By- Shailendra Shukla Sir

Group 14 Elements (Carbon Family)

Group 14 consists of in all five elements namely, Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

Carbon is the seventeenth most abundant element in the earth's crust by mass. 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. In combined state, it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. In fact, carbon is the most versatile element in the world. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes i.e. C^{12} and C^{13}. In addition to these there is a third isotope of carbon i.e. C^{14} which is radioactive in nature with a half life of 5770 years and used for radiocarbon dating.

Silicon is the second most abundant element on the earth's crust (27.7 % by mass) and is present in nature in the form of silica and silicates. It is a very important component of ceramics, glass and cement.

Germanium exists only in traces in nature.

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.

The important atomic and physical properties of the group 14 elements along with their electronic configuration are listed here-

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)	77	118	122	140	146
Ionic radius, M^{3+} (pm)	-	40	53	69	78

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Ionic radius, M^+ (pm)		**-**	**-**	**73**	**118**	**119**
Ionization enthalpy (kJ mol^{-1})	**Δ_iH_1**	**1086**	**786**	**761**	**708**	**715**
	Δ_iH_2	**2352**	**1577**	**1537**	**1411**	**1450**
	Δ_iH_3	**4620**	**3228**	**3300**	**2942**	**3081**
	Δ_iH_4	**6220**	**4354**	**4409**	**3929**	**4082**
Electronegetivity		**2.5**	**1.8**	**1.8**	**1.8**	**1.9**
Density (g cm^{-3})		**3.51**	**2.34**	**5.32**	**7.26[f]**	**11.34**
Melting point (K)		**4373**	**1693**	**1218**	**505**	**600**
Boling point (K)		**3923**	**2740**	**2676**	**2353**	**1730**
$E^0_{M3+/M}$ (Volt)		**-**	**3550**	**3123**	**2896**	**2024**
$E^0_{M+/M}$ (Volt)		**10^{14} - 10^{16}**	**50**	**50**	**10^{-5}**	**10^{-5}**

Electronic Configuration

The valence shell electronic configuration of Gr. 14 elements is ns^2np^2. However, these elements differ in inner core of their electronic configurations.

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 elements is higher than that of the corresponding members of group 13 elements. Here also, the influence of inner core electrons is clearly visible. In general, the ionisation enthalpy decreases down the group. Small decrease in ionization enthalpy (Δ_iH) from Si to Ge and the Ge to Sn and slight increase in ionization enthalpy (Δ_iH) from Sn to Pb is the

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consequence of poor shielding effect of intervening d and f orbitals and increase in atomic size on moving down the group.

Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity 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

(1)Oxidation states

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. Due to inert pair effect, in heavier members, the tendency to show +2 oxidation state increases down the group. For lead, +4 oxidation state is more stable than +2 oxidation state.

Being electron precise molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot expand its covalence beyond 4, other elements of the group can do so. It is because of the presence of d orbitals in their outermost shell. Due to presence of d orbitals, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like $[SiF_6]^{2-}$, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ etc. exist where the central atom is sp^3d^2 hybridized.

(2)Reactivity towards oxygen

All members when heated in oxygen form their oxides. There are mainly of two types i.e. monoxide (MO) and dioxide (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

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GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Amongst monoxides, CO is neutral, GeO is distinctly acidic while, SnO and PbO are amphoteric in nature.

Ques. Which member of group 14-
(i) forms the most acidic dioxide,
(ii) commonly found in +2 oxidation state
(iii) used as semiconductor.

Solution
(i) Carbon
(ii) Lead
(iii) Silicon and germanium

(3)Reactivity towards water

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

$$Sn + 2H_2O \xrightarrow{\Delta} SnO + 2H_2$$

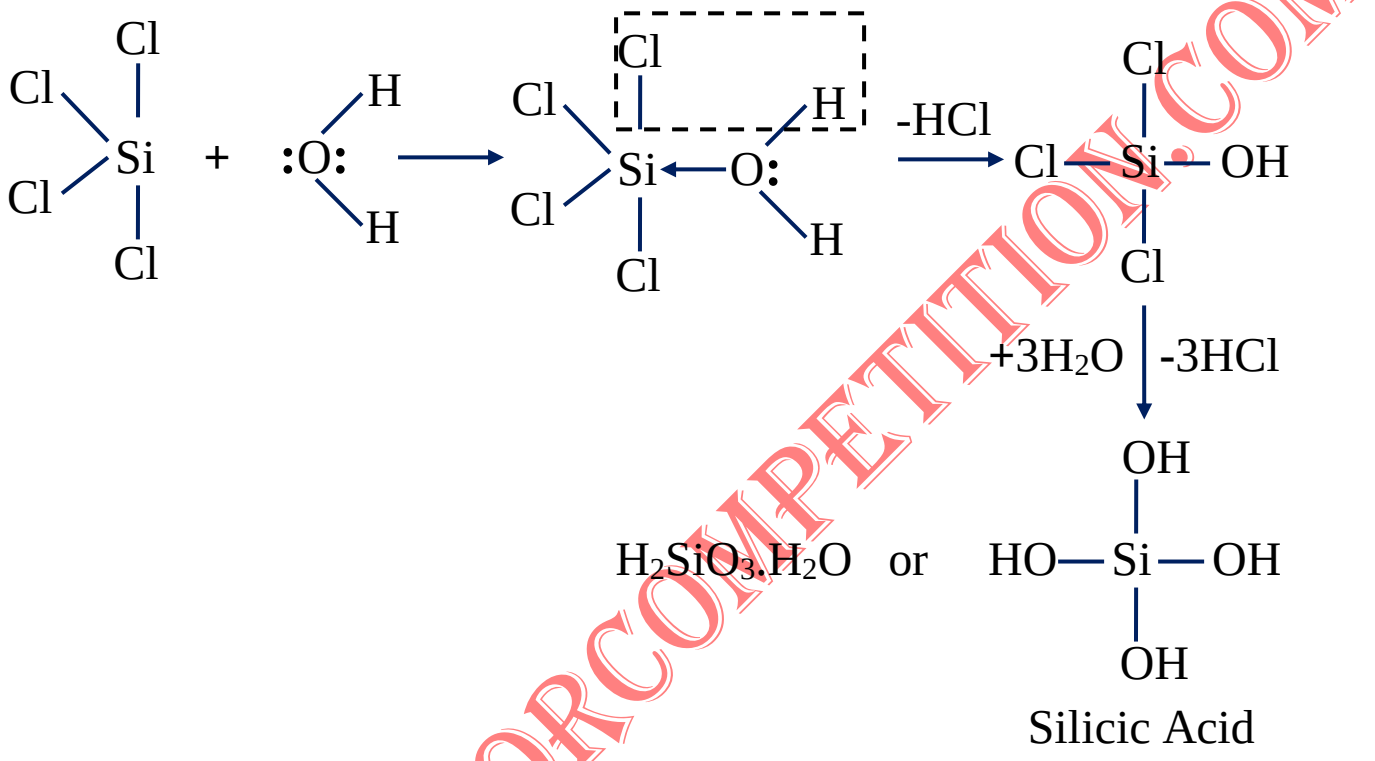
Lead is unaffected by water. It is probably due to the formation of a protective oxide film over its surface.

(4)Reactivity towards halogen

These elements can form halides of type MX_2 and MX_4 (where, X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to form their halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides involes sp^3 hybridisation and therefore, the molecules are tetrahedral in shape. SnF_4 and PbF_4 being ionic in nature are the exceptions. 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, all other tetrachlorides are easily hydrolysed by water because the

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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-



Ques.-$[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

Solution-The main reasons are-

(i) Six large sized chloride ions cannot be accommodated around Si^{4+} ion due to limitation of its size.

(ii) Interaction between lone pair of chloride ion and Si^{4+} is not very strong.

Important Trends and Anomalous Behaviour of Carbon

(1)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 pair of electrons around it. This would limit the maximum covalence of carbon to 4 whereas other members can expand their covalence beyond 4 due to the presence of d orbitals in their outermost shell.

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(2)Carbon also has unique ability to form pπ-pπ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are- C=C, C≡C, C=O, C=S, and C≡N. Heavier elements do not form pπ-pπ bonds because their atomic orbitals are too large and diffused to have effective overlapping.
(3)Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. It is because of very high bond strength of C-C bonds. Down the group the atomic size increases and electronegativity decreases, and thereby, the tendency to show catenation decreases. This can be clearly seen from bond enthalpies values.

Bond	Bond enthalpy/kJ mol^{-3}
C-C	348
Si-Si	297
Ge-Ge	260
Sn-Sn	240

The order of tendency to show catenation for different elements of group 14 is as under-

C >> Si > Ge ≈ Sn

Lead does not show catenation. Due to property of catenation and pπ- pπ bond formation, carbon is able to show allotropic forms.

Allotropes of Carbon

Carbon exists in many crystalline as well as amorphous allotropic forms. 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.

(1) Diamond

It is one of the crystalline allotropes of carbon, where each carbon atom is sp^3 hybridized and remains linked tetrahedrally to four other carbon atoms. Here, carbon-carbon bond length is 154 pm.

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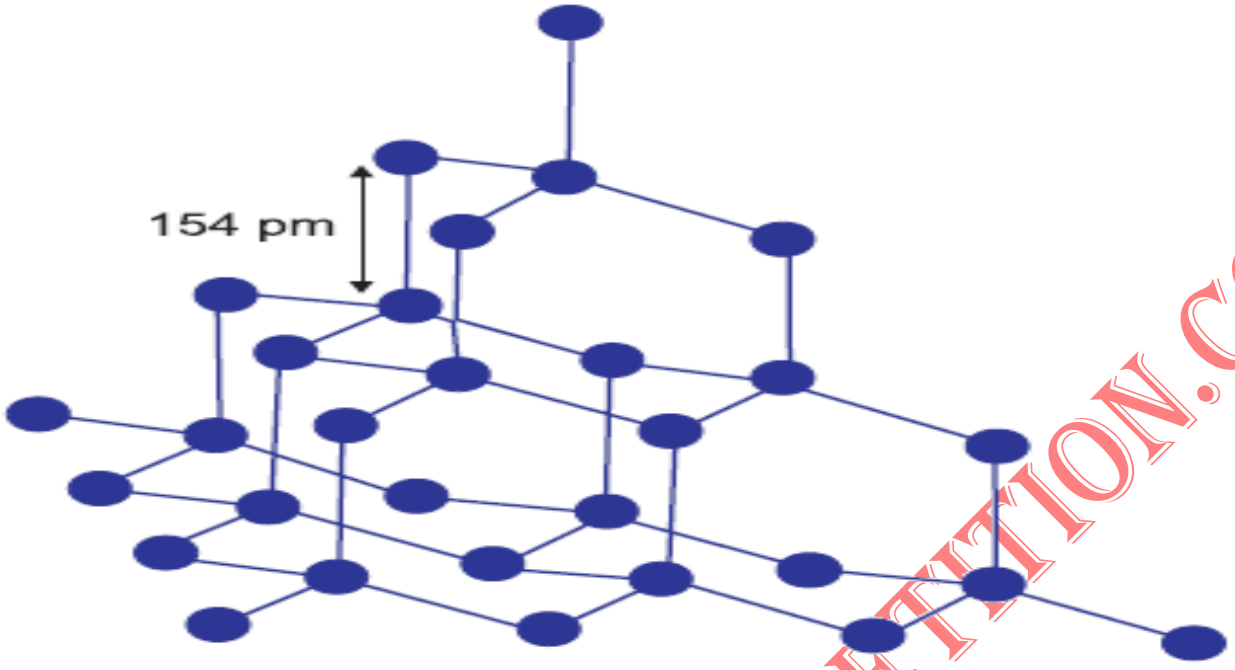


Fig.- Structure of Diamond

In fact, diamond has a rigid three dimensional network of carbon atoms, where, directional covalent bonds are present throughout the lattice.
It is very difficult to break extended covalent bonding and, therefore, diamond is the hardest substance on the earth.
Diamond is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Ques.-Diamond is covalent, yet it has high melting point. Why?
Ans.-Diamond has a three-dimensional network involving strong C-C bonds, which are very difficult to break. Hence, it has very high melting point.

Graphite

Graphite is one of the crystalline allotropes of carbon, where each carbon atom is sp^2 hybridized. It has layered structure where, different layers remain held together by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. carbon-carbon bond length within the layer is 141.5 pm. Here, each carbon makes three sigma bonds with three neighbouring carbon atoms using its three valence electrons, while fourth valence electron forms a π bond. The pi electrons are

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delocalised over the whole sheet. These electrons are mobile and, therefore, graphite is a good conductor of electricity and is used as electrode.

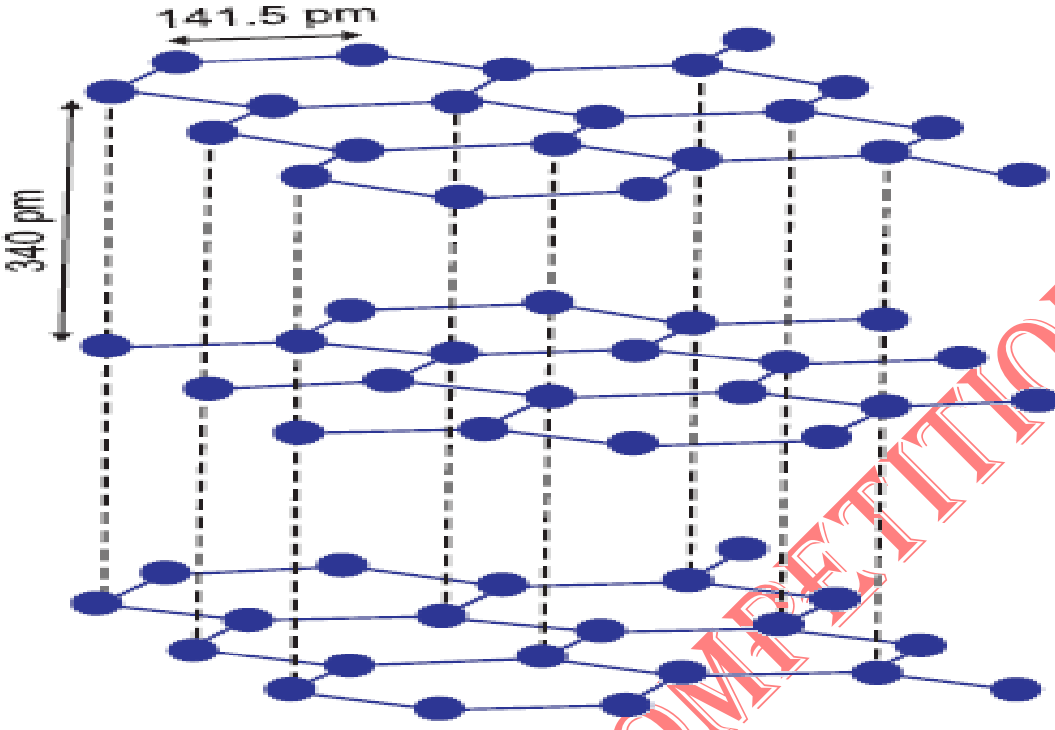


Fig.- Structure of Graphite

Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. Hence, it is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes

Fullerenes are newly discovered crystalline allotropes of carbon. It is produced by heating graphite in an electric arc in the presence of inert gases such as helium or argon. Here, the sooty material formed by condensation of vapourised carbon contains small molecules (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. C_{60} molecule has a shape like soccer ball and is called Buckminsterfullerene.

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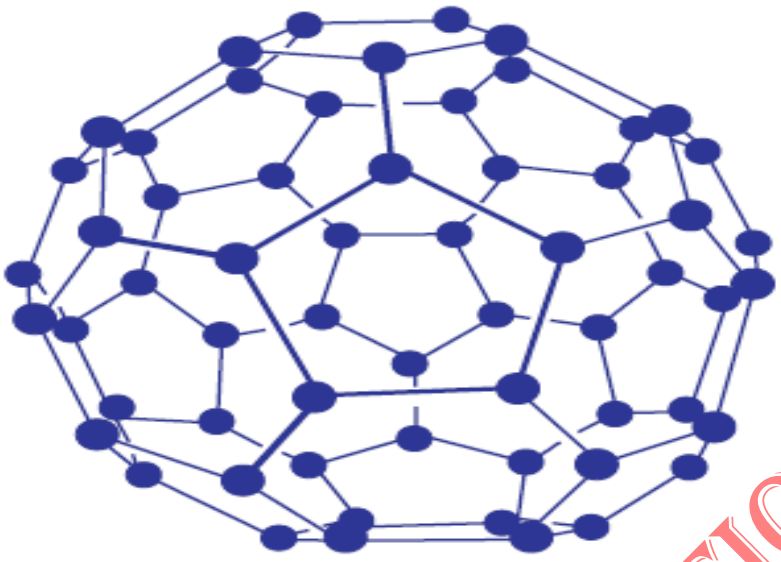


Fig.- Structure of C_{60} (Buckminsterfullerene (soccer ball shaped)

It contains 20 six- membered rings and 12 five membered rings. Here, a six membered ring remains fused either with six or five membered rings, but a five membered ring remains fused with six membered rings. All the carbon atoms are equal and involve 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. Graphite is thermodynamically most stable allotrope of carbon and, therefore, standard enthalpy of formation ($\Delta_f H^0$) of graphite is taken to be zero.

The standard enthalpy of formation ($\Delta_f H^0$) 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.

Uses of Carbon

(1)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.

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(2)Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
(3)Crucibles made from graphite are inert to dilute acids and alkalies.
(4)Being highly porous, activated charcoal is used in adsorbing poisonous gases, in water filters to remove organic contaminators and in airconditioning system to control odour.
(4)Carbon black is used as black pigment in black ink and as filler in utomobile tyres.
(5)Coke is used as a fuel and largely as a reducing agent in metallurgy.
(6)Diamond is a precious stone and used in making jewellery. It is measured in carats (1 carat = 200 mg).

Important Compounds of Carbon and Silicon

Oxides of Carbon

Following are two important oxides of carbon-
(1) Carbon monoxide (CO)
(2) Carbon dioxide, (CO_2)

(1)Carbon Monoxide

Preparation Methods

(1)Direct oxidation of carbon in limited supply of oxygen or air yields carbon monoxide.

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

(2)On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K.

$$HCOOH(l) + O_2(g) \xrightarrow[\text{Conc. } H_2SO_4]{273\text{ K}} 2CO(g) + H_2O(l)$$

(3)On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.

$$C(s) + H_2O(g) \xrightarrow{473\text{-}1273\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

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When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\ K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

Water gas and producer gas are very important industrial fuels. In fact, carbon monoxide of these gases undergoes further combustion in air forming carbon dioxide with the liberation of heat.

Properties

(1)Carbon monoxide is a colourless, odourless and almost water insoluble gas.

(2)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.

$$\underset{\text{Haematite}}{Fe_2O_3(s)} + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$\underset{\text{Zinc Oxide}}{ZnO(s)} + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

(3)In CO molecule, there are one sigma and two π bonds between carbon and oxygen atoms.

$$:C \equiv O:$$

Carbon monoxide

Because of the presence of a lone pair of electrons on carbon atom, CO molecule acts as a ligand (donor) and reacts with certain metals on heating to form metal carbonyls.

(4)Carbon monoxide is a highly poisonous gas and is also called silent killer. Its highly poisonous nature arises due to its ability to form a complex with haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. It reduces oxygen carrying capacity of blood haemoglobin and ultimately results in death.

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(2) Carbon Dioxide

Preparation

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

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

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

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

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

(3)On commercial scale it is obtained by heating limestone.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Properties

(1) It is a colourless and odourless gas.

(2)Is is sparingly soluble in water. Its low water solubility makes it of immense biochemical and geo-chemical importance.

(3)In water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps-

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

(4)H_2CO_3/HCO_3^- buffer system is found in blood and maintains the pH of blood from 7.26 to 7.42.

(5)Being acidic in nature, it combines with alkalies to form metal carbonates.

(6) Atmospheric air contains about 0.03 % of CO_2 by volume and is used by plants in photosynthesis to prepare food. The overall chemical change involved in photosynthesis is as under-

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$$6CO_2(g) + 12H_2O(l) \xrightarrow[\text{Chlorophyl}]{h\upsilon} C_6H_{12}O_6(s) + 6O_2 + 6H_2O(l)$$

By this process plants make food for themselves as well as for animals and human beings.

(7)Unlike carbon monoxide, CO_2 is not poisonous. However, the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years has increased the CO_2 content of the atmosphere. This may lead to increase in green house effect and therefore, raise the temperature of the atmosphere which might have serious consequences.

Uses of Carbon dioxide

(1) Solid CO_2 is called dry ice. It is obtained by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food.

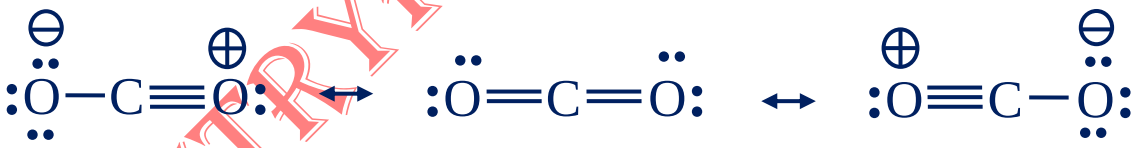
(2) Gaseous CO_2 is extensively used in carbonate soft drinks.

(3) Being heavy and non-supporter of combustion, it is used as fire extinguisher.

(4) A substantial amount of CO_2 is used in manufacture of urea.

Structure of CO_2 Molecule

In CO_2 molecule, central carbon atom is sp hybridised. Here, both the sp hybridised orbitals of carbon overlap with p orbital of two oxygen atoms separately to form two sigma bonds. The rest two unhybrised orbitals of carbon are involved in pπ-pπ bonding with oxygen atom. Thus, CO_2 molecule is linear in shape and is resonace hybrid of following resonance structures-



Resonance Structure of CO_2

Due to resonce, both the C-O bonds in CO_2 have same bond length of 115 pm. Due to linear geometry, the dipole moment of CO_2 molecule is zero.

Silicon dioxide, SiO_2

Aout 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.

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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, while each oxygen atom is covalently bonded with two silicon atoms. Each corner is shared with another tetrahedron. The entire crystal is in fact, a giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.

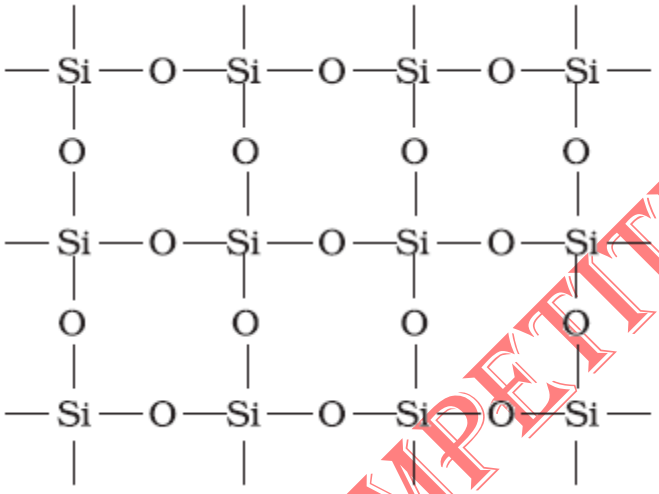


Fig.- Three dimensional structure of SiO_2

Chemical Properties

(1) 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.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Uses of Silica

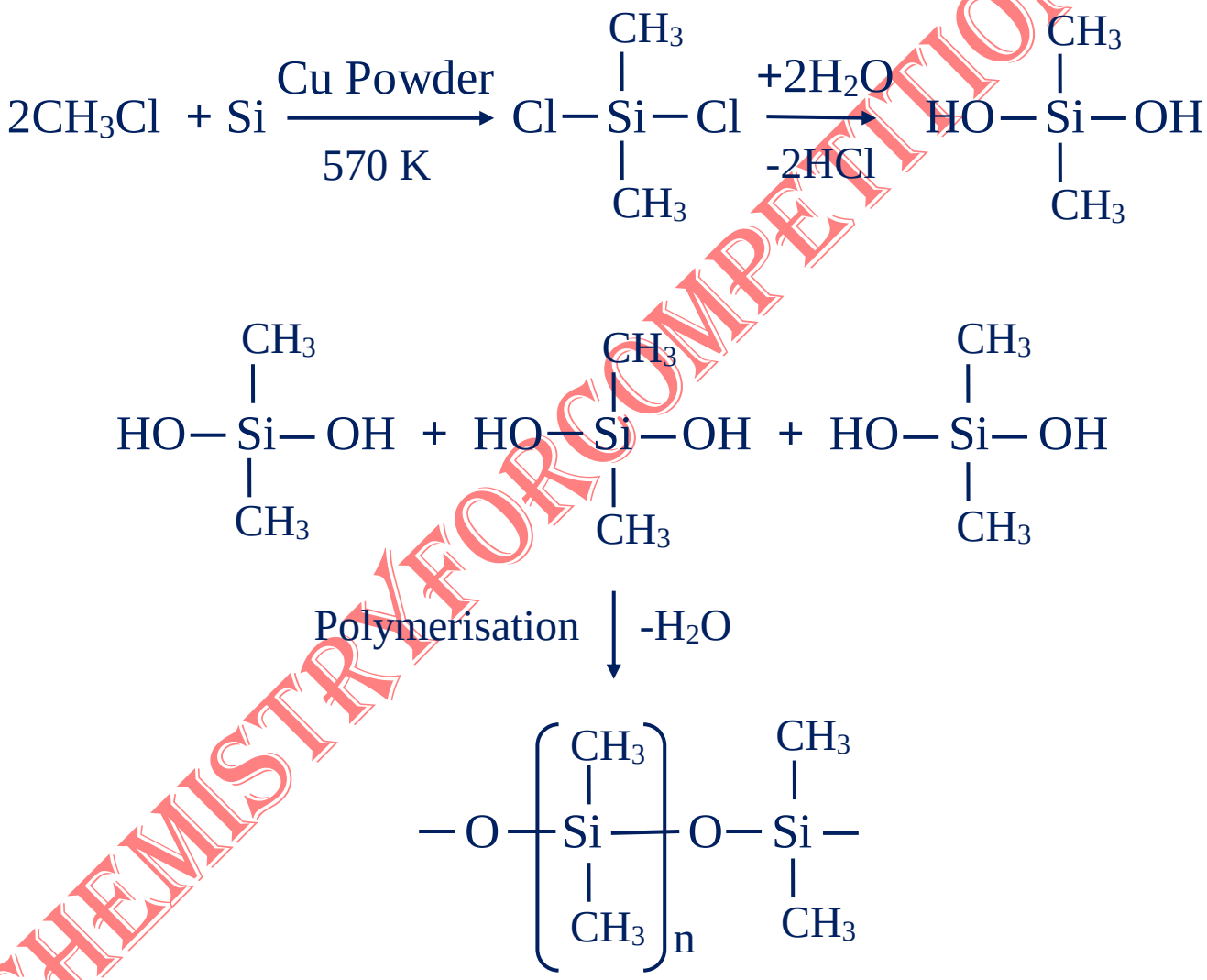
(1) Quartz is extensively used as a piezoelectric material.
(2) It has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.
(3) Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.
(4)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

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Silicones

Silicones are organosilicon polymers having (R_2SiO) as a repeating unit. The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, where R is alkyl or aryl group.

For example, when methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilanes of formula $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl with small amount of Me_4Si are formed. Hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.



Silicone

The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends and stops further polymerisation.

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

Uses of Silicones

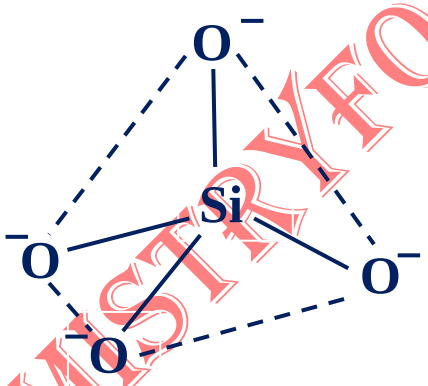
Silicones have wide applications. They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Silicates

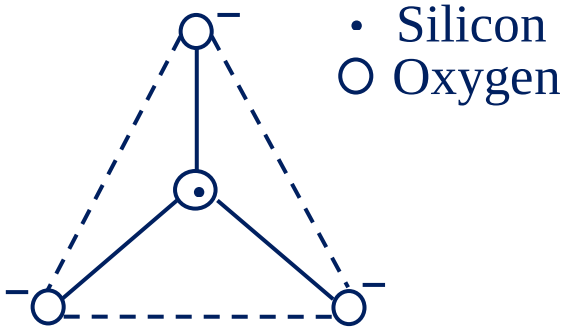
Silicates are the natural minerals of silicon. Some of the most examples of silicate are feldspar, zeolites, mica, asbestos, etc.

The basic structural unit of silicates is SiO_4^{4-} where silicon atom is tetrahedrally bonded to four oxygen atoms. Silicates contain either discrete units or a number of such units joined together through 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.



Tetrahedral SiO_4^{4-} ion



Representation of SiO_4^{4-} unit

Two important man-made silicates are glass and cement.

Zeolites

These are the aluminosilicate which are obtained by replacing few silicon atoms of three-dimensional network of silicon dioxide by aluminium atoms. After this replacement the three-dimensional network of silicon dioxide acquires a negative

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charge. Cations such as Na^+, K^+ or Ca^{2+} balance these negative charges. Examples are feldspar is another example of aluminosilicate.

Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation. For example, 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.

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