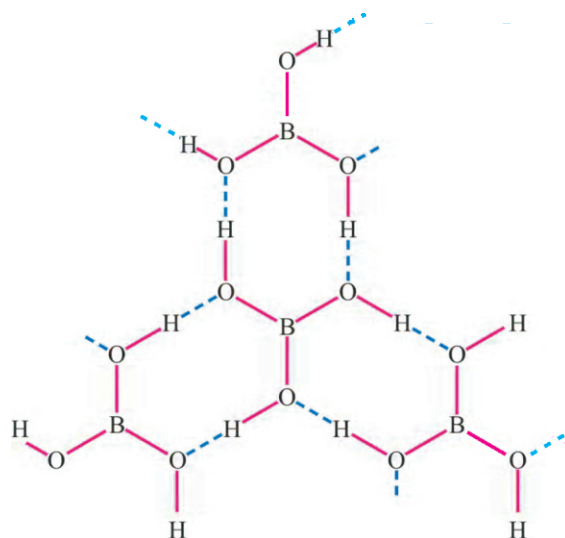


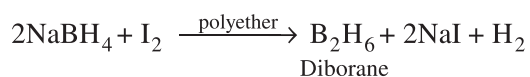
Fig. 5.2 Structure of boric acid having H-bond
(The dotted lines represent hydrogen bonds)

Uses :

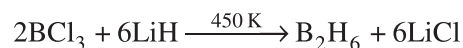
- In food industry it is used as a preservative for the preservation of food.
- Used in the preparation of pigments and borax.
- It is used (in medicine) as an eye wash.
- Used in the manufacturing of enamels and pottery glazes.

(3) Boron hydrides : Boron forms a number of hydride compounds having general formula B_nH_{n+4} and B_nH_{n+6} . **Boron hydrides are also called Boranes.** B_2H_6 (diborane) is a boron hydride.

Preparation of Diborane (B_2H_6) : In the laboratory, diborane is prepared by the reaction of iodine with sodium-borohydride in the presence of polyether as a solvent.

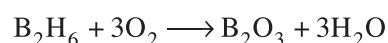


On an industrial scale, diborane is obtained by the reaction of boron trifluoride or boron trichloride with lithium hydride at 450 K temperature.



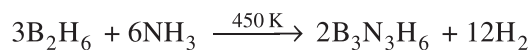
Properties :

- Diborane is colourless and highly toxic gas.
- Diborane has strong affinity for O_2 and therefore it catches fire spontaneously on exposure to air and releases energy. The heat of combustion is very high.

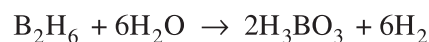


$$\Delta H = -2008 \text{ kJ mol}^{-1}$$

- At 450 K temperature, if diborane is heated with NH_3 , forms **Borazine ($B_3N_3H_6$)** having structure like benzene and hence it is also called inorganic benzene.



- Diborane on hydrolysis gives boric acid and liberates H_2 gas.



- The structure of diborane is given in Figure 5.3.

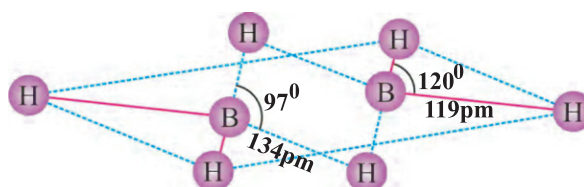


Fig. 5.3 The structure of diborane, B_2H_6

Uses of Boron and its Compounds :

- Isotope of boron ^{10}B has ability to absorb neutrons and therefore used as metal borides, in nuclear reactor as a **protective shield** and the **controlling rods** and also used in chemotherapy to cure cancer.
- Boron fibres are used in making light composite materials for air craft industries.
- Boron and boric acid are used in manufacturing of **heat resistant borosilicate pyrex glass**. They are also used in metallurgy as a **flux for soldering** metals.

- (iv) Borax is used for making **porcelain enamels**.
- (v) In laboratory, borax powder is used in **borax bead test** for detection of coloured metallic ions.
- (vi) Aqueous solution of boric acid is used as **a mild antiseptic**.
- (vii) In leather industry borax is used for cleaning **skin (leather)** while in food industry it is used as a **preservative**.
- (viii) The heat of combustion for diborane is very high, so it is used as a high energy fuel.

5.4 Properties of Aluminium

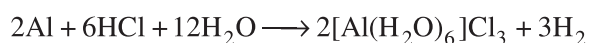
- (i) Aluminium is a light, silvery white metal.
- (ii) It has high **tensile strength**, high electrical and thermal conductivity. (twice than that of Cu).
- (iii) It is highly electropositive.
- (iv) It readily reacts with O₂ and forms a protective layer of Al₂O₃ on its surface, which makes it passive.

Uses :

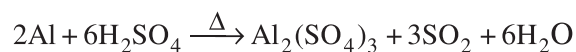
- (i) Aluminium is used extensively in industries and in daily life.
- (ii) It forms useful alloys with Cu, Mn, Mg, Si and Zn.
- (iii) Al and its alloys are used in making utensils, aeroplane parts and also in some preparations.
- (iv) It is used in **Aluminothermite process** for obtaining the chromium and manganese metals from their oxides.
- (v) Aluminium is used as a **strong reducing agent**.

Reaction of Aluminium with acids and bases : Aluminium reacts both with acid and base. Thus, it is amphoteric.

With acid : Aluminium dissolves in dil HCl, dil H₂SO₄ and liberates H₂ gas slowly.

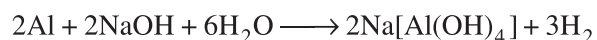


On heating with concentrated H₂SO₄ aluminium produces SO₂ gas.



Aluminium reacts with concentrated HNO₃ and forms inactive, passive protective layer of Al₂O₃ on surface which stops the further reaction on its surface.

Reaction with base : Aluminium dissolves in strong alkali (NaOH or KOH) to form sodium aluminate or potassium aluminate and H₂ gas is evolved.



5.5 General Introduction of Group 14 Elements

Group 14 includes the elements. Carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn) and Lead (Pb). The first element of this group is carbon, so they are also called carbon group elements. **Carbon shows catenation characteristic due to its small size, high electronegativity** and very high carbon-carbon bond enthalpy. Due to typical character of catenation, it forms chain and cyclic compounds having carbon-carbon σ-bond as well as π-bond. Moreover, one carbon can form one or more than one bond with another carbon or with other atoms. also e.g. C = C, C ≡ C, C - O, C = O, C - N, C = N, C ≡ N and compounds having such type of bonding are studied in Organic Chemistry. Compounds of carbon with metals, metalloids and with non-metals are called binary inorganic compounds. The compounds like calcium carbide, silicon carbide, carbon monoxide, carbon dioxide, hydrogen cyanide are inorganic compounds. Organic compounds have their contribution in the fields like living organism, non-living organism, medicine, plastic etc.

Electronic Configuration : Carbon group elements have **electronic configuration ns² np² in outermost valence orbital** where n = 2 to 6. The electronic configurations of carbon group elements are given in Table 5.5.

Table 5.5 Electronic Configurations of Elements of Group 14

Element	Atomic No.	Electronic Configuration	
		Complete	With inert gas core
Carbon (C)	6	$1s^2 2s^2 2p_x^1 2p_y^1$	$[\text{He}] 2s^2 2p_x^1 2p_y^1$
Silicon (Si)	14	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$	$[\text{Ne}] 3s^2 3p_x^1 3p_y^1$
Germanium(Ge)	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p_x^1 p_y^1$	$[\text{Ar}] 3d^{10} 4s^2 4p_x^1 4p_y^1$
Tin (Sn)	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ $5s^2 5p_x^1 5p_y^1$	$[\text{Kr}] 4d^{10} 5s^2 5p_x^1 5p_y^1$
Lead (Pb)	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ $4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p_x^1 6p_y^1$	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2$ $6p_x^1 6p_y^1$

Occurrence : Carbon is the seventeenth most abundant element by weight out of elements obtained from the earth's crust. In earth's crust it occurs in form of coal, petroleum and metal carbonate of electropositive metals. In atmosphere it is in the form of CO_2 . All living organisms contain carbon in form of organic compounds. Silicon is present in nature in the form of silica (SiO_2) and silicates. Moreover it is an important component used in ceramics, glass and cement. Silicon is the second most abundant (27.7 %) by

weight in the earth's crust. Germanium occurs as a trace element and is mainly recovered from the flue dust arising from roasting of zinc ores. Tin and Lead are found in nature in the amount 2 ppm and 13 ppm respectively. **Galena (PbS)** is the principal ore of lead. Found along with **zinc blende (ZnS)**. Other ores of lead are **anglesite (PbSO_4)** and **cerussite (PbCO_3)**

Variation in properties : Group 14 elements have variation in some properties as shown in Table 5.6.

Table 5.6 Some Physical Properties of Group 14 Elements

Property	Elements					
	C	Si	Ge	Sn	Pb	
Atomic number	6	14	32	50	82	
Atomic mass	12.01	28.09	72.60	118.71	207.2	
Covalent radius / for M(II) state	77	118	122	140	146	
Ionic radius (M^{4+})(pm)	—	40	53	69	78	
Ionic radius (M^{2+}) (pm)	—	—	73	118	119	
Ionisation enthalpy (M^+) (kJ mol ⁻¹)	(I)	1086	786	761	708	715
	(II)	2352	1577	1537	1411	1450
	(III)	4620	3228	3300	2942	3081
	(IV)	6220	4354	4409	3929	4082

Electronegativity (Pauling scale)	2.5	1.8	1.8	1.8	1.9
Density (g cm⁻³) at 293 K	3.51 (for diamond)	2.34	5.32	7.26	11.34
	2.21 (for graphite)				
Melting point (K)	4373	1693	1218	505	600
Boiling point (K)	—	3550	3123	2896	2024
Electrical resistivity (ohm cm)	10 ¹⁴ –10 ¹⁶	50	50	10 ⁻⁵	2 × 10 ⁻⁵

(i) Atomic radii : On moving down the group the atomic radii of group 14 elements go on increasing as the atomic number increases, but from silicon and onwards, Ge, Sn and Pb due to intervening of d and f - orbitals in electronic configuration and because of the ineffective shielding effect the atomic radii increases gradually.

(ii) Ionisation enthalpy : On moving down in the group 14 as the atomic number increases, the order of change one notices in ionisation enthalpy is **C > Si > Ge > Sn < Pb**. From C to Sn as the atomic number increases the atomic size also increases and hence the ionisation enthalpy decreases but instead of decreasing the ionisation enthalpy of Pb slightly increases because of the intervening of d and f- both types of orbitals in electronic configuration of Pb. So the force of attraction towards the nucleus increases due to poor shielding effect of that orbital and hence, ionisation enthalpy decreases.

(iii) Electropositivity (Metallic character) : On moving down the group 14 the electropositivity increases, so the carbon behaves totally as non-metal. Silicon is essentially a non-metal and Germanium is metalloid (having pronounced metallic character) while tin and lead are typical metals. Elements of group 14 are less electropositive, hence, the metallic character observed is less.

(iv) Electronegativity : The elements of group 14 are more electronegative than elements of group 13. The electronegativity decreases as the atomic number increases due to increase in the atomic size. But it remains almost same from Si to Pb.

(v) Melting points and Boiling points :

The melting points and boiling points of group 14 elements are much higher than those of group 13 elements, because elements of group 14 form four covalent bonds, hence there exists a strong binding between the atoms. Therefore the melting points and boiling points are higher. The intermolecular forces decrease as the atomic number increases in group 14 and therefore, melting point and boiling point also decrease.

(vi) Density : On moving down in the elements of group 14, that means from carbon to lead, regular increase in density is seen because there is a greater increase in atomic mass than increase in atomic size, so the density increases.

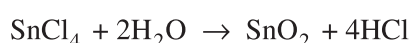
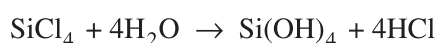
(vii) Catenation : Group 14 elements show catenation property in the order **C >> Si > Ge ≈ Sn >> Pb**. Because the atomic size of carbon is less and electronegativity is higher, further the C – C bond enthalpy is also very high, so it indicates maximum catenation properties at the same time remarkable decrease in silicon.

(viii) Allotropy : Elements of group 14 show allotropy. Carbon has number of allotropic forms out of which **diamond, graphite and fullerene** are the crystalline forms of carbon. Tin has two allotropes, **white tin or β-tin**. It gets stable at room temperature whereas **grey tin or α-tin** remains unstable, and it can be obtained from β-tin at 286 K temperature.

white tin (β -tin) $\xrightleftharpoons{286\text{ K}}$ grey tin (α -tin)

Oxidation states and trends in chemical reactivity : Group 14 elements have outermost valence shell electronic configuration $ns^2 np^2$ and hence, these elements have common oxidation state +4. Now due to intervening of d and f-orbitals in Ge, Sn and Pb the inert pair effect becomes more and more prominent so they all show oxidation state +2 with +4 and the stability of +2 oxidation state increases in order, which can be given as $\text{Ge} < \text{Sn} < \text{Pb}$. Thus, the divalent state of lead is more prominent. The trends in chemical reactivity are given below :

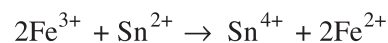
- (i) Simple M^{4+} ions in this group are not known.
- (ii) Except carbon the other elements of the group form compounds with co-ordination number higher than 4, like e.g. $[\text{SiF}_5]^-$, $[\text{SiF}_6]^{2-}$, $[\text{PbCl}_6]^{2-}$.
- (iii) In divalent state, stable compounds of MX_2 type for carbon and silicon are rare. The stability of divalent state increases in the order **$\text{Ge} < \text{Sn} < \text{Pb}$** .
- (iv) Tendency of catenation decreases in the order as **$\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn} > \text{Pb}$** .
- (v) Ability to form $p\pi - p\pi$ bonds with element itself and ability to form such bond with other elements like dinitrogen and dioxygen decreases from carbon to lead. So, CO_2 is a gas but silica is a solid.
- (vi) Si, Ge, Sn, and Pb form MX_4 type tetrahedral and covalently bonded compounds. The ionic character and thermal stability of halides decreases with increasing atomic number of halogen and they are hydrolysed by water, e.g.



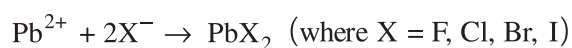
Ge, Sn and Pb also form MX_2 type halides. The stability of dihalides increases in order



The divalent state becomes more stable on moving down the group. $\text{Sn}(\text{II})\text{Cl}_2$ is obtained by dissolving Sn in con. HCl. On cooling this solution, $\text{Sn}(\text{II})\text{Cl}_2$ crystallises in form of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Anhydrous SnCl_2 acts as a reducing agent in acidic solution.



$\text{Pb}(\text{II})$ halides are obtained by adding halide ions into a soluble lead salts.



PbI_2 is yellow, other halides are colourless and sparingly soluble in water.

- (vii) Si, Ge, Sn and Pb form MO_2 type oxides. In silica, silicon and oxygen atoms combine by covalent bond and form infinite three dimensional network of four oxygen atoms. In SiO_2 each Si atom is covalently bonded to four oxygen atoms. In SiO_2 is Si atom combines with oxygen atoms tetrahedrally.

Crystalline silicon dioxide occurs in **quartz, cristobalite and tridymite minerals**. Quartz is used as a **piezoelectric crystal, crystal oscillator** and **in transducers**. Silica gel is obtained by acidification of sodium silicate. When this gel is dehydrated, the **obtained silica gel is extensively used in chromatography and for the drying of other substances**, and therefore, it acts as a drying agent.

GeO_2 , SnO_2 and PbO_2 are solid and exist in several modifications. **SiO_2 is acidic but GeO_2 and SnO_2 are amphoteric while PbO_2 is basic.** $\text{Sn}(\text{IV})$ oxide is prepared by heating Sn and O_2 or reaction of Sn with con HNO_3 . SnO_2 is used in polishing powder and in manufacturing of glass and pottery. PbO_2 is prepared by reaction of Pb_3O_4 with dil HNO_3 .



PbO_2 is a strong oxidising agent and liberates O_2 when treated with acids. Sn and Pb

both form MO type stable oxides. SnO is obtained by heating tin oxalate.



PbO exists in red, orange and yellow colour depending upon the method of preparation. It can be prepared by heating lead carbonate. On heating PbO with air in a reverberatory furnace at 773 K temperature gives red Pb_3O_4 . It is a combination mixture of $2(\text{PbO}) \cdot (\text{PbO}_2)$.

Anomalous behaviour of carbon :

Carbon differs from the other members of its group, because the atomic size of carbon is small and has higher electronegativity. The ionisation enthalpy of carbon is high and also lacks d-orbital in its electronic configuration. Due to following characteristics, it differs from the other members of its group.

- (i) Carbon forms only four covalent bonds while other elements have d or d and f-orbitals. So they can form more covalent bonds. (5 or 6)
- (ii) Carbon atom forms single bond. Moreover, double or triple bond with the other carbon atoms and some other atoms like O, N and S which are small in size and have high electronegativity forms $\text{C} = \text{O}$, $\text{C} = \text{S}$, $\text{C} = \text{N}$, $\text{C} \equiv \text{N}$ with $p\pi - p\pi$ bonding. If the atomic size of some other atoms are very big then overlapping of $p\pi - p\pi$ orbital does not remain effective.
- (iii) The trend of catenation in carbon is maximum due to its high value of carbon-carbon single bond enthalpy (348 kJ mol^{-1}). So it forms number of organic compounds having chain and cyclic structure while in other elements, this trend goes on decreasing.
- (iv) Carbon forms only $p\pi - p\pi$ type bonding while other elements form $p\pi - p\pi$ and also $d\pi - p\pi$ type of bonding.

5.6 Carbon Catenation

The carbon atom has tendency to link with another carbon atom by covalent bond and forms chain or cyclic structure of carbon which is called catenation. This trend is observed due to small size and high electronegativity of carbon atom. Tendency of catenation depends upon the bond

enthalpy of covalent bond between two carbon atoms; higher the bond enthalpy more is the tendency of catenation. The bond enthalpy of $\text{C} - \text{C}$ is 348 kJ mol^{-1} which is the highest than the other elements in its group so it forms a number of chain and cyclic structure compounds due to catenation and $p\pi - p\pi$ bond formation the carbon exhibits different allotropes.

Allotropes : Due to catenation in carbon and $p\pi - p\pi$ bond formation, it exhibits many allotropes. The diamond and graphite are the crystalline allotropes. In 1985, H.W.Kroto, R.E.Smalley and R. I. Curl discovered the third crystalline allotrope fullerene. Coal wood charcoal, animal charcoal lamp black, coke, gas carbon etc are amorphous allotropes of carbon. The structure and properties of crystalline allotropes are given below :

(i) Diamond : Due to **sp^3 hybridisation** in carbon, it combines with other four carbon atoms by single covalent bond. The bonded four carbons are arranged towards the corner of the tetrahedron as shown in Fig. 5.4. Each carbon atom, due to sp^3 hybridisation joins with other four carbon atoms by single covalent bond and forms three dimensional network structure. The distance between two carbon atoms is **154 pm**. All the carbon atoms are bound to each other by covalent bonding and these bonds are very strong. So diamond is extremely hard solid substance.

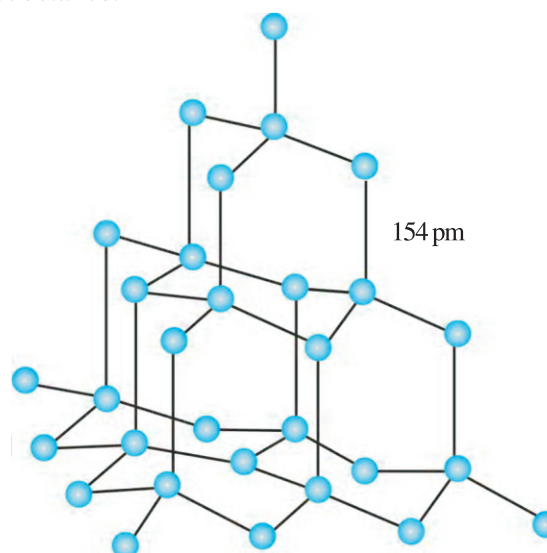


Fig 5.4 Diamond

(ii) Graphite : As the result of **sp^2 hybridisation** in carbon atom, it combines with other

three carbon atoms and as a result hexagonal layer structure is formed as shown in Figure 5.5. The distance between two carbon atoms is **141.5 pm** and distance between two layers is **340 pm** and have weak van der Waals attractive forces between the two layers. According to the circumstances there might be a little change possible between the two layers. Due to weak van der Waals forces the graphite is soft.

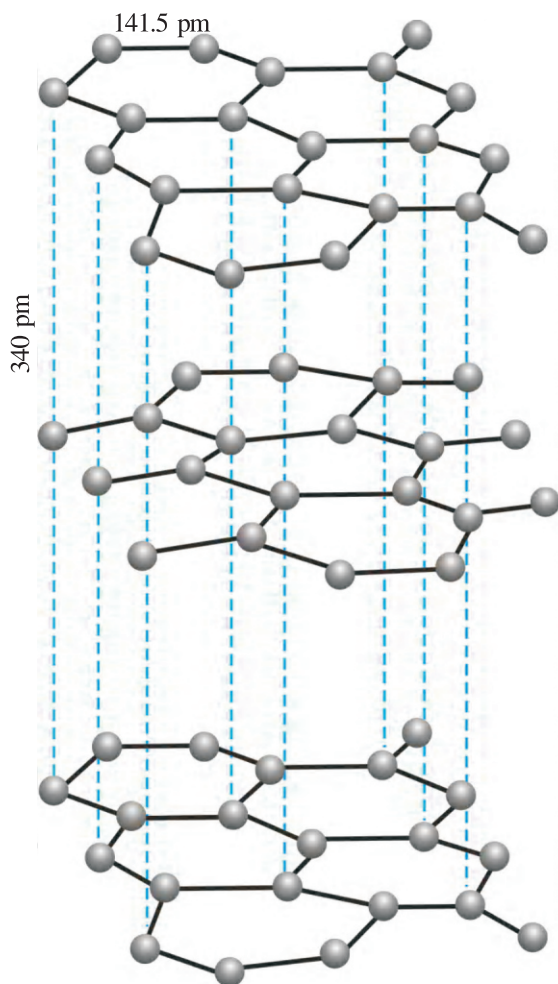


Fig 5.5 Graphite

(iii) Fullerene : The crystalline form of carbon is made up of **porous cage** like molecules. It possesses C_{2n} structure. The two important members are having number of carbon atoms C_{60} and C_{70} . Crystalline fullerene was first prepared by evaporation of graphite using lasers but presently preparation involves the heating of graphite in an electric arc in the presence of an inert gas such as He or Ne, that gives sooty material on condensation, mainly C_{60} with small quantity of C_{70} and traces of other fullerene,

consisting of even number of carbon atom upto 350 or above. As shown in Figure 5.6 the C_{60} molecule has shape like **soccer ball** and also called Buckminster Fullerene as given in Figure 5.6.

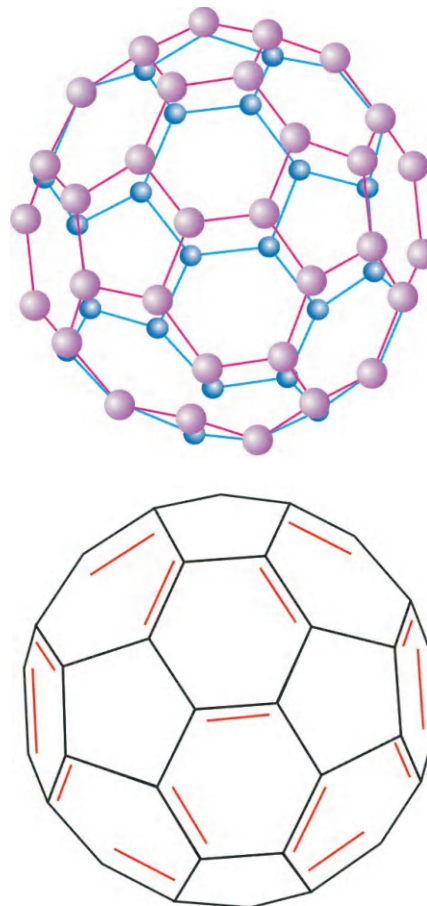


Fig 5.6 Fullerene

The shape of fullerene resembles to shape of football. The special shape of fullerene is also called **bucky ball**. It contains twelve rings having five carbon atoms and twenty rings having six carbon atoms. The ring structure having six carbon atoms is fused to both types of ring, while the ring structure having five carbon atoms is fused only to six membered ring. All the carbon atoms in Fullerene are equivalent and they undergo **sp^2 hybridisation**. So each carbon atom combines with other three carbon atoms with σ -bond. The remaining electron forms π -bond and hence, the π -bond electron gets delocalised in molecular orbital which gives aromatic character in fullerene. In fullerene the carbon-carbon single and double bonds with distance 143.5 pm and 138.3 pm are there respectively. **C_{60} and C_{70} fullerene are soluble**

in toluene solvent and give purple and orange-red coloured solution. Fullerenes are the only pure forms of carbon because they have no dangling bond so possess smooth structure.

Physical Properties of Carbon :

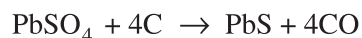
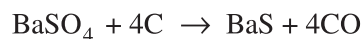
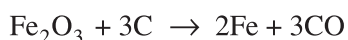
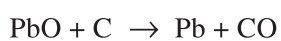
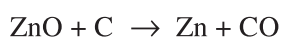
- (i) Carbon has a number of allotropes from which diamond, graphite and fullerene are crystalline, and different types of coal, coke, gas carbon are the amorphous allotropes.
- (ii) Diamond is hard whereas graphite is soft.
- (iii) Diamond is insulator while graphite is good conductor of electricity.
- (iv) Fullerene is the crystalline synthesized form of carbon. It has cage like structure.
- (v) Diamond and graphite have network structure while fullerene has molecular structure.
- (vi) Diamond and graphite are insoluble in liquid solvent, while fullerene is soluble in suitable solvent (benzene).
- (vii) Charcoal is porous, hence, it possesses the adsorption property.

Chemical Properties (Chemical reactions)

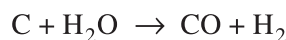
- (i) All the allotropic forms of carbon burn in air and form CO or CO₂. If the proportion of O₂ is limited, then CO is formed and if the proportion of O₂ is more, then CO₂ is formed. This combustion reaction is exothermic reaction.



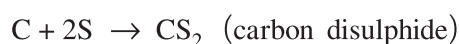
- (ii) **Reduction properties :** Carbon is a strong reducing agent. It reduces many metallic oxides and form corresponding metals. During reduction, sulphide is obtained from metal sulphate.



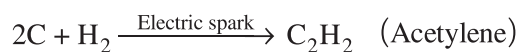
On passing water vapour over red hot coke H₂ gas can be evolved.



- (iii) **Reaction with other elements :** Passing vapour of sulphur over the red hot carbon gives CS₂.



When an electric spark is struck between carbon electrodes in the presence of H₂, acetylene is formed.



When carbon is heated with beryllium, it forms beryllium carbide.



- (iv) **Reaction with acid :** When charcoal is heated with hot and dil HNO₃, it slowly dissolves and gives brown substance which is known as artificial tannin. When carbon reacts with con. HNO₃ it gets oxidised and forms CO₂



Carbon reacts with hot con. H₂SO₄, it gets oxidised to CO₂ and H₂SO₄ is reduced to SO₂ and a small quantity of mellitic acid (Beneze hexacarboxylic acid) is also formed.



Uses of some important compounds of carbon :

- (1) **Halides of carbon :** The reaction of carbon with halogen forms carbon tetrahalides. CF₄ is a gaseous, CCl₄ is liquid while CBr₄ and CI₄ are solids. Its order of stability is CF₄ > CCl₄ > CBr₄ > CI₄

Uses :

- (i) CCl_4 is used as a solvent and **fire extinguisher**.
- (ii) CF_2Cl_2 , which is known as **Freon**, was earlier used in refrigerator as a coolant.
- (iii) CCl_4 is used as medicine for hookworm in intestine.

(2) Carbon disulphide : (CS_2) :**Uses :**

- (i) It is used in the manufacture of Viscose Yarn.
- (ii) It is used as an insecticide for curing infected seeds.
- (iii) It is used in vulcanisation of rubber.
- (iv) It is used as solvent in the manufacture of varnishes and match-sticks.
- (v) It is used in the manufacture of carbon tetrachloride

(3) Carbide Compounds : The compounds of carbon with high electropositive elements are known as carbide compounds. e.g. SiC , Fe_3C , CaC_2 , WC , Al_4C_3 , Be_4C

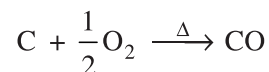
Uses :

- (i) SiC , which is known as **carborandum**, is very hard, so used as **refractory** and **abrasive for** sharpening and grinding metals and other substances.
- (ii) WC is used for making tools and mould, for making coins etc.
- (iii) CaC_2 is used for preparing acetylene and it is used for **welding** and in manufacturing of number of organic compounds such as ethyl alcohol, acetic acid etc.
- (iv) Be_4C is very hard and is used as a shield against radioactive radiation.

(4) Oxides of carbon : Carbon can burn in air or O_2 and gives carbon monoxide (CO) and carbon dioxide (CO_2).

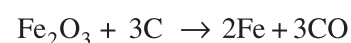
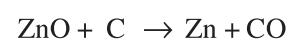
(i) Carbon Monoxide (CO) :**Preparation :**

(i) Carbon monoxide is prepared by incomplete combustion of carbon or carbon containing compounds in a limited supply of O_2

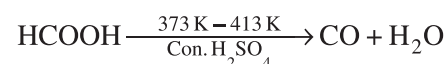


Incomplete combustion of petrol and diesel produces CO .

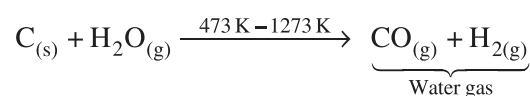
(ii) CO is prepared by the reduction of oxides of heavy metals with carbon.



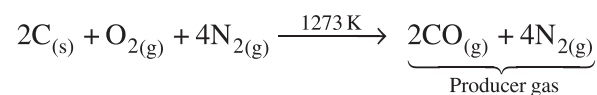
(iii) Pure CO can be prepared in a laboratory on small scale by heating formic acid (HCOOH) with con H_2SO_4 at about 373 K to 413 K temperature. Here, H_2SO_4 acts as a dehydrating agent.



(iv) On commercial scale CO is prepared by passing water vapour at 473 K to 1273 K temperature over hot coke and produce mixture of CO and H_2 which is known as watergas or synthesis gas.

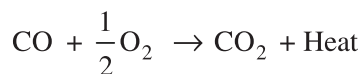


Instead of water vapour if air is used then it produces mixture of CO and N_2 which is known as producer gas.

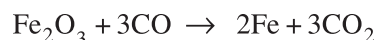
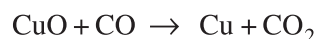
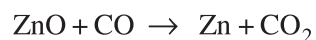
**Properties :**

- (i) Carbon monoxide is colourless and odourless gas, and it is sparingly soluble in water.
- (ii) It is highly toxic in nature because it forms stable (nearly 300 times) complex with haemoglobin present in blood and stops the oxygen carrying capacity of the blood, hence it causes death.

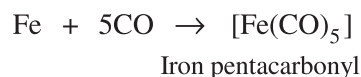
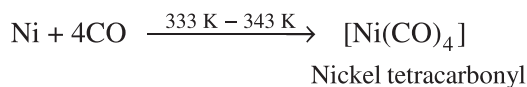
(iii) CO on combustion gives pale blue flame



(iv) Reducing character : It reacts with many metal oxides and reduces to corresponding metals e.g.



(v) Formation of metal carbonyl character : Co combines as ligand with many transitional metals, such as Ni, Fe, Co etc and form metal carbonyl complex compounds. e.g.

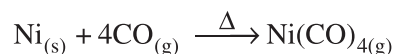


Uses :

(i) CO is useful for extraction of some metals from their oxide. For example, used in blast furnace.



(ii) CO is used to prepare tetracarbonyl nickel in **Mond's carbonyl process** to obtain pure nickel metal from impure nickel metal.



(iii) In industrial field CO is used as a fuel in the form of water gas and producer gas.

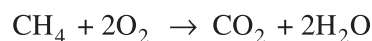
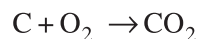
(iv) It is used in manufacturing of methyl alcohol and formic acid.

(v) It is used in manufacturing of **magnetic tapes** (Iron carbonyl) for tape recorder.

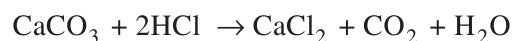
(ii) Carbon Dioxide (CO₂) :

Preparation :

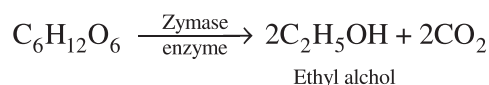
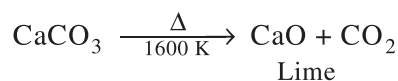
(i) Carbon dioxide is prepared by burning carbon, hydrocarbon like CH₄ or carbon monoxide in excess of air.



(ii) In laboratory, CO₂ is obtained by reaction of CaCO₃ with dil HCl



(iii) On industrial scale, CO₂ is obtained as a by-product during manufacturing of lime and manufacturing of ethyl alcohol.



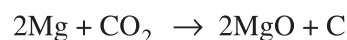
Properties :

(i) It is colourless, odourless gas and about 1.5 times heavier than air.

(ii) It is not poisonous but it does not support life of animal and human being but they die in its presence due to lack of O₂ gas.

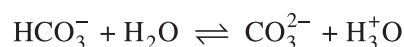
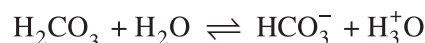
(iii) At room temperature and 50 to 60 atm. pressure CO₂ gas can be liquefied, when liquid CO₂ is allowed to evaporate rapidly i.e. expands rapidly, it is converted into solid which is known as dry ice.

(iv) CO₂ gas is neither combustible nor supporter of combustion. However, in its presence certain active metals such as Na, K, Mg etc. continue to burn.

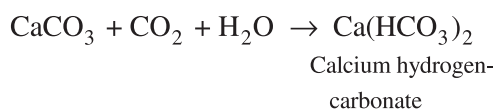
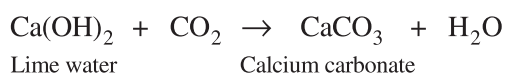


(v) CO₂ turns blue litmus paper red so it is acidic in nature.

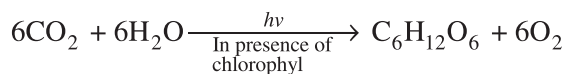
(vi) It is sparingly soluble in water but when dissolved in water, **carbonic acid (soda water (H₂CO₃))** can be obtained which is dibasic acid and it dissociates in two stages.



- (vii) On passing CO_2 through lime water it turns milky due to formation of insoluble CaCO_3 and on passing it in excess milky appearance disappears due to formation of soluble calcium hydrogencarbonate (calcium bicarbonate)



- (viii) In the presence of sunlight and chlorophyll of green plants, CO_2 reacts with water to form glucose. This reaction is called photosynthesis.



Uses :

- (i) Mixture of ether and solid CO_2 creates low temperature upto 165 K, hence it is used in liquefying other gases and **act as a coolant in cold storage.**
- (ii) CO_2 is neither combustible nor supporter of combustion. Therefore it is used as a fire extinguisher.
- (iii) CO_2 is used in preparation of soft drinks and soda water.
- (iv) CO_2 used in manufacturing of washing soda (Solvay's Process).
- (v) Dry ice is used in curing of local burns and in hospital for surgical operation of sores.
- (vi) During artificial respiration for the victims of CO poisoning it is used in form of **carbogen (95% O_2 + 5% CO_2 mixture known as carbogen).**
- (vii) CO_2 is used for the purification of cane sugar juice in manufacturing of sugar.

- (viii) CO_2 is used in photosynthesis by green plants.

- (ix) To control the pH(7.26 to 7.42) of blood CO_2 gas is used in **carbonic acid buffer system ($\text{H}_2\text{CO}_3 + \text{HCO}_3^-$).**

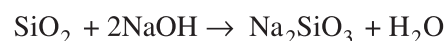
- (x) Large amount of CO_2 is used in production of fertiliser like urea.

Important Compounds of Silicon :

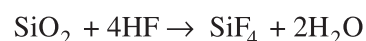
(1) Silicon hydrides : Hydride compounds of silicon have general formula $\text{Si}_n\text{H}_{2n+2}$. The value of bond enthalpy for silicon-silicon is 297 kJmol^{-1} hence, catenation character is observed in it so it forms limited hydride compounds **$\text{Si}_n\text{H}_{2n+2}$** where $n = 1$ to 8. This compound is also known as **silane**. The stability of silanes are less compared to hydrides of carbon, hence, they have more reduction power.

(2) Silicon dioxide : (Silica) SiO_2 : It is a solid substance having three dimensional structure. A silicon atom combines with four oxygen atoms by covalent bonding. Thus, SiO_2 does not exist as a single molecule but the arrangement of number of atoms form a giant crystal. More than 22 allotropic structures are known in which some are crystalline like quartz, tridimite, cristobelite etc., while amorphous like silica gel and kieselgur. SiO_2 are acidic, hence, it dissolves in liquid alkali or alkali carbonate to form silicate compounds.

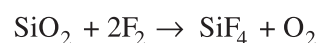
At high temperature SiO_2 reacts with NaOH to form Na_2SiO_3 .



SiO_2 react with HF and gives SiF_4



SiO_2 reacts with halogen (only F_2) and SiF_4 is obtained and O_2 is liberated.



- (ii) Silicones resist the organic reagent, oxidation and thermal decomposition. Hence, they are chemically inert.
- (iii) Silicones are heat resistant and electric insulator substances; more over, possess the character of water repellent.



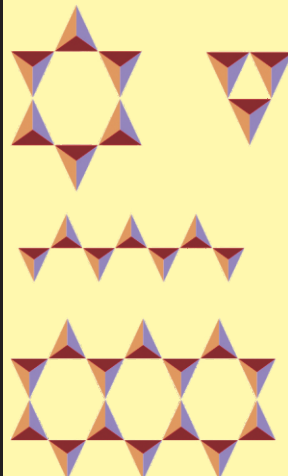
Uses :

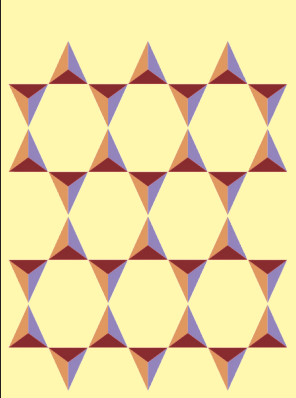
- (i) For making water-proof paper, wool, textiles, wood. etc they are coated with a thin film of silicones.
- (ii) Silicones are used as sealants and electrical insulators.
- (iii) Used as lubricant at high and low temperatures.
- (iv) Used as surgical implants.
- (v) Used as antifoaming agents in cosmetics

General Information and Structure of Silicates : Approximately 95% of the earth crust consists of silicates and silica. Silicate compounds contain independent SiO_4^{4-} or such type of ions joined to form combined silicate ions and their charges are being balanced by cations such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} . The basic structural building block in silicates is the SiO_4^{4-} having tetrahedral structure.

Types of silicates : In the structure of silicates depending upon the number of corner (0, 1, 2, 3, 4) of the SiO_4^{4-} tetrahedron shared with other tetrahedrons and based on that they are classified which are indicated in Table 5.7. In a three dimensional structure of SiO_2 , Si^{4+} is partially substituted by Al^{3+} which gives aluminosilicate called feldspar. In aluminosilicate the SiO_4^{4-} and AlO_4^{5-} tetrahedrons join with each other in a simple way to form three dimensional networks known as zeolites.

Table 5.7 Classification of silicates

No. of corner of SiO_4^{4-}	Structural arrangement	Type	Anion unit	Examples
0		Orthosilicate	SiO_4^{4-}	Zircon (ZrSiO_4), Forsterite (Mg_2SiO_4)
1		Pyrosilicate	$\text{Si}_2\text{O}_7^{6-}$	Thortveitite $\text{Sc}_2(\text{Si}_2\text{O}_7)$, Hemimorphite $\text{Zn}_2\text{Si}_2\text{O}_7$ $\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$
2		Cyclic silicate Ring silicate Chain silicate (a) Linear silicate (b) Cross link Chain	$\text{Si}_3\text{O}_9^{6-}$ $\text{Si}_6\text{O}_{18}^{12-}$ $(\text{SiO}_3^{2-})_n$ OR $(\text{SiO}_3)_n^{2n-}$ $(\text{Si}_4\text{O}_{11}^{6-})_n$	Wollastonite $\text{Ca}_3\text{Si}_3\text{O}_9$ Beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ Spodumene $\text{LiAl}(\text{SiO}_3)_2$ Diopside $\text{CaMg}(\text{SiO}_3)_2$ Tri-molyte $\text{Ca}_2\text{Mg}_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$

3		Sheet silicate	$(\text{Si}_2\text{O}_5)_n^{2n-}$ OR $(\text{Si}_2\text{O}_5^{2-})_n$	Stearite $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$ Muscovite $\text{KAl}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$
4		Three dimensional	SiO_2	Feldspar, Zeolite, (alumino-silicate) different types of silica (quartz, trydimite cristobalite)

Uses of zeolite : Zeolite has a network of cavities linked by channels. In these channels only small molecules can enter, hence, zeolite is used as a molecular sieve for separating small molecules from big molecules; zeolite is used as a catalyst

(shape-selective catalyst). One important catalyst of zeolite is ZSM-5. It is used in petrochemicals. It converts alcohol directly into gasoline (petrol) by dehydration and the mixture of hydrocarbons is formed.

SUMMARY

The elements (except He atom) having outermost valence shell electronic configuration $ns^2 np^1$ to $ns^2 np^6$ are called p-block elements. Since p-orbital can accommodate six maximum electrons, six groups 13 to 18 are there in p-block elements. We shall study group 13 and 14 i.e. Boron and carbon group elements in this unit. Generally in a row or period electronegativity, ionisation enthalpy and oxidising power are increasing as the atomic number increases while in group it decreases as the atomic number increases. Generally, in group covalent radius, van der Waals radius and metallic character increases as the atomic number increases. It is a characteristic of the p-block elements that metal, non-metal and metalloid are included in the same group.

The group 13 includes elements, Boron, Aluminium, Gallium, Indium and Thallium. Aluminium is the third most abundant element found in earth's crust. The important ores of aluminium are bauxite and cryolite. Variation in some properties of group 13 elements are like atomic radii and ionic radii, ionisation enthalpy, metallic character, electronegativity, melting point and boiling point, density, character as reducing and nature of compound are observed in elements of boron group i.e. Group 13 elements having electronic configuration $ns^2 np^1$. Hence, they possess +3 oxidation state and their stability goes on decreasing as the atomic number increases. These elements also possess +1 oxidation state and the stability goes on increasing as the atomic number increases.

The chemical reactivity of group 13 elements are as given below. Group 13 elements do not combine directly with hydrogen but they combine indirectly to form hydride compounds. Boron forms a number of hydrides having molecular formula $\text{B}_n \text{H}_{n+4}$ and $\text{B}_n \text{H}_{n+6}$ which are known as boranes. The other elements of this group form

polymeric hydrides. Group 13 elements form MX_3 type trihalides, where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I is unknown. AlCl_3 exists in dimer form. The group 13 elements form oxides and hydroxides having formula M_2O_3 and $\text{M}(\text{OH})_3$ respectively. As the atomic number of elements goes on increasing, the acidic character of oxide and hydroxide goes on decreasing. Elements of these group form octahedral complexes. Aluminium sulphate reacts and forms double salts with sulphate of NH_4^+ and alkali metal ions having formula $\text{M}_2\text{SO}_4 \cdot \text{A}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ or $\text{MAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ where $\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+$ and NH_4^+ . The first element (Boron) of group 13 shows anomalous behaviour. Boron is chemically less reactive and almost inert with normal chemical reagents at normal temperature but reacts with strong oxidising agents and with some typical reagents like non-metal, acid alkali and metals. Some important compounds of boron are borax powder, boric acid and boron hydride. The properties and uses of aluminium are as given in the text. Aluminium reacts with acid and base so it is amphoteric in nature.

The group 14 includes elements carbon, silicon, germanium, tin and lead. The first element of this group is carbon, so it is also known as carbon group elements. Carbon shows catenation property due to its small size, high electronegativity and very high carbon-carbon bond energy. Due to typical characteristic of catenation it forms number of compounds which are studied in organic chemistry. It also forms compounds with metals and non-metals. Group 14 elements have variation in properties like atomic radii, ionisation enthalpy electropositive character, electronegativity, melting points and boiling points density, catenation and allotropy. The oxidation state of group 14 elements are +2 and +4. The trends in chemical reactivity are as given in the text. The carbon shows anomalous behaviour. The crystalline allotropes of carbon are diamond, graphite and fullerenes. The physical properties and chemical properties are as given in the text. Some important compounds of carbon are halides of carbon, carbon disulphide, carbide compounds, carbon monoxide and carbon dioxide, and the method of preparation and uses are as given in the text. The important compounds of silicon are silicon hydrides having general formula $\text{Si}_n\text{H}_{2n+2}$. The value of bond enthalpy for silicon-silicon is 297 kJmol^{-1} hence catenation character is observed in silicon and it forms limited hydride compounds, having formula $\text{Si}_n\text{H}_{2n+2}$ where $n = 1$ to 8, and these compounds are also known as silanes. The stability of silane compounds are less compared to hydrides of carbon and hence reducing power is more. Silicon also forms silicon dioxide known as silica and more than 22 allotropic structures are known in which some are crystalline and some are amorphous. Silica is acidic and hence it dissolves in liquid alkali or alkaline carbonate to form silicate compounds. Silicon reacts with only F_2 and form SiF_4 while reacts with Cl_2 and form SiCl_4 . The hydrolysis of SiCl_4 gives silicic acid and the mechanism for hydrolysis are in two steps. The silicones are synthetic materials containing $\text{Si}-\text{O}-\text{Si}$ bond linkage. These compounds are polymeric substances containing R_2SiO repeating unit. The general formula is $(\text{R}_2\text{SiO})_n$, where R is methyl or phenyl group. The empirical formula is R_2SiO which is similar to that of organic compound, ketone, so it is called silicone. The preparation, properties and uses are as given in the text.

Approximately 95% of earth's crust consists of silicates and silica compounds, containing independent SiO_4^{4-} having tetrahedral structure. The types of silicates depending upon the number of corners (0, 1, 2, 3 and 4) of the SiO_4^{4-} tetrahedron are shared with other tetrahedrons and based on that they are classified as given in the text. In a three dimensional structure of SiO_2 , its Si^{4+} partially substituted by Al^{3+} gives aluminosilicate are called feldspar and zeolites. In zeolites the SiO_4^{4-} and AlO_4^{5-} tetrahedron joined together in simple way to form three dimensional network. The uses of silicates are as a molecular sieves and shape selective catalyst. One important catalyst of silicate is ZSM-5 used in petrochemical industry which converts alcohol directly into gasoline.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) What is the general electronic configuration for valence orbital of p-block elements ?
 (A) $ns^2 np^1$ (B) $ns^2 np^6$ (C) $ns^2 np^{1-6}$ (D) $ns^2 np^{1-5}$
- (2) Which is the correct order of ionisation enthalpy of group 13 elements ?
 (A) $B > Al > Ga > In > Tl$ (B) $B < Al < Ga < In < Tl$
 (C) $B > Al < Ga > In < Tl$ (D) $B > Al > Ga < In < Tl$
- (3) What is the general formula for boron hydride ?
 (A) $B_n H_{2n+4}$ (B) $B_n H_{n+6}$ (C) $B_n H_{2n+6}$ (D) $B_{2n} H_{n+6}$
- (4) Mention the colour of borax bead when it comes in contact with Cr^{3+} ion solution ?
 (A) Brown (B) Blue (C) Pink (D) Green
- (5) Which substance is known as inorganic benzene ?
 (A) Boron (B) Diborane (C) Hexaborane (D) Borazine
- (6) Which element has second order in abundance in earth's crust ?
 (A) Carbon (B) Germanium (C) Silicon (D) Aluminium
- (7) Which halide is colourless ?
 (A) PbCl_2 (B) PbBr_2 (C) PbF_2 (D) All
- (8) Which substance is used to stop the radioactive rays ?
 (A) Be_4C (B) WC (C) CaC_2 (D) Al_4C_3
- (9) Which mixture is known as producer gas ?
 (A) $\text{CO} + \text{N}_2$ (B) $\text{CO} + \text{H}_2$
 (C) $\text{CO} + \text{H}_2\text{O}$ (D) $\text{N}_2 + \text{O}_2$

- (10) Which substance is obtained on the hydrolysis of SiCl_4 ?
(A) SiO_2 (B) SiH_4 (C) Na_4SiO_4 (D) H_4SiO_4
- (11) What type of silicate is the talc ?
(A) ring (B) branch (C) pyro (D) sheet
- (12) Give use of ZSM-5 ?
(A) isomerism in petrol (B) direct gasoline from alcohol
(C) preparation of hydrocarbons (D) all
- (13) Which compound is more stable ?
(A) CF_4 (B) Cl_4 (C) CCl_4 (D) CBr_4
- (14) What is observed when excess of CO_2 is passed in lime water ?
(A) Lime water becomes milky
(B) Milky colour of lime water disappears
(C) O_2 gas is produced in lime water
(D) CaCO_3 is obtained in lime water
- (15) Which proportion is are correct for boron isomers ?
(A) ^{10}B 20% (B) ^{11}B 20% (C) ^{11}B 40% (D) ^{10}B 80%

2. Write the answers of the following question in short :

- (1) Which groups are known as p-block elements ?
- (2) Write the names of elements of group 13 ?
- (3) Give the name of ore of indium.
- (4) Write the increasing order of atomic radii of group 13 elements.
- (5) State the oxidation state of gallium.
- (6) Which hydrides of group 13 elements are in polymeric form ?
- (7) Hydroxides of which elements of group 13 are amphoteric ?
- (8) Give three forms of borax.
- (9) State the effect of heat on boric acid.
- (10) Draw structure of diborane.

- (11) Write equation for reaction of Al with dil HCl.
- (12) What is catenation ?
- (13) Give the names of elements of group-14.
- (14) Write allotropes of tin.
- (15) Write the order of stability of dihalides of carbon group elements.
- (16) Write uses of SnO_2 .
- (17) Which substance was earlier used as a coolant in refrigerators ?
- (18) Write uses of tungsten carbide.
- (19) Write equation for production of pure CO.
- (20) What is carbogen ?
- (21) Write uses of silica gel.
- (22) Which ions are present in aluminosilicate ?
- (23) Write uses of ZSM-5
- (24) Give the equation for reaction of con HNO_3 with carbon.
- (25) Mention the general and empirical formula of silicones

3. Write the answers of the following questions :

- (1) Why the first ionisation enthalpy of In is less than Tl ?
- (2) Why does boron form covalent bond instead of ionic bond ?
- (3) Why does the stability of +3 oxidation state go on decreasing as the atomic number increases in group 13 ?
- (4) Explain double salts with suitable example.
- (5) Write the equation of reaction B with H_2SO_4 and NaOH.
- (6) Explain the equation of preparation of borax from boric acid.
- (7) Write the uses of boric acid.
- (8) Explain metallic character of elements of group 14.
- (9) Write uses of silica.
- (10) Write the anomalous behaviour of carbon.

- (11) Explain the properties of carbon as strong reducing agent.
- (12) Write uses of CS_2 .
- (13) Give the equation for preparation of producer gas and water gas.
- (14) Write properties of CO .
- (15) Write uses of CO_2 .
- (16) Give the equation for preparation of silicon hydride.
- (17) Write equations for preparation of silicones.
- (18) Write uses of silicones.
- (19) Write uses of zeolites.
- (20) What is aluminosilicate ? Explain.
- (21) Which is the pure form of carbon ? Why ?
- (22) Write the equation for preparation of borax bead.
- (23) Write uses of borax powder.
- (24) Draw structure of Al_2Cl_6 and write uses of AlCl_3 .

4. Write the answers of the following questions in detail :

- (1) Explain the chemical reactivity of group 13 elements.
- (2) Explain the preparation and properties of boric acid.
- (3) Write the uses of boron and its compounds.
- (4) Explain the chemical properties of carbon.
- (5) Write the preparation and properties of CO .
- (6) Write the properties and uses of CO_2 .
- (7) Explain the preparation of silicon tetrachloride and its hydrolysis.
- (8) Write short notes :
 - (1) Silicones
 - (2) Silicate compounds

