

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 02 (Class XI – Semester 2)
Module Name/Title	The p- block elements: The Carbon family – Part 2
Module Id	Kech_21102
Pre-requisites	Knowledge of the concept of periodic table, periodic properties of elements in the periodic table and atomic physical and chemical properties of the elements of Boron family etc.
Objectives	After going through this lesson, the learners will be able to: <ol style="list-style-type: none">1. Understand the atomic, physical and chemical properties of the group 14 elements.2. Understand the important trends and anomalous behaviour of carbon3. Describe the structure and properties of various allotropes of carbon4. Understand the chemistry of some important compounds of carbon and silicon.5. Understand the important application and uses of carbon silicon and their compounds
Keywords	<i>p</i> - block elements, carbon, diamond, graphite, fullerenes, carbon monoxide, carbon dioxide, silicon dioxide, silicones, silicates and zeolites

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Table of Contents:

1. Introduction
2. Group 14 Elements: The Carbon Family
 - 2.1. *Electronic Configuration*
 - 2.2. *Covalent Radii*
 - 2.3. *Ionization Enthalpy*
 - 2.4. *Electronegativity*
 - 2.5. *Physical Properties*
 - 2.6. *Chemical Properties*
 - Oxidation State and Trends in Chemical Reactivity
 - i. Reactivity towards Air
 - ii. Reactivity towards Water
 - iii. Reactivity towards Halogens
3. Important Trends and Anomalous Behaviour of Carbon
4. Allotropes of Carbon
 - 4.1. Diamond
 - 4.2. Graphite
 - 4.3. Fullerenes
5. Uses of Carbon
6. Some Important Compounds of Carbon and Silicon
 - 6.1 Carbon Monoxide
 - 6.2 Carbon Dioxide
 - 6.3 Silicon Dioxide, SiO_2
 - 6.4 Silicones
 - 6.5 Silicates
 - 6.6 Zeolites

1. Introduction

We have learnt a great deal about the atomic physical and chemical properties of the group 13 elements: The boron family in module 1 of this unit. In this module, we shall learn about the atomic physical and chemical properties of the group 14 elements: The carbon family in detail. We shall also learn about the existence of various allotropes of carbon and discuss the anomalous behaviour of carbon in the family in detail. We shall also learn about the chemistry of some important compounds of carbon and silicon and their applications.

2. Group 14 Elements: The Carbon Family

Carbon, silicon, germanium, tin, lead and flerovium are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond; however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C . In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS . Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices. Flerovium is synthetically prepared radioactive element. Symbol of Flerovium is Fl. It has atomic number 114, atomic mass 289 g mol^{-1} and electronic configuration $[\text{Rn}] 5f^{14} 6d^{10} 7s^2 7p^2$. It has been prepared only in small amount. Its half life is short and its chemistry has not been established yet. The important atomic and physical properties along with their electronic configuration of the elements of group 14 leaving flerovium are given in Table 1. Some of the atomic, physical and chemical properties are discussed below:

2.1. Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2 . The inner core of the electronic configuration of elements in this group also differs.

2.2. Covalent Radii

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.

2.3. Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general, the ionisation enthalpy decreases down the group. Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.

2.4. 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.

Table 1: Atomic and Physical Properties of Group 14 Elements

Property		Element				
		Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic Number		6	14	32	50	82
Atomic mass (g mol ⁻¹)		12.01	28.09	72.60	118.71	207.2
Electronic configuration		[He]2s ² 2p ²	[Ne]3s ² 3p ²	[Ar]3d ¹⁰ 4s ² 4p ²	[Kr]4d ¹⁰ 5s ² 5p ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²
Covalent radius/pm ^a		77	118	122	140	146
Ionic radius M ⁴⁺ /pm ^b		–	40	53	69	78
Ionic radius M ²⁺ /pm ^b		–	–	73	118	119
Ionization enthalpy / kJ mol ⁻¹	$\Delta_i H_1$	1086	786	761	708	715
	$\Delta_i H_2$	2352	1577	1537	1411	1450
	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082
Electronegativity ^c		2.5	1.8	1.8	1.8	1.9
Density ^d /g cm ⁻³		3.51 ^e	2.34	5.32	7.26 ^f	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity / ohm cm (293 K)		10 ¹⁴ –10 ¹⁶	50	50	10 ⁻⁵	2 × 10 ⁻⁵

^a for M IV oxidation state; ^b 6–coordination; ^c Pauling scale; ^d 293 K; ^e for diamond; for graphite, density is 2.22; ^f β -form (stable at room temperature)

2.5. Physical Properties

All members of group 14 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.

2.6. Chemical Properties

Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence $\text{Ge} < \text{Sn}$

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 MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2 , SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Problem 1: Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

Solution: (i) carbon (ii) lead (iii) silicon and germanium.

ii. Reactivity towards water

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



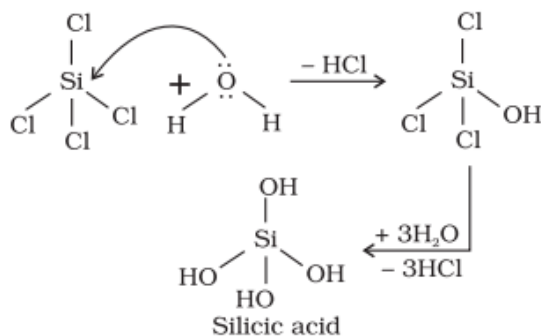
Lead is unaffected by water, probably because of a protective oxide film formation.

iii. Reactivity towards halogen

These elements can form halides of formula MX_2 and MX_4 (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4 , which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. 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 . Except CCl_4 , 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.

Hydrolysis can be understood by taking the example of SiCl_4 . It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si, finally leading to the formation of Si(OH)_4 as shown below :



Problem 2: $[\text{SiF}_6]^{2-}$ is known whereas $[\text{SiCl}_6]^{2-}$ not. Give possible reasons.

Solution: The main reasons are: (i) six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size. (ii) Interaction between lone pair of chloride ion and Si^{4+} is not very strong.

3. Important Trends and Anomalous Behaviour of Carbon

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy 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.

Carbon also has unique ability to form π – π multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{S}$, and $\text{C}\equiv\text{N}$. Heavier elements do not form π – π bonds because their atomic orbitals are too large and diffuse to have effective overlapping. 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 $\text{C}-\text{C}$ bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values.

Bond	Bond enthalpy / kJ mol^{-1}
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

The order of catenation is $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn}$. Lead does not show catenation. Due to property of catenation and $p\pi-p\pi$ bond formation, carbon is able to show allotropic forms.

4. 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.

4.1. 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 (Fig. 1) 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.

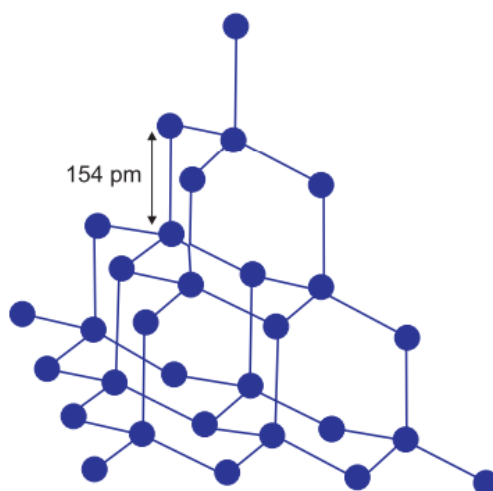


Fig. 1: The Structure of Diamond

It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Problem 3: Diamond is covalent, yet it has high melting point. Why?

Solution Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

4.2. Graphite

Graphite has layered structure (Fig.2). 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.

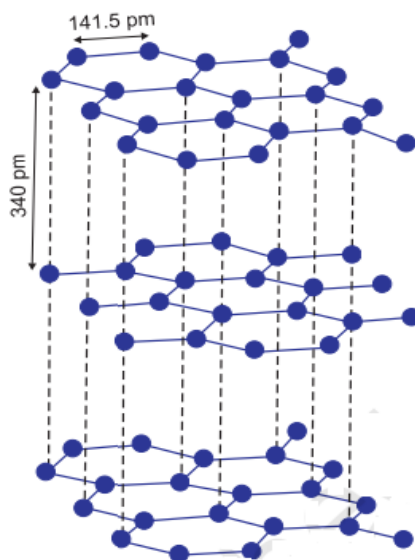


Fig. 2: The Structure of graphite

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. 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.

4.3. 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 vapourised 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.

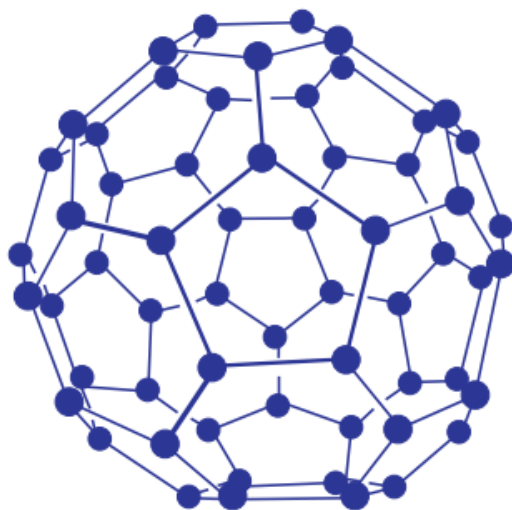


Fig. 3: The structure of C_{60} , Buckminsterfullerene: Note that molecule has the shape of a soccer ball (football).

Fullerenes are the only pure form of carbon because they have smooth structure without having ‘dangling’ bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called Buckminsterfullerene (Fig. 3). 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 in short.

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\ominus$ of graphite is taken as zero. $\Delta_f H^\ominus$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol⁻¹, respectively. 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.

5. Uses of Carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites 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 filters to remove organic contaminants and in airconditioning 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).

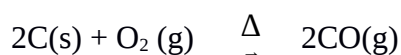
Some Important Compounds of Carbon and Silicon

Oxides of Carbon

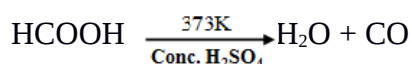
Two important oxides of carbon are carbon monoxide, CO and carbon dioxide, CO₂.

5.1. **Carbon Monoxide**

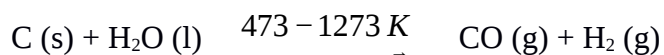
Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



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

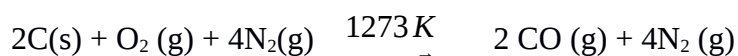


On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H₂ thus produced is known as **water gas** or **synthesis gas**.



Water gas

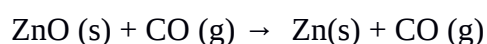
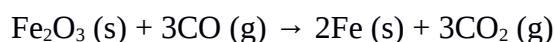
When air is used instead of steam, a mixture of CO and N₂ is produced, which is called **producer gas**.



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.

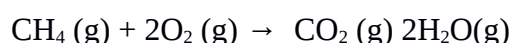
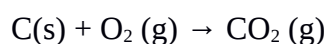
Carbon monoxide is a colourless, odourless and almost water insoluble gas. It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals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



In CO molecule, there are one sigma and two π bonds between carbon and oxygen, $:\text{C} \equiv \text{O}:$. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form metal carbonyls. The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin, 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.

5.2. Carbon Dioxide

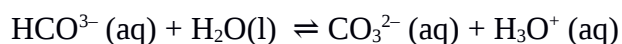
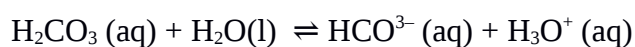
It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.



In the laboratory it is conveniently prepared by the action of dilute HCl on calcium carbonate.

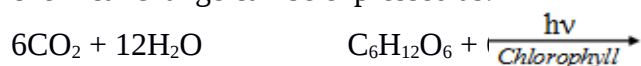


On commercial scale it is obtained by heating limestone. It is a colourless and odourless gas. Its low solubility in water makes it of immense biochemical and geo-chemical importance. With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:



$\text{H}_2\text{CO}_3/\text{HCO}_3^-$ buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

Carbon dioxide, which is normally present to the extent of $\sim 0.03\%$ by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

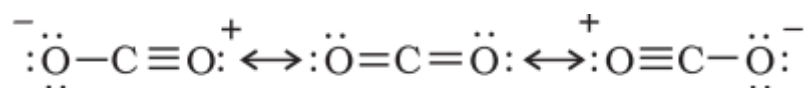


By this process plants make food for themselves as well as for animals and human beings. Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

Carbon dioxide can be obtained as a solid in the form of dry ice by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food. Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of

combustion it is used as fire extinguisher. A substantial amount of CO₂ is used to manufacture urea.

In CO₂ molecule carbon atom undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in *pπ– pπ* bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



Resonance structures of carbon dioxide

5.3. 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 interconvertible at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram (Fig 4). Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.

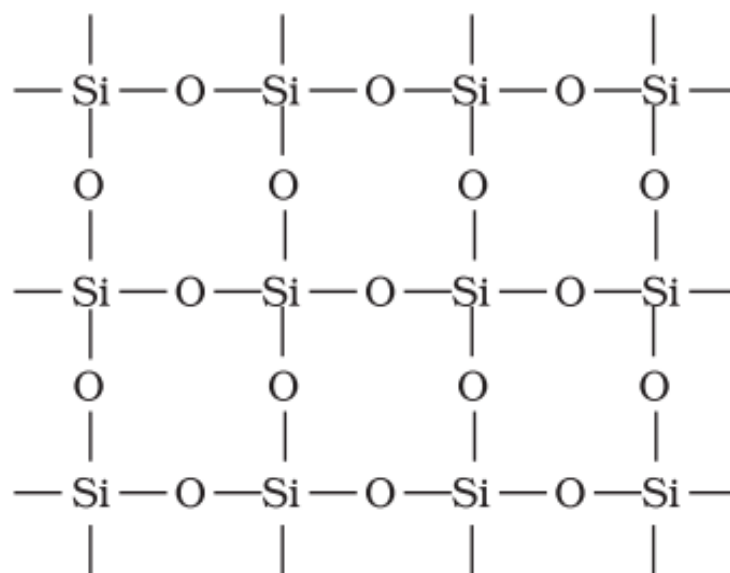
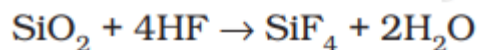


Fig. 4: Three dimensional structure of SiO₂

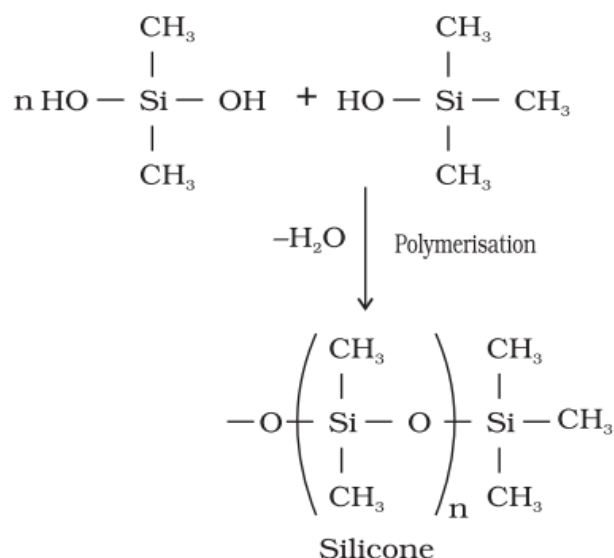
Silica in its normal form is almost nonreactive because of very high Si—O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH.



5.4. Silicones

[illegible]

The chain length of the polymer can be controlled by adding $(\text{CH}_3)_3\text{SiCl}$ which blocks the ends as shown below:



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.



5.5. 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-} (Fig. 5) in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion.

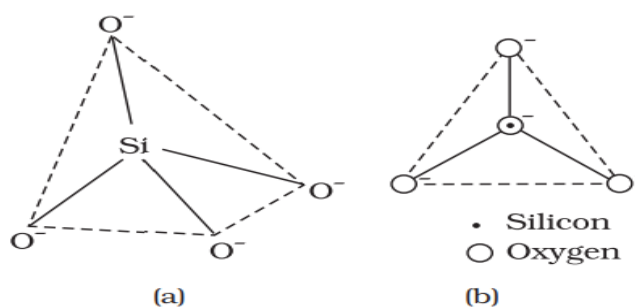


Fig. 5 (a) Tetrahedral structure of SiO_4^{4-} anion; (b) Representation of SiO_4^{4-} unit

In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1, 2, 3 or 4 oxygen atoms per silicate units.

When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures. Negative charge on silicate structure is neutralised by positively charged metal ions. If all the four corners are shared with other tetrahedral units, three-dimensional network is formed. Two important man-made silicates are glass and cement.

5.6. 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. 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.

Summary

Carbon is a typical non-metal forming covalent bonds employing all its four valence electrons ($2s^2 2p^2$). It shows the property of catenation, the ability to form chains or rings, not only with C–C single bonds but also with multiple bonds ($\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$). The tendency to catenation decreases as $\text{C} \gg \text{Si} > \text{Ge} \sim \text{Sn} > \text{Pb}$. Carbon provides one of the best examples of allotropy. Three important allotropes of carbon are diamond, graphite and fullerenes. The members of the carbon family mainly exhibit +4 and +2 oxidation states; compounds in +4 oxidation states are generally covalent in nature. The tendency to show +2 oxidation state increases among heavier elements. Lead in +2 state is stable whereas in +4 oxidation state it is a strong oxidising agent. Carbon also exhibits negative oxidation states. It forms two important oxides: CO and CO_2 . Carbon monoxide is neutral whereas CO_2 is acidic in nature. Carbon monoxide having lone pair of electrons on C forms metal carbonyls. It is deadly poisonous due to higher stability of its haemoglobin complex as compared to that of oxyhaemoglobin complex. Carbon dioxide as such is not toxic. However, increased content of CO_2 in atmosphere due to combustion of fossil fuels and decomposition of limestone is feared to cause increase in ‘green house effect’. This, in turn, raises the temperature of the atmosphere and causes serious complications. Silica, silicates and silicones are important class of compounds and find applications in industry and technology.