

Inorganic chemistry II  
Second stage / Second semester

The Sixth lecture

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**COMPARISON OF CARBON AND SILICON**

Carbon and silicon, the first two elements of group 14 have a number of similarities in their properties as both have same number of electrons in the outermost shell. They show many dissimilarities in properties also because the number of electrons in the penultimate shells are different.

**Points of Similarities**

(a) Electronic configuration: Both the elements have 4 electrons, *i.e.*,  $s^2 p^2$  grouping in their valence shell.

C; 2, 4

Si; 2, 8, 4

(b) Occurrence : Both are widely distributed in nature. Carbon is the essential constituent of vegetable and animal kingdom while silicon is an essential constituent of mineral kingdom.

(c) Non-metallic : Both are typical non-metallic. They form oxides of type  $MO_2$  which are acidic in nature. Their monoxides CO and SiO are neutral, SiO is comparatively unstable.

(d) Valency : Both show tetravalency both form covalent compounds by sharing of electrons. Both show tetravalency on account of  $sp^3$  hybridization.

(e) Allotropy : Both show allotropy

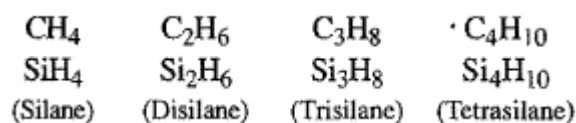
(f) Catenation: Both carbon and silicon possess the property of catenation. Their atoms join with one another in large numbers forming the long chains and rings.

(g) Similar compounds:

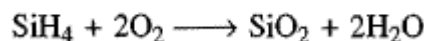
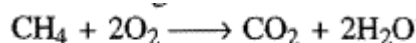
(i) Formation of oxides: Both burn in oxygen to form acidic oxides.



(ii) Formation of hydrides: Both form a number of similar hydrides.



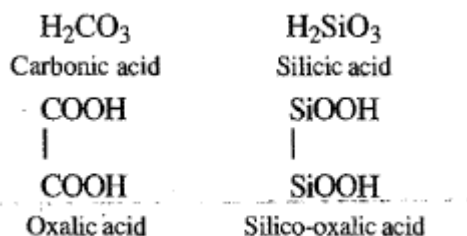
These are all colourless gases and burn in air to form oxides



(iii) Formation of halides : Both form covalent halides of same formula.

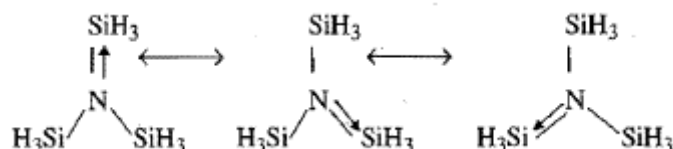


(iv) Formation of acids : Both form similar types of acids

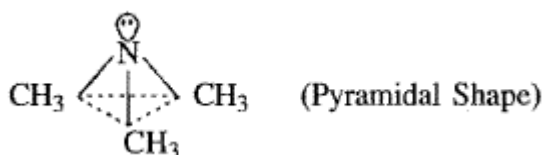


**(v) Structure of trimethyl ammonia and trisilyl ammonia :**

Trimethyl ammonia is pyramidal whereas trisilyl ammonia is a planar molecule. In silicon atom, there is vacant *d*-orbital hence electron pair of nitrogen is donated to silicon by  $p_\pi-d_\pi$  overlapping in trisilyl ammonia. Thus, trisilyl ammonia has planar structure.



Trimethyl ammonia has pyramidal shape due to presence of lone pair of electron at nitrogen.



**Points of Difference (Dissimilarities)**

No.	Carbon	Silicon
1.	It has 2 electrons in the penultimate shell.	It has 8 electrons in the penultimate shell.
2.	It is black solid. It does not melt.	It is reddish brown solid. It melts at 1410 °C.
3.	Some allotropic forms of carbon, <i>e.g.</i> , graphite are good conductors of electricity.	It is bad conductor of heat and electricity.
4.	Caustic alkalies have no action on carbon.	It reacts with alkalies to evolve hydrogen. $\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2$
5.	<p>The dioxide, carbon dioxide, is a gas. It has a linear structure. Carbon atom is linked to two oxygen atoms by double covalent bonds. Carbon is <i>sp</i> hybridized. These hybrid orbitals overlap with the <i>p</i>-orbital of each oxygen atom. The remaining <i>2p</i>-orbital of each oxygen atom form <math>\pi</math>-bonds with <i>p</i>-orbitals of carbon atom</p> $\text{O} \begin{array}{c} \text{p-p} \\ \hline \text{p-sp} \end{array} \text{C} \begin{array}{c} \text{p-p} \\ \hline \text{sp-p} \end{array} \text{O}$ <p>CO<sub>2</sub> molecules are held together by weak van der Waals' forces hence it exists as a gas at ordinary temperatures. Carbon dioxide dissolves in water and behaves as weak acid.</p> $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ <p style="text-align: center; margin-left: 100px;">Carbonic acid</p> $2\text{NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	<p>The dioxide, silica, is a solid. It has a giant structure. The silicon atom is linked with oxygen atoms by single covalent bonds.</p> <p>Silica has a three dimensional infinite structure in which silicon is tetrahedrally bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms by covalent bonds. Hence, silica has high melting point and is a solid. Silica is insoluble in water and acts as a very weak acid.</p> $2\text{NaOH} + \text{SiO}_2 \longrightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$

6.	The lower oxide, carbon monoxide, is known. It is stable and neutral in nature.	The SiO is unstable.
7.	It forms a large number of hydrides known as hydrocarbons which are stable. These are not hydrolysed by water.	It forms lesser number of hydrides which are not very stable. These act as reducing agents. These are hydrolysed by water with evolution of hydrogen.
8.	It does not directly react with Cl <sub>2</sub> or Br <sub>2</sub> .	It reacts with Cl, or Br, at 500°C. $\text{Si} + 2\text{Cl}_2 \xrightarrow{500^\circ\text{C}} \text{SiCl}_4$
9.	CCl <sub>4</sub> is a stable compound and it is not hydrolysed by water. The hydrolysis does not occur because water molecules cannot be coordinated to carbon as its maximum covalency is four.	SiCl <sub>4</sub> is less stable and it is hydrolysed by water. The hydrolysis is due to the fact that water molecules can be coordinated to Si as its maximum covalency is six.
10.	The oxyacid, H <sub>2</sub> CO <sub>3</sub> , is unstable. It is best known in the form of salts, carbonates.	The oxyacid, H <sub>2</sub> SiO <sub>3</sub> , is stable. It is also known in the form of salts, silicates.
11.	It does not form complex ions as <i>d</i> -orbitals are not present and maximum covalency is four.	It forms a number of complex ions as <i>d</i> -orbitals are present and maximum covalency is six.

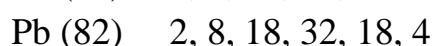
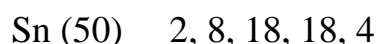
## Comparison Of Tin And Lead

Tin and Lead are the last two members of group 14. Both resemble each other in many respects but lead being the last member having higher atomic mass differs in some respects with tin.

### Points of Similarities

#### 1. Electronic configuration :

Both have same electron configuration having 4 electrons in the outermost shell and 18 electrons in the penultimate shell



#### 2. Metallic nature :

Both of them are metals. They have low melting and boiling points.

Element	m.pt. (°C)	b.pt. (°C)
Sn	232	2275
Pb	327	1620

Both are malleable in nature.

#### 3. Valency :

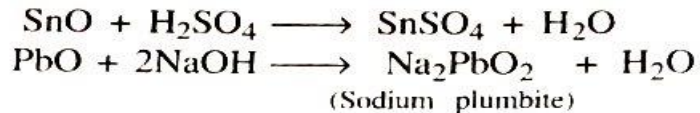
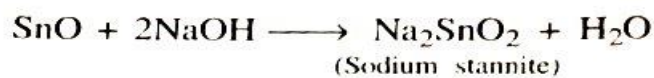
Both show valency of 4 and 2 in their compounds. It is based on the fact that either 4 or 2 electrons from the outermost shell act as valency electrons. The lower valency, *i.e.*, 2 is shown on account of the inertness of *ns* pair of electrons. The compounds having divalency are electrovalent while compounds having tetravalency show covalent nature. Both are electropositive metals but also exhibit an electronegative character in some of their compounds. Similar to silicates, the stannates and plumbates are known.

#### 4. Action of alkalis :

Both react with hot alkali solution and liberate hydrogen.



5. Both form amphoteric oxides of the type  $MO$  and  $MO_2$ .



6. Both form tetrachlorides of the type  $MCl_4$ . These are hydrolysed by water.



These tetrachlorides combine with HCl to form chloro acids.



Chlorostannic acid

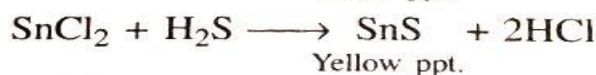


Chloroplumbic acid

Tetrachlorides decompose on heating.



7. Sulphides of both are precipitated by passing  $\text{H}_2\text{S}$  through their salt solutions.



8. Both form tetrahydrides which are unstable.

9. Both form organometallic compounds.



Tin tetraethyl



Lead tetraethyl

#### Points of Difference (Dissimilarities)

No.	Tin	Lead
1.	Tin shows allotropy.	Lead does not show allotropy.
2.	Tin does not leave any mark on paper	Lead leaves a mark on paper.
3.	Ductile.	Not very ductile.
4.	Tin is a metalloid	Lead is a metal.
5.	SnO does not combine with silica.	PbO combines with silica showing PbO is more basic than SnO. $\text{PbO} + \text{SiO}_2 \longrightarrow \text{PbSiO}_3$
6.	SnCl <sub>2</sub> is soluble in both dil. and conc. HCl.	PbCl <sub>2</sub> is insoluble in dil. HCl but soluble in conc. HCl forming complex H[PbCl <sub>3</sub> ], H <sub>2</sub> [PbCl <sub>4</sub> ].

7.	SnS is soluble in yellow ammonium sulphide showing its acidic nature.	PbS is insoluble in yellow ammonium sulphide showing its basic nature.
8.	Stannic compounds are stable. Stannous compounds act reducing agents.	Plumbous compounds are stable. Plumbic compounds act as oxidising agents.
9.	Tin is not attacked by organic acids. The reaction is not retarded with sulphuric acid as sulphates of tin are soluble. Sn forms metastannic acid with concentrated nitric acid.	Lead dissolves in organic acids. The reaction with sulphuric acid is retarded by the formation of insoluble PbSO <sub>4</sub> . Pb forms lead nitrate with concentrated nitric acid.
10.	Tin combines with sulphur to form stannic sulphide. $\text{Sn} + 2\text{S} \longrightarrow \text{SnS}_2$	Lead combines with sulphur to form lead sulphide. $\text{Pb} + \text{S} \longrightarrow \text{PbS}$

Q/ Carbon atom is tetravalent inspite of the fact that there are only two unpaired electrons in it.

### CARBON

#### 1. Unique properties of carbon in the group

1. Carbon has the smallest atomic radius and lowest atomic volume amongst all the elements of group 14.
2. It is most compact. It is the hardest and has highest melting and boiling points amongst the elements of group 14.
3. It has the highest ionisation energy and is most electronegative element of group 14.
4. Its maximum covalency is 4 as *d* electrons are absent in the valency shell.
5. It has maximum property of catenation. It can form multiple bonds. As a result, carbon forms a large number of compounds.
6. Carbon dioxide, CO<sub>2</sub>, is a gas while the dioxides of other elements are solids.
7. CCl<sub>4</sub> does not undergo hydrolysis while the tetrahalides, MX<sub>4</sub>, of other elements undergo hydrolysis.

#### 2. Occurrence

Carbon is one of the most widely distributed elements in nature. It occurs free as well as in the combined state. It occurs free in crystalline form as diamond, graphite, and in the amorphous form as coal. It is present in all living organisms, plants and animals, in the combined state in the form of proteins, carbohydrates, fats and other complicated compounds. It is present as hydrocarbons in natural gas and petroleum. It Occurs as carbon dioxide and carbon monoxide in atmosphere. In mineral world, it occurs in the form of carbonates such as limestone, CaCO<sub>3</sub> magnesite, MgCO<sub>3</sub> calamine, ZnCO<sub>3</sub> dolomite, MgCO<sub>3</sub>CaCO<sub>3</sub> siderite, FeCO<sub>3</sub> : cerussite, PbCO<sub>3</sub> etc.

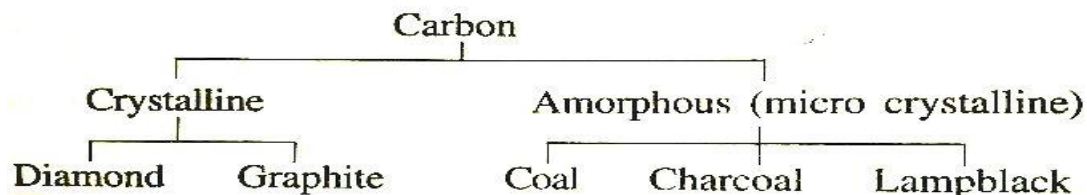
#### 3. Allotropic forms of carbon

The property due to which an element exists in two or more forms which differ in their physical and some of the chemical properties is known as allotropy and the various forms

are called allotropes or allotropic modifications. This phenomenon is due to the difference either in the number of atoms in the molecules [as in the case of oxygen (O<sub>2</sub>) and ozone (O<sub>3</sub>)] or arrangement of atoms in the molecules (as in the case of various forms of carbon).

Carbon exists in two allotropic forms:

(a) Crystalline and (b) amorphous. The crystalline forms are diamond and graphite while the amorphous forms are coal, charcoal, lampblack, etc.



### (a) Diamond :

(i) It is the purest form of carbon.

(ii) It is found naturally as well as obtained artificially.

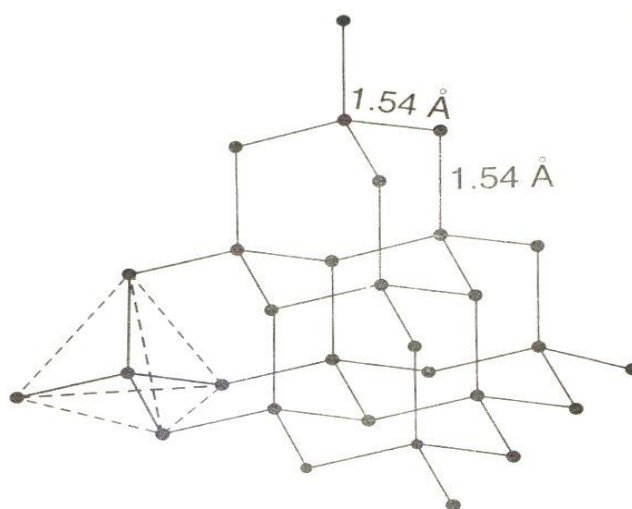
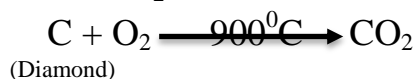
(iii) It is the hardest natural substance known.

(iv) It is transparent and has a specific gravity 3.52.

(v) It is a bad conductor of heat and electricity. It is transparent to X-rays and glows in ultraviolet rays with bluish green colour.

(vi) Its refractive index is high (2.45) and when properly cut, it produces maximum total internal reflection which is responsible for its brilliance.

(vii) It is chemically inert. It is not attacked by acids, alkalies and salts. It burns in air on heating at 900°C to form CO<sub>2</sub>. It reacts with fluorine at 700°C to form CF<sub>4</sub>



Structure of diamond



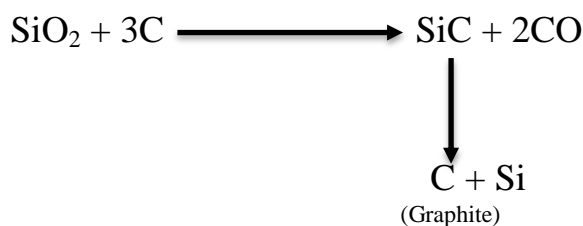
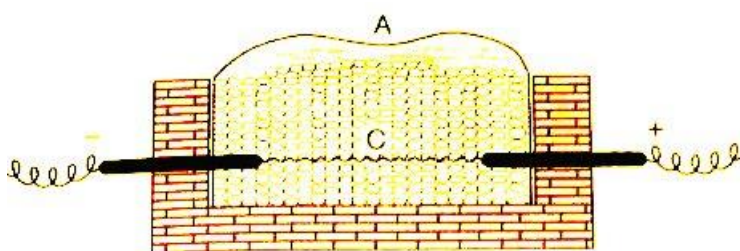
The important properties of diamond are related to its structure. In diamond, each carbon atom is in  $sp^3$  hybridized state and linked to four other carbon atoms tetrahedrally by covalent bonds. This gives a giant three dimensional polymeric structure in which C-C distance is 1.54 Å and bond angle is 109.5°.

As the atoms are held firmly by strong covalent bonds, diamond is the hardest substance, possesses very high melting point (3600°C) and chemically inert. Since there is no mobile electron present, diamond is non-conductor of electricity.

**Uses :** Diamond is used as a gem stone on account of reflection and refraction of light. Impure diamonds (black) are used in knives for cutting glass, "Diamond studded saws" in drill bits, as rock borers and is also used as polishers.

**(b) Graphite :** (i) It is found in nature and also manufactured by Acheson process. Anthracite is heated with sand in an electric furnace of the resistance type. It is fitted with two carbon electrodes joined by a thin carbon rod through which an alternating current is passed (Fig. below ).

The charge is heated at 3000°C for 24-30 hours. Silicon carbide is formed first which decomposes at high temperature into graphite and silicon. Silicon volatilizes away leaving behind graphite.



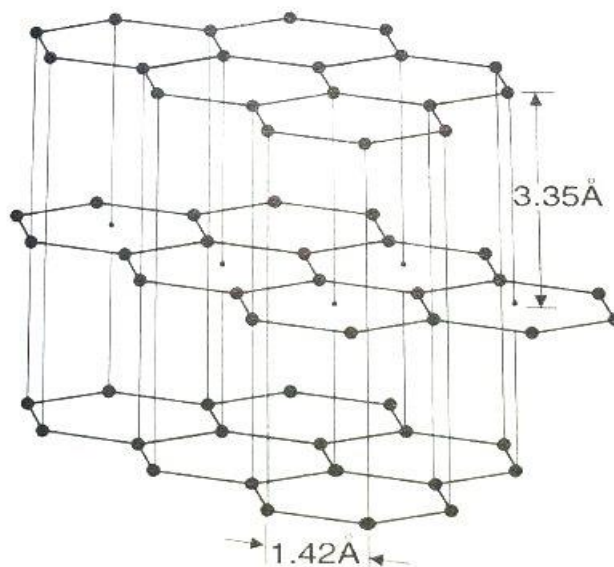
(ii) It is a soft, greasy, dark greyish coloured crystalline solid.

(iii) Its density is 2.5 g mL<sup>-1</sup>.

(iv) It is good conductor of electricity and its conductivity increases with temperature.

(v) It leaves a black mark on paper and is called black lead or plumbago.

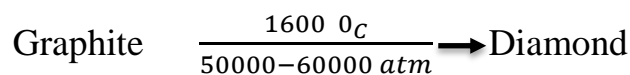
(vi) It is chemically more active than diamond. It ignites in air or oxygen at 700°C to form CO<sub>2</sub>. It is not attacked by alkalis and dilute acids. However, when treated with concentrated HNO<sub>3</sub> or concentrated H<sub>2</sub>SO<sub>4</sub>, it is oxidised to insoluble yellowish green substance known as graphitic acid, C<sub>4</sub>H<sub>11</sub>O<sub>5</sub>. With alkaline potassium permanganate, it is oxidised to mellitic acid [C<sub>6</sub>(COOH)<sub>6</sub>] and oxalic acid. It forms CO<sub>2</sub> with chromic acid.



It has a two dimensional sheet structure. Each carbon atom is in  $sp^2$ - hybridized state and is linked to three other carbon atoms in a hexagonal planar structure. As there are four valence electrons in each carbon atom, after forming three C-C bonds, each carbon atom is left with one spare electron in its  $p$ -orbital. This electron then overlaps with each other to form a  $\pi$ -bond. Hence, the C-C distance in graphite is shorter (1.42 Å) than that of diamond (1.54 Å). The  $\pi$ -electrons are free to move throughout the entire layers, graphite is good conductor of electricity. The adjacent layers are held by weak van der Waals' forces and the distance between two layers is sufficiently large (3.4 Å). Thus, two adjacent layers can easily slide over each other and hence graphite is soft and possesses low density. The more reactivity of graphite is due to the presence of mobile electrons. Graphite is of two forms:  $\alpha$  and  $\beta$ .

In  $\alpha$ -graphite layers are arranged in sequence  $ABAB$ , with the third layer exactly above first layer. In  $\beta$ -graphite, the layers are arranged as  $ABCABC\dots$ . The two forms are interconvertible.

Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.



When graphite is heated with vapours of K, Rb, Cs at  $300^\circ\text{C}$ , it forms  $\text{C}_8\text{M}$ . Graphite is diamagnetic but  $\text{C}_8\text{M}$  is paramagnetic.

**Uses :** Graphite is used:

- (i) for lining and making electrodes of electric furnaces.
- (ii) in making refractory crucibles.
- (iii) in making lead pencils.
- (iv) as a moderator in nuclear reactor.



(v) as a lubricant in machinery.

**(c) Coal :** It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air. It is found in various forms which represent the different stages of transformation of vegetable matter. The successive stages of transformation are: peat, lignite, bituminous, steam coal and anthracite. The carbon contents of these forms along with calorific values are given below:

	Peat	Lignite	Bituminous	Steam	Anthracite
Carbon content %	60	67	88	93	95
Calorific value (B.Th.U. per lb)	9900	11.700	14.950	15.720	16.200

[1 B.Th.U. = 252 calories or 397 B.Th.U. = 1 kcal.]

The common variety of coal is bituminous. It is hard like stone and burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame.

When coal is subjected to destructive distillation by heating in the absence of air, it loses volatile constituents such as coal gas, ammonia, benzene, phenol and tar, the residue left behind is coke. Thus, coke an artificial product. It is coal minus volatile matter.

**Uses :** Coal is mainly used: (i) as a fuel. (ii) for the manufacture of coal gas, coal tar and coke. (iii) in the manufacture of synthetic petrol.

Coke is used (i) as a reducing agent in iron and steel industry. (ii) as a fuel. (It burns without smoke) (iii) for making fuel gases and graphite.

**(d) Charcoal :** This form of carbon is obtained by burning wood, cellulose or any other carbonous matter in a limited supply of air. Charcoal is of various forms such as wood charcoal, sugar charcoal, coconut charcoal, animal charcoal, etc. These forms contain varying amounts of carbon content. A very pure form of carbon is obtained from sugar. Wood charcoal is porous and has a very large surface area per unit weight. It is, therefore, used as an adsorbent. When charcoal is given a special treatment in order to increase its absorption capacity, the resulting material is known as activated charcoal and the process of treatment is called activation. Activation is carried out by heating the charcoal in retorts at 800-850°C in a current of superheated steam. This removes the impurities sticking on the surface and blocking the capillary pores.

Charcoal is the most active form of carbon. It easily burns in air to form CO<sub>2</sub>. It reacts with many oxidising agents. It is affected by conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>.



Uses : Charcoal is used

- (i) in removing offensive odour from air in the air conditioning processes.
- (ii) in making filters in cigarettes as to remove vapours of nicotine.

(iii) in removing fused oil from crude spirit.

(iv) in decolourising sugar syrup and refining oils, fats, glycerine, etc.

(v) in treatment of drinking water after chlorination as it adsorbs excess of chlorine.

(vi) in gas masks as it adsorbs poisonous gases.

**(e) Lampblack or carbon black or soot:** It is obtained by burning substances rich in carbon content such as kerosene, petroleum, turpentine oil, acetylene, etc., in a limited supply of air. These substances yield a large amount of smoke which is passed into chambers having wet blankets. The soot collected on these blankets is called lampblack.

It is almost pure carbon. The carbon content is as high as 98-99% with a small impurity of hydrocarbon, Lampblack is a soft black powder. It is used for making printing inks, black paints, Indian ink, boot polishes and ribbons of typewriters. The main application, at present, is as a filler in making rubber tyres.

### Chemical properties of carbon

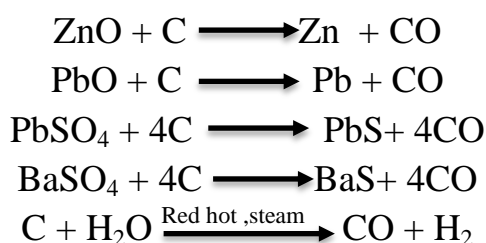
Charcoal has the enormous surface area and hence, it is the most reactive form of carbon. The other forms such as diamond, graphite, coal, etc., which are denser, are less reactive in nature.

**(a) Combustion:** All the allotropic forms of carbon burn in air or oxygen forming carbon dioxide (when oxygen supply is sufficient) and carbon monoxide (when oxygen supply is insufficient).

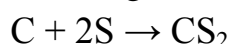


This property shows that all the allotropic forms are chemically identical.

**(b) Reducing agent :** Carbon is a strong reducing agent. It reduces many metallic oxides to corresponding metals, sulphates into sulphides and water to hydrogen. These reactions occur at high temperatures.



**(c) Combination with other elements :** It combines with sulphur when the vapours of sulphur are passed over red hot carbon forming carbon disulphide.



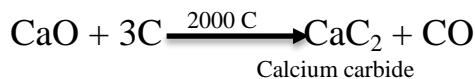
When electric arc is struck between carbon electrodes in presence of hydrogen, acetylene is formed.



Beryllium when heated with carbon forms carbide.



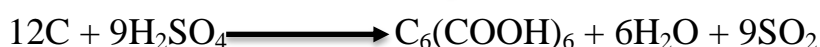
Various carbides are formed when carbon is heated with certain oxides



**(d) Reactivity towards acids :** Charcoal dissolves slowly in hot dilute  $\text{HNO}_3$  forming a brown coloured substance, artificial tannin. Conc.  $\text{HNO}_3$  oxidises carbon to carbon dioxide



Hot and conc.  $\text{H}_2\text{SO}_4$  also oxidises it to carbon dioxide. A small quantity of mellitic acid (benzene hexacarboxylic acid) is also formed.



## COMPOUNDS OF CARBON

### 1. Oxides of Carbon

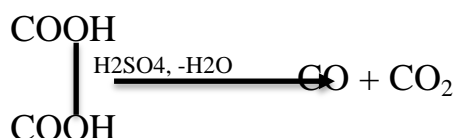
Two oxides of carbon, carbon monoxide and carbon dioxide are important and described below

#### (a) Carbon Monoxide, CO

It is found in small amounts in volcanic gases, chimney gases, exhaust gases of internal combustion engines and coal gas.

**Preparation:** The following methods can be applied for the preparation of carbon monoxide:

**(i) By heating oxalic acid with concentrated sulphuric acid :** A mixture of CO and  $\text{CO}_2$  is obtained. Sulphuric acid acts as a dehydrating agent.  $\text{CO}_2$  is removed by passing the gaseous mixture through caustic soda or caustic potash solution.



Similarly by heating formic acid with concentrated  $\text{H}_2\text{SO}_4$ , only CO is obtained.



**(ii) By the reduction of oxides of heavy metals with carbon :** On heating oxides of heavy metals with carbon, CO is formed.



**(iii) By reduction of carbon dioxide :**  $\text{CO}_2$  can be reduced with carbon or zinc at high temperatures.  $\text{CO}_2$  when passed over red hot zinc, a mixture of CO and  $\text{CO}_2$  is obtained.

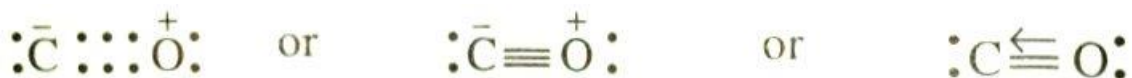


Similarly, when  $\text{CO}_2$  is passed over red hot charcoal, the reduction of  $\text{CO}_2$  into CO occurs with the formation of a mixture of  $\text{CO}_2$  and CO. The gaseous mixture is passed through NaOH or KOH solution as to remove  $\text{CO}_2$ .

**Uses:**

- (i) It is used as a fuel in the form of water gas ( $\text{CO} + \text{H}_2$ ) and producer gas ( $\text{CO} + \text{N}_2$ ).
- (ii) CO is used in the manufacture of methanol, synthetic petrol, formic acid and phosgene gas (highly poisonous gas).
- (iii) It is used as a reducing agent in the extraction of iron.
- (iv) It is used in the extraction of nickel (Mond's process).

**Structure :** The electronic structure of carbon monoxide may be represented as follows:



Carbon atom is *sp* hybridized. One *sp*-orbital is being used to form a single bond with oxygen atom while the other *sp*-orbital which points away from the C-O bond contains a lone pair of electrons. The remaining two unhybridized *p*-orbitals form two  $\pi$ -bonds with two *p*-orbitals of oxygen atoms. The presence of a triple bond is evidenced by the following facts:

- (i) The bond length between carbon and oxygen is  $1.13 \text{ \AA}$  which corresponds to carbon-oxygen triple bond.
- (ii) The value of dipole moment is small.
- (iii) Due to presence of lone pair of electrons on carbon. carbon monoxide molecule acts as a ligand and can form a coordinate bond with certain metals ( $\leftarrow \text{M} \equiv \text{C} \text{ O}$ )

### (b) Carbon Dioxide, $\text{CO}_2$

#### Occurrence :

It is present in atmosphere to the extent of 0.03-0.05 per cent. It comes to the atmosphere from animal breathing, decay of vegetable matter, burning of carbon and carbonous matter, etc. It is also utilised by plants in photosynthesis. Thus, a carbon dioxide cycle is operating in nature and the proportion of  $\text{CO}_2$  in the atmosphere remains about the same. It is found in combined state in the form of carbonates.

**Preparation :** The following methods are used for its preparation

- (i) By the complete combustion of carbon : Carbon is burnt in free supply of air.



If CO is formed, it also burns with pale blue flame forming carbon dioxide.



- (ii) By the action of dil. mineral acids on carbonates and bicarbonates: Mineral acids react with carbonates and bicarbonates and evolve carbon dioxide.



This method is used in the laboratory for the formation of carbon dioxide. Marble pieces ( $\text{CaCO}_3$ ) are taken in Woulfe bottle which is fitted with a thistle funnel and a delivery tube. The other end of the delivery tube is kept into a dry cylinder through a card board disc. Pieces of marble are first covered with water and then concentrated HCl is added through the funnel.  $\text{CO}_2$  is formed which is collected by upward displacement of air.

Sulphuric acid is not used for the preparation because calcium sulphate formed gets deposited on the pieces of marble. This prevents the further action of  $\text{H}_2\text{SO}_4$  on marble pieces.

(iii) By heating carbonates and bicarbonates : The carbonates of less electropositive metals on heating decompose evolving carbon dioxide.



Bicarbonates of all the metals decompose on heating with evolution of  $\text{CO}_2$ .



### Uses :

(i) It is used in the manufacture of aerated water.

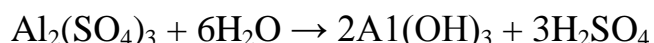
(ii) Solid  $\text{CO}_2$  (dry ice) is used in refrigeration. It is superior refrigerant than common ice because it can produce very low temperatures and does not form liquid on melting. A mixture of solid  $\text{CO}_2$  and ether is used to produce low temperature of the order of  $-80^\circ\text{C}$  to  $-100^\circ\text{C}$ .

(iii) Carbogen is a mixture of  $\text{O}_2$  and  $\text{CO}_2$  (5-10%). It is used for artificial respiration in the case of pneumonia patients and victims of CO poisoning.

(iv) It is used in the manufacture of white lead and sodium carbonate (Solvay process).

(v)  $\text{CO}_2$  is used as fire extinguisher. The use of common fire extinguisher is based on the production of  $\text{CO}_2$ . A soda acid fire extinguisher contains a concentrated solution of sodium bicarbonate and a bottle containing concentrated sulphuric acid. When the apparatus is turned upside down the acid flows out of the bottle and reacts with sodium bicarbonate to produce  $\text{CO}_2$ .

Aluminium sulphate in place of conc.  $\text{H}_2\text{SO}_4$  is used in foam type fire extinguishers. When solution of  $\text{NaHCO}_3$  and aluminium sulphate react,  $\text{CO}_2$  is liberated along with the hydrolysis of aluminium sulphate producing aluminium hydroxide in the form of foam.



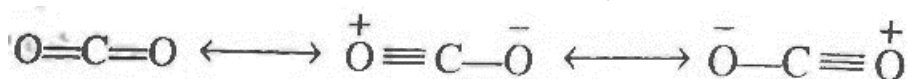
$\text{Al}(\text{OH})_3$  deposits on the burning articles and thus cuts off their contact with the air,

(vi)  $\text{CO}_2$  is used by plants in the form of food.

**Structure:**  $\text{CO}_2$  has a linear structure since its dipole moment is zero. Both the oxygen atoms are linked by double bonds.

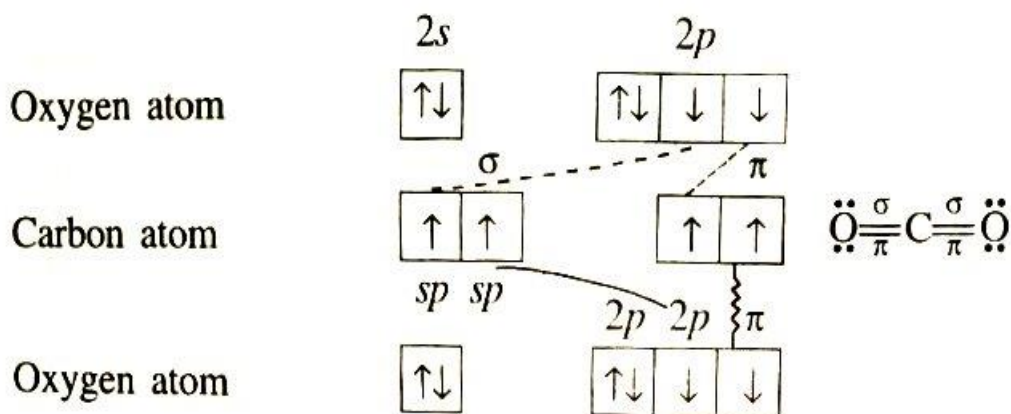


The C-O bond length is  $1.15 \text{ \AA}$  which is less than calculated value of double bond  $\text{C}=\text{O}$ . Thus, it is believed that  $\text{CO}_2$  molecule is a resonance hybrid of the following structures :

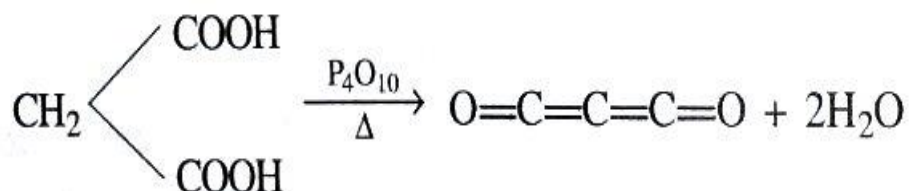


The formation of the molecule can be explained on the basis of hybridization. Carbon is  $sp$ -hybridized. The hybrid orbitals form sigma bonds with  $p$ -orbitals of each oxygen

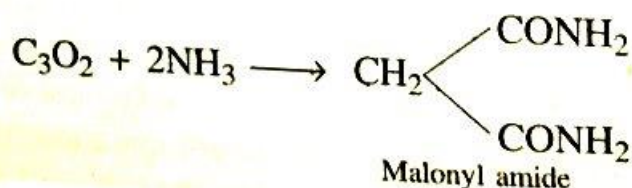
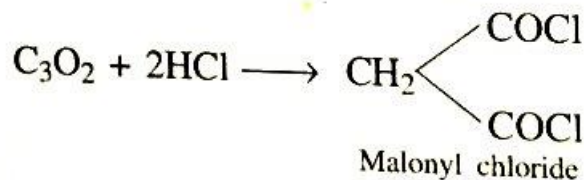
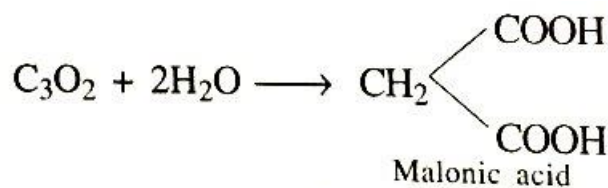
atoms. The unhybridized two  $p$ -orbitals of carbon atom form two  $\pi$ -bonds with two oxygen atoms.



Carbon forms some less stable oxides, e.g.,  $C_3O_2$ ,  $C_5O_2$  and  $C_{12}O_9$ . Graphite oxides are  $C_2O$  and  $C_2O_3$  which are still less stable. Carbon suboxide is formed by dehydration of malonic acid.



Some important reactions of carbon suboxide are:



**Carbonic Acid, Carbonates and Bicarbonates** Carbon dioxide is an acidic oxide, The solution of  $\text{CO}_2$  in water shows feeble acidic nature. This is believed due to the formation of carbonic acid.

$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  ( $\text{CO}_2$  is called carbonic anhydride.) Carbonic acid is known only in solution and has never been isolated in free state.

The carbonic acid is a dibasic acid and it form two series of salts by replacement of one or both the hydrogen atoms.

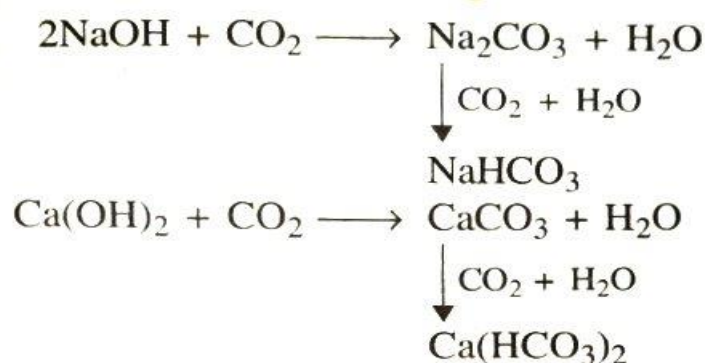


a) Acid salts are also called bicarbonates or hydrogen carbonates . these contain  $\text{HCO}_3^{1-}$  ions

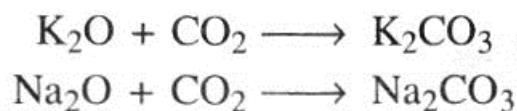
b) normal salt , are also called carbonates .these contain  $\text{CO}_3^{2-}$  ions.

The metallic carbonates or bicarbonates are prepared by following methods.

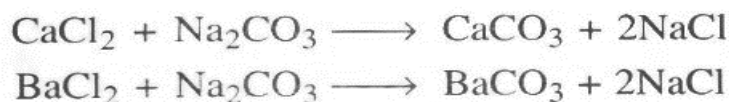
(i) By passing  $\text{CO}_2$  through the solution of base :



(ii) By reacting basic oxides and  $\text{CO}_2$  :



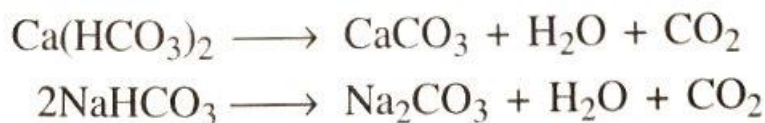
(iii) By double decomposition, i.e., by using sodiu carbonate :



### Properties :

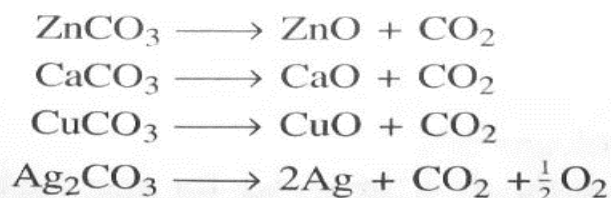
(i) Solubility:: (a) Except alkali metals carbonates, all other carbonates are insoluble in water. (b) The bicarbonates are soluble in water. The bicarbona of alkali metals are known in solid state while the bicarbona of alkaline earth metals are only known in solutions.

(ii) Action of heat : (a) All bicarbonates decompose on heating evolving carbon dioxide. The carbonate formed may further decompose except alkali metal carbonates.

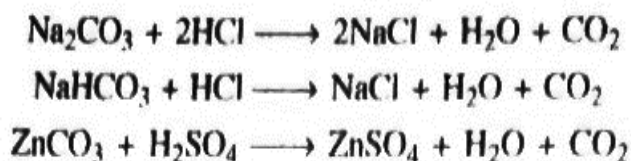


(b) Alkali metal carbonates except  $\text{Li}_2\text{CO}_3$  do not decmpose on heating.

(c) All other carbonates decompose on heating evolution of carbon dioxide.



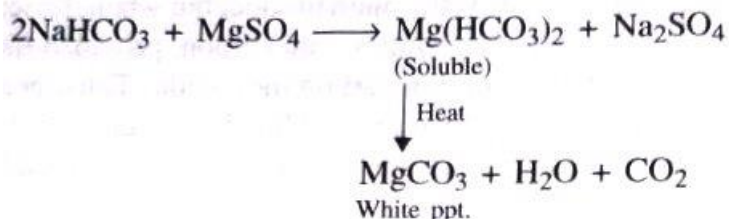
(iii) Action of acids :both carbonates and bicarbonates are decomposed by the action of acids with evolution of  $\text{CO}_2$  (effervescences).



(iv) Action of  $\text{MgSO}_4$  This is the reagent with which carbonates and bicarbonates can be distinguished and tested. Soluble carbonates form an insoluble white precipitate with magnesium sulphate in cold.



Bicarbonates do not form any white precipitate with magnesium sulphate in cold. However, when such solution is heated, a white precipitate appears.



(v) Effect of phenolphthalein : Soluble carbonates produce pink colour with phenolphthalein showing higher pH value while bicarbonates do not give pink colour with phenolphthalein.

### 3. Gaseous Fuels

Fuels are the substances which undergo combustion. As a result of their burning, they produce heat energy. During combustion, no undesirable product should be formed. The heat energy production depends on the presence of combustible substances such as carbon, carbon monoxide, carbonous matter, hydrogen, etc. in the fuels. Most common fuels are

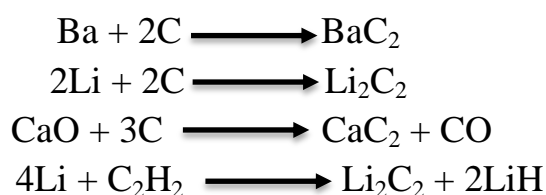
- (a) Solid fuels: Wood, lignite, peat, coke, charcoal, etc.
- (b) Liquid fuels: Petroleum products such as petrol, kerosene, spirits, etc.
- (c) Gaseous fuels: Water gas, producer gas, coal gas, oil gas, natural gas, etc.

#### Characteristics of good fuel:

- (i) It should have high calorific value
- (ii) It should yield very little ash content.
- (iii) It should not give any offensive odour or any undesirable product during burning,
- (iv) Its cost of production should be low and it should be easily available.
- (v) The combustion should be of moderate speed.

### 4. Carbides

Carbides are binary compounds of carbon with elements of lower or about equal electronegativity. Carbides are classified into three types on the basis of chemical bonding. These are salt-like carbides, covalent carbides and interstitial or alloy like carbides. Carbides are generally prepared by heating the element or its oxide with carbon or hydrocarbon at very high temperatures.



**Salt-like carbides:** These carbides are formed by the metals of groups IA, IIA and IIIA (except boron), coinage metals, zinc, cadmium and some lanthanides. Depending on the

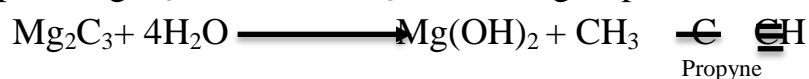


nature of the hydrocarbon formed during hydrolysis by water or dilute HCl, the ionic carbides can be further classified into the following types:

(i) Acetylides: These are the ionic carbides which yield acetylene on hydrolysis. These are regarded as derivatives of acetylene and are thus called acetylides. The alkali metals and copper, silver and gold form  $M_2C_2$  type compounds. The alkaline earth metals, zinc and cadmium give  $MC_2$  type carbides. These carbides are believed to contain  $[C \equiv C]^{2-}$  groups. Two types of crystal structures characterise these carbides. Both are tetragonal and are derived from sodium chloride structure by replacement of  $Cl^{1-}$  ions by  $C_2^{2-}$  ions.

(ii) Methanides : These carbides evolve allylene on hydrolysis. These are regarded as derivatives of methane and are called methanides.  $Al_4C_3$ ,  $Be_2C$ ,  $Mn_3C$ , etc., are some examples of methanides. These contain  $C^{4-}$  groups.

(iii) Alkylides : These carbides evolve allylene (methyl acetylene) on hydrolysis. The only example of this type is  $Mg_2C_3$ . It contains  $C_3^{4-}$  discrete groups.



(iv) Mixed carbides: These carbides yield a mixture of hydrocarbons on hydrolysis. Carbides of iron group,  $UC_2$  and  $ThC_2$  belong to this class.

**Covalent carbides :** The only true covalent carbides are those of silicon (SiC carborundum) and boron ( $B_4C$  and  $B_{13}C_2$ ). These are chemically inert and extremely hard materials. On account of hardness, these carbides are used as abrasives.

Silicon carbide is produced by heating quartz or sand with an excess of coke in an electric arc furnace.



**Metallic or interstitial carbides :** In these carbides, small carbon atoms occupy interstitial positions in the crystal lattices of the metals. These are of two types:  $MC$  ( $M = Ti, Zr, Hf, V, Nb, Ta, Mo, W$ ) and  $M_2C$  ( $M = V, Mo$  and  $W$ ). These carbides possess metallic lustre, high electrical conductivity and are chemically inert. These are extremely hard like diamond and possess very high melting points.

#### Uses:

(i) Calcium carbide is used to prepare acetylene. Acetylene is the starting material for many organic compounds. It is also used for production of oxy-acetylene flame employed for welding purposes.

(ii) SiC, being hard substance, is used as abrasive. Boron carbide is also used as abrasive and shield from radiations. It is used for the construction of atomic reactors.

(iii) Carbides which can withstand high temperature are used widely in furnace lining.

(iv) Tungsten carbide, WC, is used for the manufacture of high speed tools.