

Carbon Family

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

Electronic configuration

Elements	Electronic configuration ($ns^2 np^2$)
${}_6\text{C}$	$1s^2, 2s^2 2p^2$ or $[\text{He}]2s^2 2p^2$
${}_{14}\text{Si}$	$1s^2, 2s^2 2p^6, 3s^2 3p^2$ or $[\text{Ne}]3s^2 3p^2$
${}_{32}\text{Ge}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^2$ or $[\text{Ar}]3d^{10} 4s^2 4p^2$
${}_{50}\text{Sn}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^2$ or $[\text{Kr}]4d^{10} 5s^2 5p^2$
${}_{82}\text{Pb}$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^2$ or $[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^2$

Physical properties

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(7) Ionization energy

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

Ionization energy (kJ mol^{-1})

	C	Si	Ge	Sn	Pb
IE_1	1086	786	761	708	715
IE_2	2352	1577	1537	1411	1450
IE_3	4620	3284	3300	2942	3081
IE_4	6220	4354	4409	3929	4082

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

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

(8) Oxidation state

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

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

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

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

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

(9) Catenation

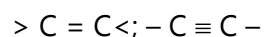
(i) The tendency of formation of long open or closed atom chains by the combination of same atoms in themselves is known as catenation.

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

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

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

(iv) Only carbon atoms also form double or triple bonds involving $p\pi-p\pi$ multiple bond within itself.



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

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

(vii) The reason for greater tendency of carbon for catenation than other elements in the group may further be explained by the fact that the C-C bond energy is approximately of the same

magnitude as the energies of the bond between C and other elements. On the other hand, the Si-Si bond is weaker than the bond between silicon and other elements.

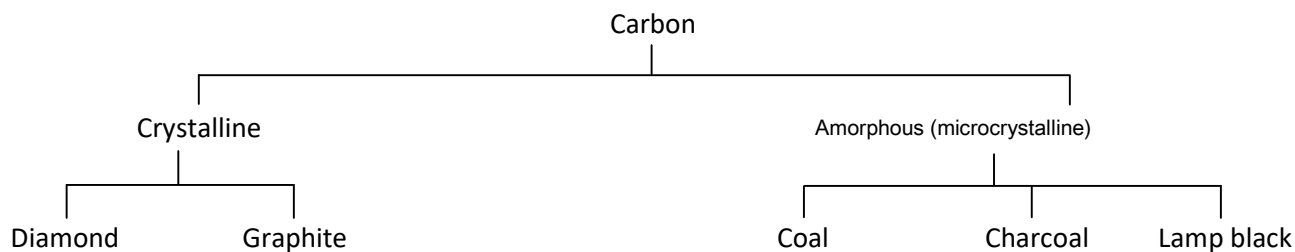
Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)
C-C	348	Si-Si	180
C-O	315	Si-O	372
C-H	414	Si-H	339
C-Cl	326	Si-Cl	360
C-F	439	Si-F	536

(10) Allotropy

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

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

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



(iv) **Diamond and Graphite:** The two allotropic forms of crystalline carbon. Diamond is the purest and hardest form of carbon. Its structure involves a giant molecular form where each carbon atom is surrounded by four other carbon atoms (sp^3 hybridization) In doing so, each carbon atom is located in the center of a regular tetrahedron with its four valencies directed towards the four corners which are

linked with four other carbon atoms ($C - C - C$ angle = $109^\circ 28'$ $C-C=154 \text{ pm} = 1.54 \text{ \AA}$). The hardness of diamond result due to the uniformity of the C-C covalent bonds. Since the C-C bond length is very small, it has very high density (3.51 g cm^{-3}) and has more compact structure than graphite (density, 2.25 g cm^{-3}) It does not melt (vaporizes at 3773K) has very high refractive index (2.45) and is insoluble in all ordinary solvents. It does not conduct electricity as all the four valence electrons are used up in forming covalent bonds with other carbon atoms Diamond, because of its hardness is used in cutting, grinding instruments such as glass and drilling equipment's Its ability to reflect and refract light makes diamond an important jewellery material.

Difference between diamond and graphite

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

Carbon also exists in three common microcrystalline or amorphous forms (charcoal, carbon black and cocke) Carbon black is formed when hydrocarbons, petroleum, turpentine oil or

substances rich in carbon contents are heated in limited supply of oxygen, $\text{CH}_{4(g)} + \text{O}_{2(g)} \rightarrow \text{C}_{(s)} + 2\text{H}_2\text{O}_{(g)}$

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

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

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

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

Graphite occurs in Nature and can also be obtained from coke. In graphite, out of four valence electrons, only three form covalent bonds (sp^2 hybridization) with three other carbon atoms. This forms hexagonal rings as sheets of one atom thickness. These sheets are held together by weak attractive forces. One electron of each carbon atom is free and this enables these thin sheets to slide over one another. For this reason graphite is a soft material with lubricating properties. Graphite is a dark, opaque and soft material (density = 2250 kg/m^3) although graphite is non-metallic still it possesses a metallic lustre. It is insoluble in ordinary solvents. Graphite is a good conductor of heat and electricity because of the presence of one free electron on each carbon

atom. Graphite is used as a dry lubricant in making electrodes in electric furnaces. It is chiefly used in lead pencils.

Chemical properties

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

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

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

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

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

CO_2 and SiO_2 is acidic, GeO_2 is weakly acidic while SnO_2 and PbO_2 are amphoteric in nature.

All the elements of group 14 except silicon form monoxides e.g., CO , GeO , SnO and PbO . Out of these monoxides only CO is neutral, while all other monoxides are basic.

(3) **Halides:** Elements of group 14 react with halogens directly to form tetrahedral and covalent halides except C where its halide is produced by the action of halogens on hydrocarbons.

$PbBr_4$ and PbI_4 do not exist because Pb^{4+} is a strong oxidant and Br^- and I^- are strong

reductants. Hence Pb^{4+} ion is difficult to survive in presence of strong reductants Br^- and I^- and is immediately reduced to Pb^{2+} .

Anomalous behaviour of Carbon

Carbon is found to differ in many properties from the rest of the members of group 14. This is because of the following:

(i) Its smallest size

(ii) Its high electronegativity

(iii) Its property to catenate

(iv) Absence of d-orbitals in it.

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

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

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

(3) It has maximum tendency to show catenation.

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

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

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

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

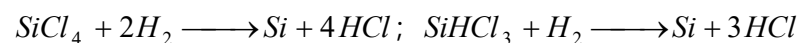
Silicon and its compounds

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

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

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

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



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

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

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

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

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

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

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

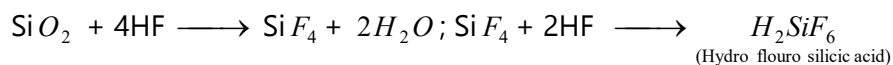
(4) **Uses of silicon** : It is added to steel as ferrosilicon (an alloy of Fe and Si) to make it acid resistant. It is used in the pure form as a starting material for production of silicon polymers (Silicones).

(5) **Compounds of silicon**

Silica or silicon dioxide (SiO_2)

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

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

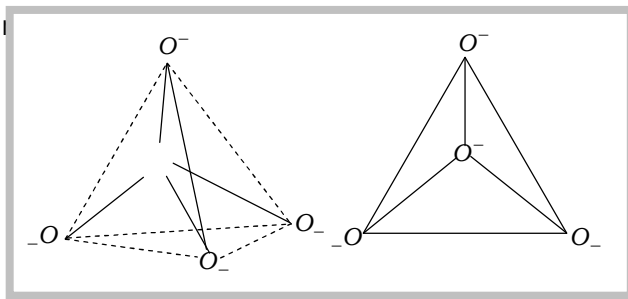


HF readily dissolves Silica, therefore HF can not be store in glass bottles which contain Silica.

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

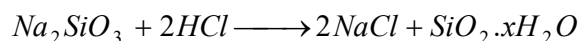
Silicates

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



Silica gel

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

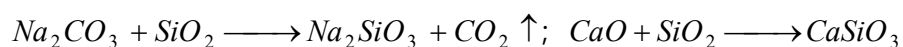


The white ppt. thus obtained is heated to lose water. When the water content is very low, the solid product is called silica gel. It possesses excellent absorptive properties due to its porous nature and is used for absorbing moisture and an adsorbent in chromatography.

Glass

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

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



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

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

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

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

Crook's glass	$K_2CO_2, PbCO_3, CeO_2$, sand	Absorbs ultra violet rays, for making lenses
---------------	---------------------------------	----------------------------------------------

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

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