The *p*-Block Elements

The *p*-Block Elements comprise those belonging to Group 13 to 18 and these together with the *s*-Block Elements they are called the Representative Elements or Main Group Elements.

The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period.

Group 13 elements--- *ns²np¹* Group 14 elements--- *ns²np²*

Main Points

- Most of p-Block elements are non-metals.
- ۲ They have variable oxidation states.
- ۲ They form acidic oxides
- ۲ They impart no characteristic colour to the flame
- ۲ Generally they form covalent compounds. Halogens form salts with alkali metals
- They have high ionization potentials.
- ۲ They have very large electron gain enthalpies.
- ۲ They are solids/liquids/gases at room temperature (Br is liquid)
- ۲ The aqueous solutions their oxides are acidic in nature.
 - why p-block elements consist of only six groups?

Ans: The number of p orbitals is three therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six. Therefore, there are six groups of p-block elements in the periodic table numbering from 13 to 18.

- Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups.
- Their valence shell electronic configuration is $ns^2 np^{1-6}$ (except for He).

GROUP 13 ELEMENTS: THE BORON FAMILY

• The boron group consists of boron (B), aluminium (AI), gallium (Ga), indium (In), thallium (TI), and ununtrium (Uut)

STD-XI-Sc-P-block elements



Oxidation states

- The atoms of these elements have three valence electrons, two in s-subshell and one in the p-subshell (ns² np¹). Therefore, all these elements can show maximum of +3 oxidation state.
- The common oxidation states, observed for group 13 elements are +3 and + 1.
- The stability of the + 1 oxidation state increases in the sequence Al < Ga < In < Tl. Except boron and aluminium, the other elements also show +1 oxidation state.
- The +1 oxidation state becomes more stable as one moves down the group from boron to thallium. In case of last element, thallium, +1oxidation state has been found to be more stable than + 3 oxidation state.

The +1 oxidation state of TI is more stable than +3 oxidation state. For e.g., thallous compounds such as TIOH and TIClO₄ are more stable than their thallic compounds. This is attributed to the inert pair effect.

GROUP 13 ELEMENTS: THE BORON FAMILY

- This group elements show a wide variation in properties.
- Boron is a typical non-metal,
- aluminium is a metal but shows many chemical similarities to boron
- Gallium, indium and thallium are almost exclusively metallic in character.

Occurrence

- Boron is a fairly rare element, mainly occurs as
 - 1. orthoboric acid, (H₃BO₃), or B(OH)₃
 - 2. borax, $Na_2B_4O_7$ ·10H₂O, and
 - 3. kernite, $Na_2B_4O_7 \cdot 4H_2O$.
- Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).
 - 1. Bauxite, Al₂O₃. 2H₂O and
 - 2. cryolite, Na_3AlF_6 are the important minerals of aluminium.

Physical Properties

• Boron is non-metallic in nature. It is extremely hard and black coloured solid.

std-xl-sc-P-block elements

- It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point.Rest of the members are soft metals with low melting point and high electrical conductivity.
- It is worthwhile to note that gallium with unusually low melting point (303K), could exist in liquid state during summer.
- Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.
- Density of the elements increases down the group from boron to thallium.

Atomic Radii

• On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen.

Ionization Enthalpy

• The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group

Electronegativity

• Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.-

What is inert pair effect ?

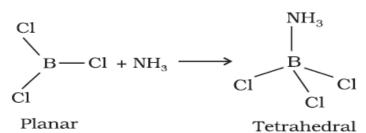
The elements of group 13 have three electrons in their valence shell (ns^2np^1) and, therefore, exhibit, oxidation state of + 3. However, it bas been observed that in addition to + 3 oxidation state, they also exhibit oxidation state of +1. The +1 oxidation state becomes more and more stable as one goes down the group from B, AI, Ga, In to TI. *In the case of last element, after the removal of one electron from p-orbital, the remaining ns*² (e.g. 6s²) electrons behave like stable noble gas and do not take part in bond formation. This reluctance of the s-electron pair to take part in chemical combination is called inert pair effect

Electron deficient molecule

Why does boron triflouride behave as a Lewis acid ?

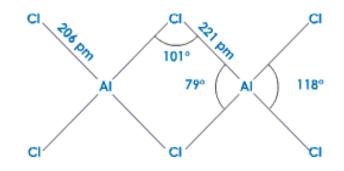
In boron triflouride, the number of electrons around the central boron atom will be only six such **electron deficient molecule have tendency** to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. In boron family tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl₃ easily accepts a lone pair of electrons from ammonia to form BCl₃·NH₃.

STD-XI-Sc-P-block elements



 Al_2Cl_6

AlCl₃ achieves stability by forming a dimer



Chemical Properties

Reactivity towards air

- Boron is unreactive in crystalline form.
- Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.

Reactivity towards air

• Amorphous boron and aluminium metal on heating in air form B₂O₃ and Al₂O₃ respectively.

$$4 \text{ B} + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3$$
$$4 \text{ AI} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$$

• With dinitrogen at high temperature they form nitrides.

STD-XI-Sc-P-block elements



Nature of oxides

The nature of these oxides varies down the group.

- Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates.
- Aluminium and gallium oxides are amphoteric
- and those of indium and thallium are basic in their properties.

Reactivity towards acids and alkalies

- Boron does not react with acids and alkalies even at moderate temperature;
- but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.
- Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2AI(s) + 6HCI_{(aq)} \rightarrow 2AI^{3+}_{(aq)} + 6CI^{-}_{(aq)} + 3H_{2(g)}$$

- concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.
- Aluminium reacts with aqueous alkali and liberates dihydrogen.

$$2AI_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \rightarrow 2Na^+[AI(OH)_4]_{(aq)} + 3H_{2(g)}$$

Sodium tetrahydroxoaluminate(III)

Reactivity towards halogens

These elements react with halogens to form trihalides (except Tl I₃).

$$2E (s)+3X_2(g) \rightarrow 2EX_3(g)$$

X=F,Cl,Br,I

Eg. $2B(s)+3Cl_2(g) \rightarrow 2BCl_3(g)$

SOME IMPORTANT COMPOUNDS OFBORON

● Borax, Na₂B₄O₇·10H₂O

 \odot Diborane B_2H_6

std-xl-sc-P-block elements



Borax

- It is the most important compound of boron.
- It is a white crystalline solid
- Borax dissolves in water to give an alkaline solution.

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

Orthoboric acid

Borax bead

• On heating, borax first loses water molecules and swells up.

On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead

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

Sodium + B_2O_3
metaborate Boric
anhydride

Orthoboric acid

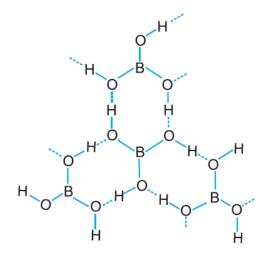
- Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch.
- It is sparingly soluble in water but highly soluble in hot water.

Preparation

It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

Orthoboric acid (structure)



Orthoboric acid (Properties)

- Boric acid is a weak monobasic acid.
- It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

$$\mathrm{B(OH)}_{3} + 2\mathrm{HOH} \rightarrow \mathrm{[B(OH)}_{4}]^{-} + \mathrm{H}_{3}\mathrm{O}^{4}$$

- On heating, orthoboric acid above 370K forms metaboric acid, HBO₂
- which on further heating yields boric oxide, B₂O₃.

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

Why is boric acid considered as a weak acid?

Answer

Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

Diborane B₂H₆

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

STD-XI-Sc-P-block elements

 $4\mathrm{BF}_3 + 3\ \mathrm{LiAlH}_4 \rightarrow 2\mathrm{B}_2\mathrm{H}_6 + 3\mathrm{LiF} + 3\mathrm{AlF}_3$

laboratory method

$$2\text{NaBH}_4 + \text{I}_2 \rightarrow \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$$

Industrial method

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Properties

- 1. Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
- 2. Diborane catches fire spontaneously upon exposure to air.
- 3. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6+3O_2 → B_2O_3 + 3H_2O;$$

 $Δ_cH^{\ominus} = -1976 \text{ kJ mol}^{-1}$

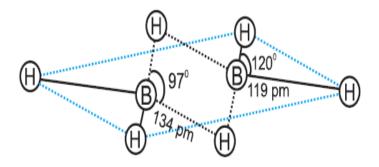
- Most of the higher boranes are also spontaneously flammable in air.
- Boranes are readily hydrolysed by water to give boric acid.

$$B_2H_6(g) + 6H_2O(I) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

• Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, BH3·L

 $B_2H_6 + 2 NMe_3 \rightarrow 2BH_3.NMe_3$ $B_2H_6 + 2 CO \rightarrow 2BH_3.CO$

Structure of diborane



The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre-two electron bonds

Anomalous behaviour of boron

Because of extremely small size of its atom and high electronegativity, boron differs in its properties from other elements of the group

Anomalous properties of boron

- 1. Boron is a non-metal whereas aluminium is a metal.
- 2. Boron is a bad conductor of electricity whereas aluminium is a good conductor.

3. Boron exists in two forms-crystalline and amorphous. Aluminium is a soft metal and does not exist in different forms.

4. The melting point and boiling point of boron are much higher than those of aluminium.

- . Boron forms only covalent compounds whereas aluminium forms even some ionic compounds.
- 6. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.

7. The trihalides of boron (BX_3) exist as monomers. On the other hand, aluminium halides exist as dimers (AI_2X_6).

8. The hydrides of boron are quite stable while those of aluminium are unstable.

USES OF BORON

- Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- The boron-10 (10B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass.
- Borax is also used as a flux for soldering metals

Aluminium

- Aluminium is a bright silvery-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.
- Aluminium is used extensively in industry and every day life. It forms alloys with Cu, Mn, Mg, Si and Zn.
- Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.
- The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

GROUP 14 ELEMENTS: THE CARBON FAMILY

- Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) constitute the group 14 of the periodic table. This group is known as carbon family
- The elements of group 14 have four electrons in the outermost orbitals. The general configuration may be written as ns²np² (one electron in the outermost p-orbitals and two electrons in the s-orbital).

Electronic configurations

Element	Symbol	Atomic No.	Electronic Configuration	Abundance in Earth's crust (in ppm)
Carbon	С	6	[He] 2s ² 2p ²	320
Silicon	Si	14	[Ne] 3s ² 3p ²	277, 200
Germanium	Ge	32	[Ar] 3d ¹⁰ 4s ² 4p ²	7
Tin	Sn	50	[Kr] 4d ¹⁰ 5s ² 5p ²	40
Lead	Pb	82	[Xe] 5d ¹⁰ 6s ² 6p ²	16

Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled *d* and *f* orbitals in heavier members.

Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. In general the ionisation enthalpy decreases down the group.

Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

Chemical Properties

i) Reactivity towards oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides, *i.e., monoxide and dioxide of formula MO and* MO₂ respectively. SiO only exists at high temperature.

(ii) Reactivity towards water

- Carbon, silicon and germanium are not affected by water.
- Tin decomposes steam to form dioxide and dihydrogen gas.

$Sn + 2H_2O \rightarrow SnO_2 + 2H_2$

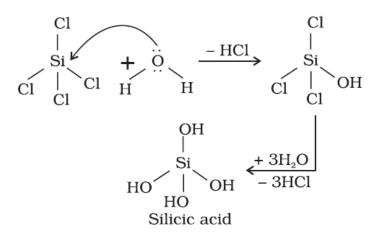
• Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

- These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I).
- Except carbon, all other members react directly with halogen under suitable condition to make halides.
- \odot Most of the MX₄ are covalent in nature.
- \bullet Heavier members Ge to Pb are able to make halides of formula MX_2 .
- Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2 , whereas PbX_2 is more than PbX_4 .

Hydrolysis

• Except CCl₄, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in *d orbital*



ANOMALOUS BEHAVIOUR OF CARBON

• Why Carbon shows ANOMALOUS BEHAVIOUR ?

- 1. It is due to its smaller size,
- 2. Higher electronegativity,
- 3. higher ionisation enthalpy
- 4. and unavailability of *d orbitals*.

In carbon, only *s* and *p* orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of *d* orbitals.

$p\pi - p\pi$ bonds

• Carbon also has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are:

$$C=C,C\equiv C, C=O, C=S, and C\equiv N.$$

• Heavier elements do not form $p\pi - p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Catenation

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation.

This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. The order of catenation is

C > > Si >Ge ≈ Sn.

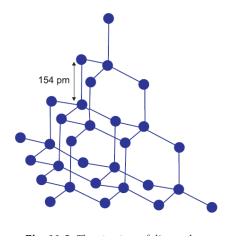
Lead does not show catenation. Due to property of catenation and $p\pi$ – $p\pi$ bond formation, carbon is able to show allotropic forms.

ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes was discovered by** H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

13

Diamond



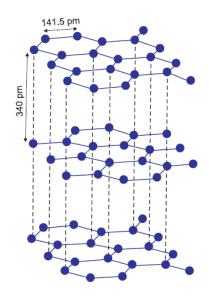
It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms. In this structure directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

Graphite

Graphite has layered structure.Layers are held by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms.Fourth electron forms a π bond. The electrons are delocalised over the whole sheet.

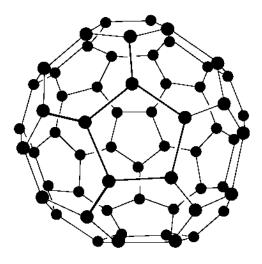
Graphite(structure)



Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery.For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vaporized C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.



C₆₀ molecule has a shape like soccer ball and called Buckminsterfullerene

It contains twenty six- membered rings and twelve five membered rings.

A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms.

The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called **bucky balls**

Other forms of carbon

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

Uses of Carbon

- The composites of carbon are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- > Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
- > Crucibles made from graphite are inert to dilute acids and alkalies.
- > Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water
- Also used in water filters to remove organic contaminators and in air conditioning system to control odour.
- > Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- > Coke is used as a fuel and largely as a reducing agent in metallurgy.
- > Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

IMPORTANT COMPOUNDS OF CARBON

- 1. Carbon Monoxide
- 2. Carbon Dioxide

1. Carbon Monoxide

Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

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

On small scale pure CO is prepared by dehydration of formic acid with concentrated H₂SO₄ at 373 K

HCOOH
$$\xrightarrow{373K}$$
 conc. H_2SO_4 $H_2O + CO$

On commercial scale it is prepared by the passage of steam over hot coke.

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

Water gas

The mixture of CO and H₂ thus produced is known as water gas or synthesis gas.

When air is used instead of steam, a mixture of CO and N₂ is produced, which is called producer gas.

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

Producer gas

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

properties

- Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals.
- This property of CO is used in the extraction of many metals from their oxides ores.

$$\begin{array}{l} \operatorname{Fe}_{2}O_{3}\left(s\right) + 3\operatorname{CO}\left(g\right) \xrightarrow{\Delta} 2\operatorname{Fe}\left(s\right) + 3\operatorname{CO}_{2}\left(g\right) \\ \operatorname{ZnO}\left(s\right) + \operatorname{CO}\left(g\right) \xrightarrow{\Delta} \operatorname{Zn}\left(s\right) + \operatorname{CO}_{2}\left(g\right) \end{array}$$

STD-XI-Sc-P-block elements

Danger of CO

The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin, called Carboxyhaemoglobin which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

Carbon Dioxide

Preparation

It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

Lab method

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

Photosynthesis

Carbon dioxide, which is present in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO₂ into carbohydrates such as glucose. By this process plants make food for themselves as well as for animals and human beings.

The overall chemical change is as follows

$$\begin{array}{c} 6\mathrm{CO}_2 + 12\mathrm{H}_2\mathrm{O} & \xrightarrow{\mathrm{h}\,\nu} & \\ & & \mathrm{Chlorphyll} \end{array} \rightarrow \mathrm{C}_6\mathrm{H}_{12}\mathrm{O}_6 + 6\mathrm{O}_2 \\ & & + 6\mathrm{H}_2\mathrm{O} \end{array}$$

18

Green house effect

The increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO₂ content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

Uses of Carbon Dioxide

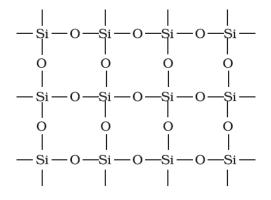
- Dry ice is used as a refrigerant for ice-cream and frozen food.
- \odot Gaseous CO₂ is extensively used to carbonate soft drinks.
- Being heavy and non-supporter of combustion it is used as fire extinguisher.
- \odot A substantial amount of CO₂ is used to manufacture urea.

IMPORTANT COMPOUNDS OF Silicon

1. Silicon Dioxide, SiO₂ 2. Silicones 3. Silicates 4. Zeolites

Silicon Dioxide, SiO₂

- 95% of the earth's crust is made up of silica and silicates.
- Silicon dioxide, commonly known as silica, occurs in several crystallographic forms.
- Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature.
- Silicon dioxide is a covalent, three-dimensional network solid



Silicon Dioxide, SiO₂ properties

- Silica in its normal form is almost nonreactive because of very high Si—O bond enthalpy.
- It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures.
- However, it is attacked by HF and NaOH.

$$\begin{split} \mathrm{SiO}_2 &+ 2\mathrm{NaOH} \rightarrow \mathrm{Na}_2\mathrm{SiO}_3 + \mathrm{H}_2\mathrm{O}\\ \mathrm{SiO}_2 &+ 4\mathrm{HF} \rightarrow \mathrm{SiF}_4 + 2\mathrm{H}_2\mathrm{O} \end{split}$$

Uses.

- Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.
- Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.
- Kieselghur, an amorphous form of silica is used in filtration plants.

Silicones

- What are silicones ?
- Simple silicones consist of

chains in which alkyl or phenyl groups occupy the remaining bonding positions on each silicon.

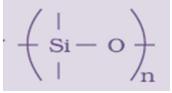
• They are hydrophobic (water repellant) in nature.

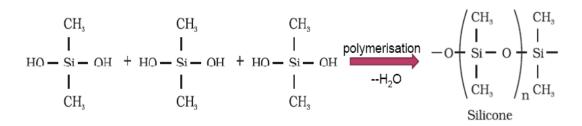
Method of preparation

Hydrolysis of dimethyldichlorosilane, (CH₃)₂SiCl₂ followed by condensation polymerisation

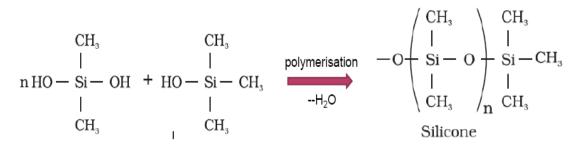
$$2CH_{3}Cl + Si \xrightarrow{Cu \text{ powder}} (CH_{3})_{2}SiCl_{2}$$

$$(CH_{3})_{2}SiCl_{2} \xrightarrow{+2H_{2}O} (CH_{3})_{2}Si(OH)_{2}$$





The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below



Properties & uses

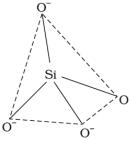
- Silicones being surrounded by non-polar alkyl groups are water repelling in nature.
- They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals.

They have wide applications.

- They are used as sealant, greases, electrical insulators and for water proofing of fabrics.
- Being biocompatible they are also used in surgical and cosmetic plants.

Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-}

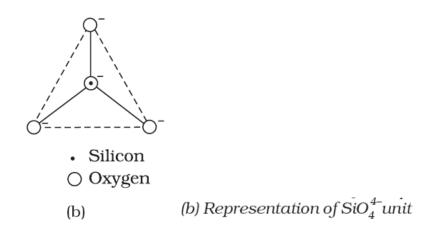


(a)

(a) Tetrahedral structure of SiO_4^{4-}

STD-XI-Sc-P-block elements

• Two important man-made silicates are glass and cement.



Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+ , K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites.

Uses

Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.