

## GROUP 13 ELEMENTS: THE BORON FAMILY

The elements of group 13 are

**B - Boron**

**Al - Aluminium**

**Ga - Gallium**

**In - Indium**

**Tl - Thallium**

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character. Al is the third most abundant element found in the earth's crust after oxygen and silicon.

### GENERAL CHARACTERISTICS (i.e., PHYSICAL PROPERTIES) OF BORON FAMILY :

**(i) Electronic configuration :** The elements of group 13 belong to p-block of the periodic table and these elements contain three electrons in the valence shell, therefore, their valence shell electronic configuration is  $ns^2np^1$

Element	At. No.	Electronic Config.	Valence Shell Config.
B	5	[He] $2s^2, 2p^1$	$2s^2 2p^1$
Al	13	[Ne] $3s^2, 3p^1$	$3s^2 3p^1$
Ga	31	[Ar] $3d^{10}, 4s^2 4p^1$	$4s^2 4p^1$
In	49	[Kr] $4d^{10}, 5s^2 5p^1$	$5s^2 5p^1$
Tl	81	[Xe] $4f^{14}, 5d^{10}, 6s^2 6p^1$	$6s^2 6p^1$

### **(ii) Atomic radii and ionic radii :**

(a) Atoms and their ions of group 13 elements have smaller size than those of alkaline earth metals of group-2, due to greater nuclear charge of former group than latter group.

(b) On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

**(iv) Ionization Enthalpy :** The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f-electrons, which have low screening effect, to compensate the increase in nuclear charge. The order of ionisation enthalpies, as expected, is  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$ .

The sum of the first three ionisation enthalpies for each of the elements is very high. This is reflected in the predominant covalent character in their compounds.

**(v) Electronegativity :** Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

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

### Chemical Properties:

#### ❖ Oxidation states :

- (a) B and Al show an oxidation state of +3 only while Ga, In and Tl show oxidation states of both +1 and +3.
- (b) As we move down in the group 13, due to inert pair effect, the tendency to achieve +3 oxidation state goes on decreasing and the tendency to acquire +1 oxidation state goes on increasing.
- (c) Stability of +1 oxidation state follows the order  $\text{Ga} < \text{In} < \text{Tl}$
- (d)  $\text{Tl}^+$  compounds are more stable than  $\text{Tl}^{3+}$  compounds.

#### ❖ Inert pair effect :

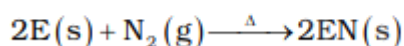
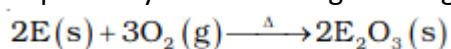
- (a) It is the reluctance of the s-electrons of the valence shell to take part in bonding and occurs due to ineffective shielding of the  $ns^2$  electrons by the intervening d and f electrons.
- (b) It increases down a group and thus the lower elements of group show lower oxidation states.

#### ❖ Nature of compounds :

- (a) The tendency of formation of ionic compounds increases from B to Tl.
- (b) Boron forms only covalent compounds whereas Al can form both covalent (e.g., anhydrous  $\text{AlCl}_3$ ) and ionic compounds (e.g., hydrated  $\text{AlCl}_3$ ) because when anhydrous  $\text{AlCl}_3$  is hydrated, the hydration energy released is sufficient to overcome the ionisation energy of Al.
- (c) Gallium forms mainly ionic compounds although anhydrous  $\text{GaCl}_3$  is covalent.

#### ❖ Reactivity towards air:

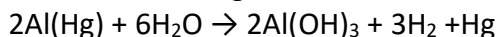
Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form  $\text{B}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  respectively. With dinitrogen at high temperature they form nitrides.



The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

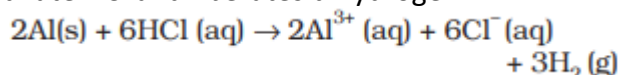
❖ **Reactivity towards water:**

(a) Both B and Al do not react with water but amalgamated aluminium does react with H<sub>2</sub>O evolving H<sub>2</sub>.

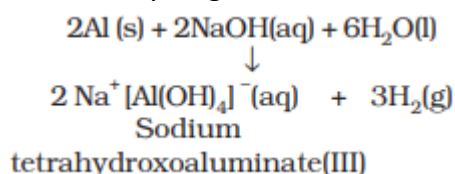


(b) Ga and In do not react with pure cold or hot water but Tl forms an oxide on the surface.

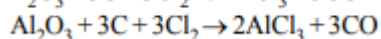
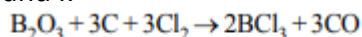
❖ **Reactivity towards acids and alkalies:** Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. Aluminium dissolves in dilute HCl and liberates dihydrogen.



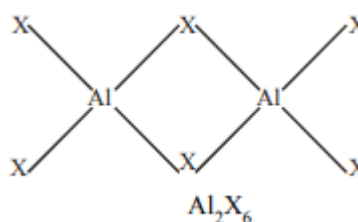
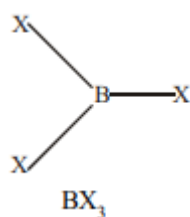
However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen



❖ **Reactivity towards halogens:** (a) All the elements of boron family (except thallium which forms thallos monohalides) form trihalides of type MX<sub>3</sub> where X = F, Cl, Br and I.



(b) All the boron trihalides, BX<sub>3</sub> and aluminium trihalides AlX<sub>3</sub> (except AlF<sub>3</sub> which is ionic) are covalent compounds whereas former exist as only monomers and latter as dimers, because boron atom is too small to coordinate with four large halide ions and in case of much smaller F<sup>-</sup> ion, the energy released during the formation of the bridge structure is not sufficient for the cleavage of the typical pπ-pπ bond in BF<sub>3</sub>.



❖ **ANOMALOUS BEHAVIOUR OF BORON :** Boron shows anomalous behaviour as compared to other member of the group, due to the following reasons.

- (i) It has smallest size in the group.
- (ii) It has high ionisation energy.
- (iii) It has highest electronegativity in the group.
- (iv) It does not have any vacant d-orbital in valance shell

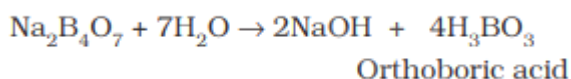
**A few points of difference are :**

- (i) It is a non-metal while other members of the group are metallic in character.
- (ii) It shows allotropy as crystalline and amorphous while other members do not.
- (iii) It has the highest m. p. and b.p. amongst the elements of group 13.
- (iv) It forms only covalent compounds while other members form both ionic and covalent compounds.
- (v) The oxides and hydroxides of boron are weak acidic while those of aluminium are amphoteric and those of other elements are basic.

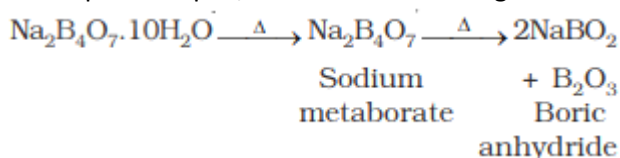
**SOME IMPORTANT COMPOUNDS OF BORON:**

**1. Borax:**

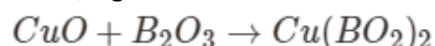
It is the most important compound of boron. It is a white crystalline solid of formula  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . In fact it contains the tetranuclear units  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  and correct formula; therefore, is  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ . Borax dissolves in water to give an alkaline solution.



On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead



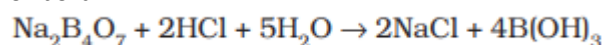
The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with copper salt on a loop of platinum wire in reducing flame, a green coloured bead is formed.



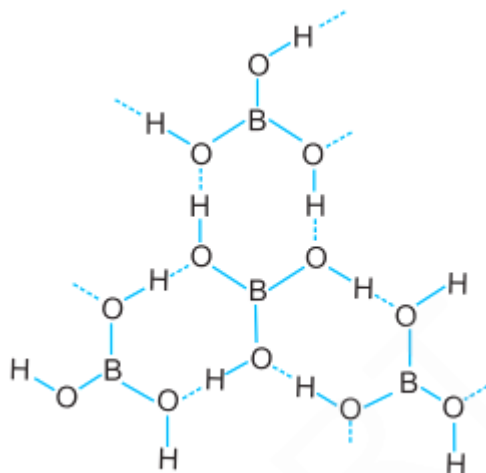
On heating in reducing flame we get  $\text{CuBO}_2$  which is subjected to cooling we get green color.

## 2. Orthoboric acid:

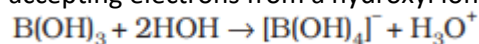
Orthoboric acid,  $\text{H}_3\text{BO}_3$  is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.



It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It has a layer structure in which planar  $\text{BO}_3$  units are joined by hydrogen bonds as shown in the following figure.



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

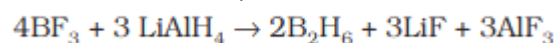


On heating, orthoboric acid above 370K forms metaboric acid,  $\text{HBO}_2$  which on further heating yields boric oxide,  $\text{B}_2\text{O}_3$ .

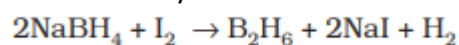


## 3. Diborane, $\text{B}_2\text{H}_6$ :

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with  $\text{LiAlH}_4$  in diethyl ether



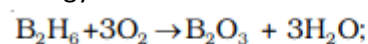
A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.



Diborane is produced on an industrial scale by the reaction of  $\text{BF}_3$  with sodium hydride.

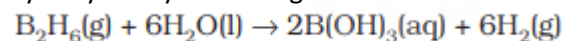


Diborane is a colourless, highly toxic gas with a b.p. of 180 K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

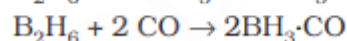
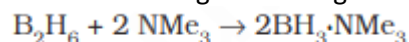


$$\Delta_c H^\ominus = -1976 \text{ kJ mol}^{-1}$$

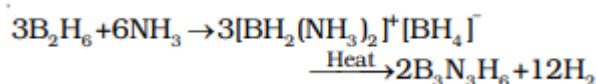
Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolysed by water to give boric acid.



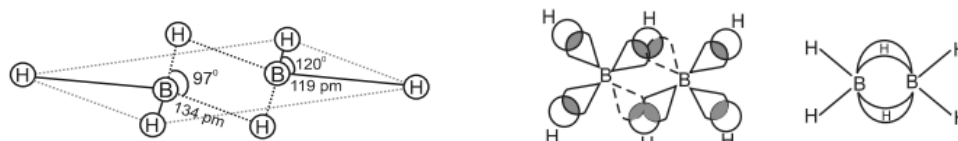
Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts,  $\text{BH}_3\cdot\text{L}$



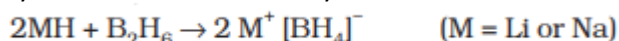
Reaction of ammonia with diborane gives initially  $\text{B}_2\text{H}_6\cdot 2\text{NH}_3$  which is formulated as  $[\text{BH}_2(\text{NH}_3)_2]^+[\text{BH}_4]^-$ ; further heating gives borazine,  $\text{B}_3\text{N}_3\text{H}_6$  known as “inorganic benzene” in view of its ring structure with alternate BH and NH groups.



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



Boron also forms a series of hydridoborates; the most important one is the tetrahedral  $[\text{BH}_4]^-$  ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with  $\text{B}_2\text{H}_6$  in diethyl ether.



Both  $\text{LiBH}_4$  and  $\text{NaBH}_4$  are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

#### ➤ USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS :

- ❖ Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications. Boron fibres are used in making bullet-proof vest and light composite material for aircraft. The boron-10 ( $_{10}\text{B}$ ) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- ❖ The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass. Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.
- ❖ Aluminium is a bright silvery-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. Aluminium is used extensively in industry and every day life. It forms alloys with Cu, Mn, Mg, Si and Zn. Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry. The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

## GROUP 14 ELEMENTS: THE CARBON FAMILY

The elements of group 14 are

**C - Carbon**

**Si - Silicon**

**Ge - Germanium**

**Sn - Tin**

**Pb - Lead**

C and Si are nonmetals, Ge is a metalloid and Sn and Pb are metals. C is black, Si is light-brown, Ge greyish white, Sn and Pb are silvery white.

Carbon is the seventeenth most abundant element by mass in the earth's crust. Naturally occurring carbon contains two stable isotopes:  $^{12}\text{C}$  and  $^{13}\text{C}$ . In addition to these, third isotope,  $^{14}\text{C}$  is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement.

- ❖ **Electronic Configuration:** The valence shell electronic configuration of these elements is  $ns^2 np^2$ . The inner core of the electronic configuration of elements in this group also differs.

### Electronic configuration :

Element	Atomic No.	Electronic configuration	Valence shell configuration
Carbon	6	[He] $2s^2 2p^2$	$2s^2 2p^2$
Silicon	14	[Ne] $3s^2 3p^2$	$3s^2 3p^2$
Germanium	32	[Ar] $3d^{10} 4s^2 4p^2$	$4s^2 4p^2$
Tin	50	[Kr] $4d^{10} 5s^2 5p^2$	$5s^2 5p^2$
Lead	82	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	$6s^2 6p^2$

- ❖ **Covalent Radius:** There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.
- ❖ **Ionization Enthalpy :** The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in  $\Delta_i H$  from Si to Ge to Sn and slight increase in  $\Delta_i H$  from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.
- ❖ **Electronegativity :** Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.
- ❖ **Melting points and Boiling points :** The melting points and boiling points decrease from carbon to lead but carbon and silicon have very high melting and boiling points due to their giant structure.

- ❖ **Catenation** : It is the tendency of an element to form long chains of identical atoms. The greater the strength of element-element bond, the greater is the strength of catenation.  $C \gg Si > Ge \gg Sn > Pb$  (catenation)

Bond $\rightarrow$	C-C	Si-Si	Ge-Ge	Sn-Sn
Bond kJ/mole	353.3	225.7	167.2	155.0

- ❖ **Allotropy** : All the elements except Pb show allotropy. Allotropic forms of carbon - Diamond, Graphite and Fullerene. Amorphous forms of carbon - coal, charcoal etc. Silicon (Si) - crystalline and amorphous. Tin (Sn) - grey tin, white tin and rhombic tin. Germanium - two crystalline forms.
- ❖ **Oxidation states** : They are as follows:

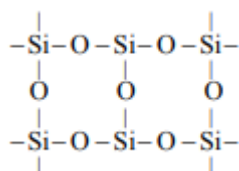
C	Si	Ge	Sn	Pb
(+2) < +4	(+2) < +4	+2 < +4	+2 < +4	+2 > +4

- The compounds of Ge and Sn in +2 oxidation state are reducing in nature. Since their higher oxidation states +4 are more stable.
  - The compounds of Pb in +4 oxidation state are powerful oxidising in nature. Since +2 oxidation state of Pb is more stable.
- ❖ **Inert-pair effect** : On descending the group, the stability of +4 oxidation state decreases and that of +2 oxidation state increases.

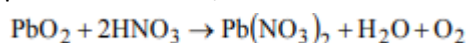
## Chemical Properties:

**(i) Reactivity towards oxygen:** All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO<sub>2</sub> 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<sub>2</sub>, SiO<sub>2</sub> and GeO<sub>2</sub> are acidic, whereas SnO<sub>2</sub> and PbO<sub>2</sub> are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

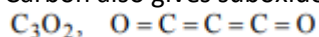
CO forms a number of coordination compounds with transition metals e.g. [Ni(CO)<sub>4</sub>], [Fe(CO)<sub>5</sub>] etc. CO<sub>2</sub> is linear, gas at ordinary temperature. Solid CO<sub>2</sub> is known as dry ice or dry ice. SiO<sub>2</sub> is solid with three dimensional network having Si bonded to four oxygen atoms tetrahedrally and covalently.



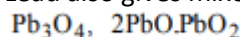
The bond energy of Si - O bond is 368 kJ/mol, therefore SiO<sub>2</sub> is chemically inert and has high melting point. SnO<sub>2</sub>, GeO<sub>2</sub>, and PbO<sub>2</sub> all are network solids. PbO<sub>2</sub> is a powerful oxidising agent



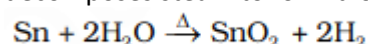
Carbon also gives suboxide



Lead also gives mixed oxide



**(ii) Reactivity towards water:** Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.



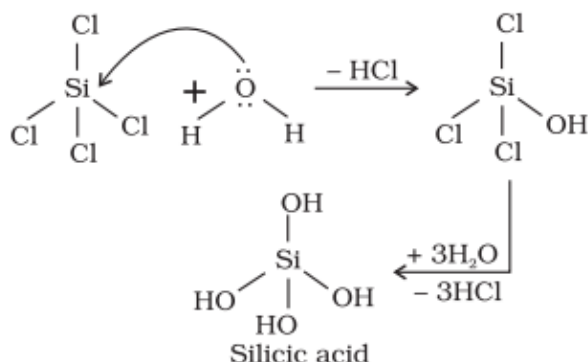
Lead is unaffected by water, probably because of a protective oxide film formation.

**(iii) Reactivity towards halogen:** These elements can form halides of formula MX<sub>2</sub> and MX<sub>4</sub> (where X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX<sub>4</sub> are covalent in nature. The central metal atom in these halides



undergoes  $sp^3$  hybridisation and the molecule is tetrahedral in shape. Exceptions are  $SnF_4$  and  $PbF_4$ , which are ionic in nature.  $PbI_4$  does not exist because  $Pb-I$  bond initially formed during the reaction does not release enough energy to unpair  $6s^2$  electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula  $MX_2$ . Stability of dihalides increases down the group. Considering the thermal and chemical stability,  $GeX_4$  is more stable than  $GeX_2$ , whereas  $PbX_2$  is more than  $PbX_4$ . Except  $CCl_4$ , other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in d orbital.

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



### ANOMALOUS BEHAVIOUR OF CARBON:

Carbon differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals.

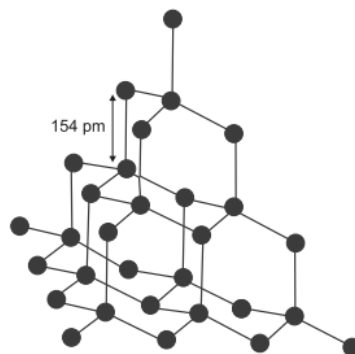
In carbon, only s and p orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals. Carbon also has unique ability to form  $p\pi-p\pi$  multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are:  $C=C$ ,  $C \equiv C$ ,  $C=O$ ,  $C=S$ , and  $C \equiv N$ . Heavier elements do not form  $p\pi-p\pi$  bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

### ALLOTROPE OF CARBON :

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

#### Diamond:

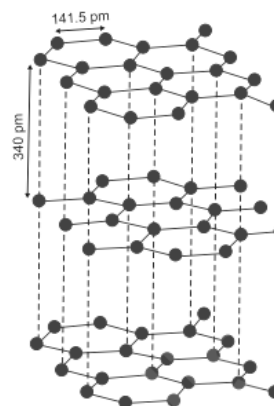
It has a crystalline lattice. In diamond each carbon atom undergoes  $sp^3$  hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C-C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms. In this structure directional covalent bonds are present throughout the lattice. It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest element on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs



### Graphite :

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

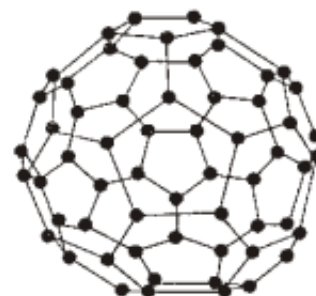
Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.



### Fullerenes:

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C<sub>n</sub> small molecules consists of mainly C<sub>60</sub> with smaller quantity of C<sub>70</sub> 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<sub>60</sub> molecule has a shape like soccer ball and called Buckminsterfullerene.

It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C—C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.



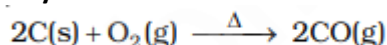
- It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore,  $\Delta_f H^0$  of graphite is taken as zero.  $\Delta_f H^0$  values of diamond and fullerene, C<sub>60</sub> are 1.90 and 38.1 kJ mol<sup>-1</sup>, respectively.  
Other forms of elemental 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.

## SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON:

### Carbon Monoxide:

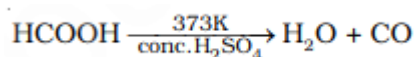
Preparation:

1. **By direct oxidation of C** in limited supply of oxygen or air yields carbon monoxide

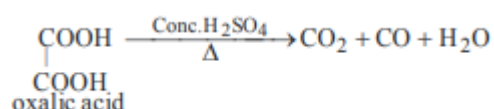


2. **Laboratory (Small scale) preparation:**

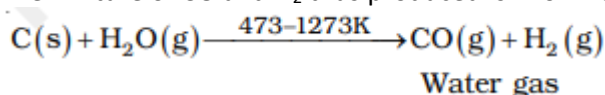
On small scale pure CO is prepared by dehydration of formic acid or oxalic acid with concentrated H<sub>2</sub>SO<sub>4</sub> at 373 K.



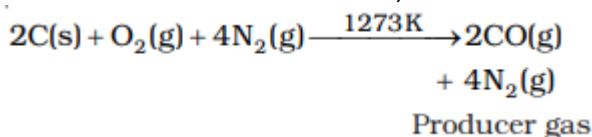
Formic acid



3. **Industrial preparation:** On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H<sub>2</sub> thus produced is known as water gas or synthesis gas.

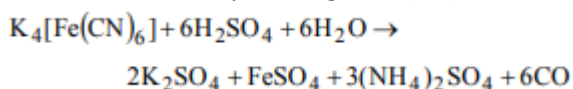


When air is used instead of steam, a mixture of CO and N<sub>2</sub> is produced, which is called producer gas.



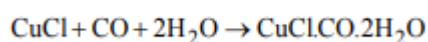
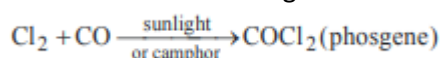
Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

4. **Other Method:** By heating K<sub>4</sub>[Fe(CN)<sub>6</sub>] with conc H<sub>2</sub>SO<sub>4</sub>

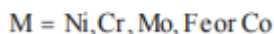
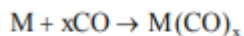


### Properties:

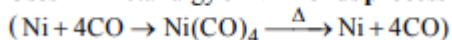
- ❖ Neutral, colourless, poisonous, burns with blue flame. Sparingly soluble in water.
- ❖ It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.
- ❖ In CO molecule, there are one sigma and two π bonds between carbon and oxygen, :C ≡ O: Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form metal carbonyls. The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.
- ❖ **Unsaturated nature** : It gives addition products



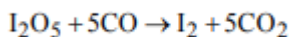
- ❖ **Formation of metal carbonyls:** It acts as lewis base



**Uses** - In metallurgy of Ni-**Monds process**



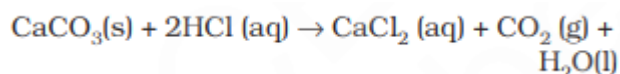
- ❖ **Test for CO:** It reduces  $I_2O_5$  to  $I_2$  which turns  $CCl_4$  layer violet (**Ditte Reaction**):



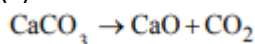
## CARBONDIOXIDE $CO_2$ :

### Preparation :

(i) **Lab method:** In the laboratory it is conveniently prepared by the action of dilute HCl on calcium carbonate

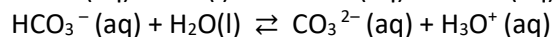
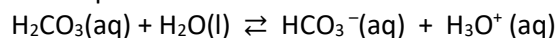


(ii) **Manufacture:** On commercial scale it is obtained by heating limestone



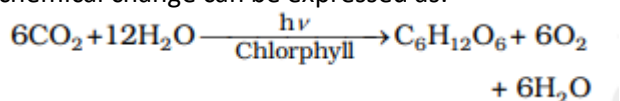
### Physical Properties :

- ❖ Colourless, 1.5 times heavier than air, can be poured downwards like  $H_2O$ . Animals die in its presence due to lack of  $O_2$ , it is also known as **black damp**.
- ❖ Its low solubility in water makes it of immense biochemical and geo-chemical importance. With water, it forms carbonic acid,  $H_2CO_3$  which is a weak dibasic acid and dissociates in two steps:



$H_2CO_3/HCO_3^-$  buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonate.

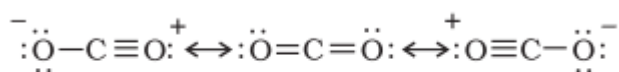
- ❖ Carbon dioxide, which is normally present to the extent of  $\sim 0.03\%$  by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric  $CO_2$  into carbohydrates such as glucose. The overall chemical change can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



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

- ❖ Carbon dioxide can be obtained as a solid in the form of dry ice by allowing the liquified  $CO_2$  to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food. Gaseous  $CO_2$  is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of  $CO_2$  is used to manufacture ure

- ❖ In CO<sub>2</sub> molecule carbon atom undergoes sp hybridisation. Two sp hybridised orbitals of carbon atom overlap with two p orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in pπ– pπ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:

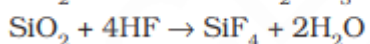
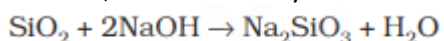
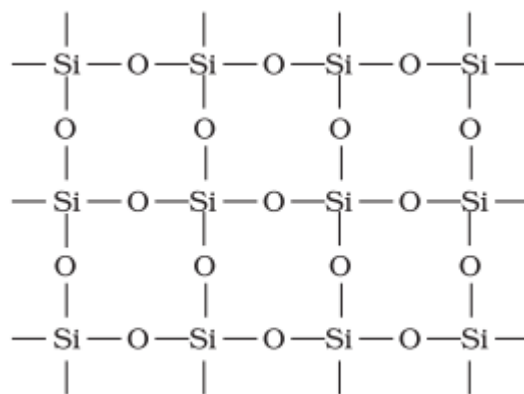


Resonance structures of carbon dioxide

- ❖ **Uses:** In household as **fire extinguisher**.
  - Dry powder fire extinguisher contains (NaHCO<sub>3</sub> + sand) which is decomposed by heat.
 
$$2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$
  - Foamite extinguisher contains baking soda and aluminium sulphate and is used for oil fires.

### Silicon Dioxide, SiO<sub>2</sub>:

95% of the earth's crust is made up of silica and silicates. Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertible at suitable temperature. Silicon dioxide is a covalent, three-dimension network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms. 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.

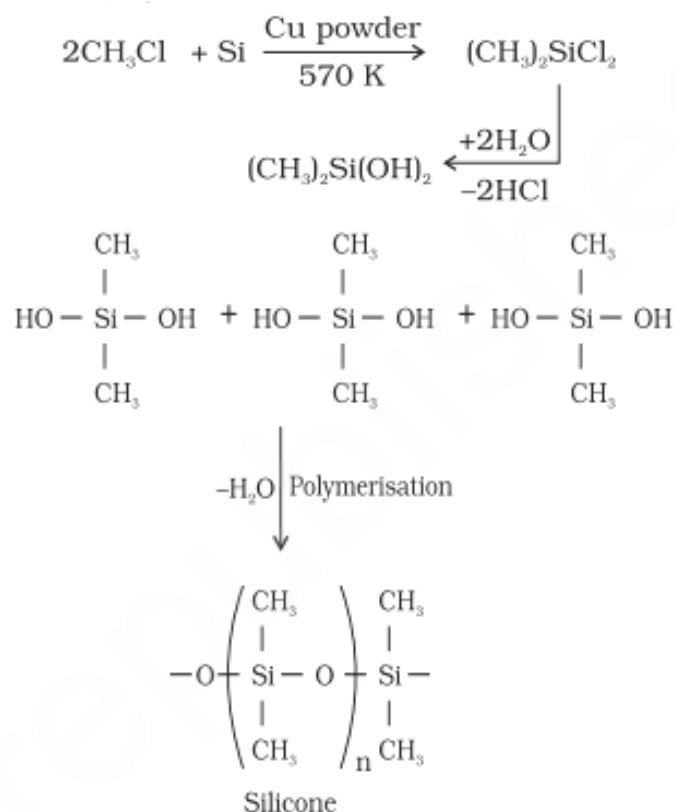


Quartz is extensively used as a **piezoelectric material**; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.

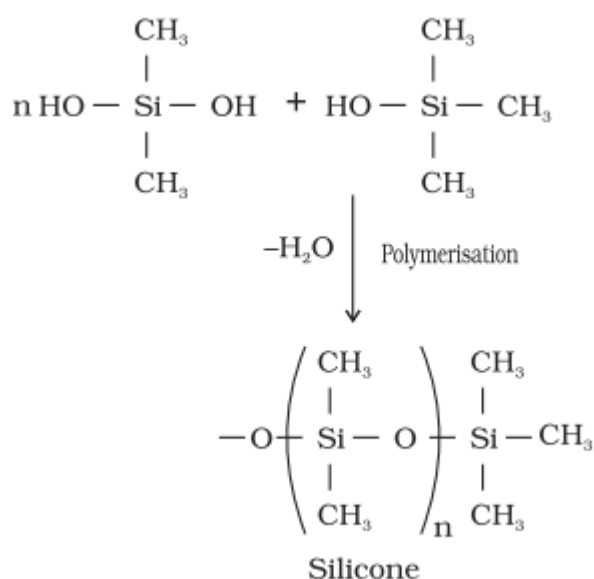
Kieselghur, an amorphous form of silica is used in filtration plants.

### Silicones:

They are a group of organosilicon polymers, which have  $(R_2SiO)$  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. When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilane 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.



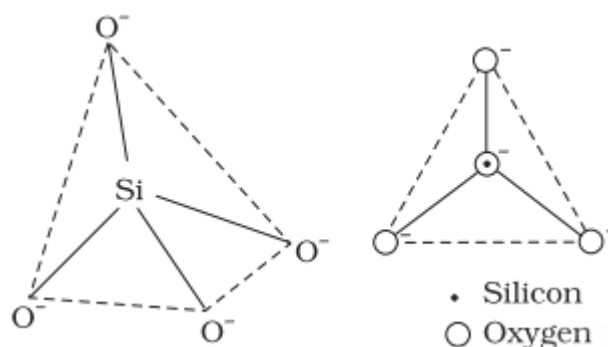
The chain length of the polymer can be controlled by adding  $(\text{CH}_3)_3\text{SiCl}$  which blocks the ends as shown below :



Silicones being surrounded by non-polar alkyl groups are water repelling in nature. They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals. They have wide applications. They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

### Silicates:

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is  $\text{SiO}_4^{4-}$  in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1,2,3 or 4 oxygen atoms per silicate units. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures. Negative charge on silicate structure is neutralised by positively charged metal ions. If all the four corners are shared with other tetrahedral units, three-dimensional network is formed. Two important man-made silicates are glass and cement.



### Type of silicates:

Silicates contain  $\text{SiO}_4^{4-}$  tetrahedra formed by  $\text{sp}^3$  hybridisation, depending upon the number of O-atoms shared between tetrahedra and fashion, Silicates have been classified into following groups.

- (i) **Orthosilicates** - They contain discrete  $\text{SiO}_4^{4-}$  tetrahedra, Examples are phenacite  $\text{Be}_2\text{SiO}_4$ , willimite  $\text{Zn}_2\text{SiO}_4$ , zircon  $\text{ZrSiO}_4$ , forsterite  $\text{Mg}_2\text{SiO}_4$ .
- (ii) **Pyrosilicates** - Here two tetrahedra units are joined by one oxygen atom forming a large discrete  $\text{Si}_2\text{O}_7^{6-}$ . Examples are thortveitite  $\text{Se}_2(\text{Si}_2\text{O}_7)$ , hemimorphite  $\text{Zn}_3(\text{Si}_2\text{O}_7) \cdot \text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$
- (iii) **Chain silicates** - Here two oxygen atoms per  $\text{SiO}_4$  tetrahedra are shared giving polymeric anion chains. Discrete unit is  $(\text{SiO}_3^{2-})_n$ . Examples: synthetic sodium silicate  $\text{Na}_2\text{SiO}_3$ , lithium silicate  $\text{Li}_2\text{SiO}_3$ , natural spodumene  $\text{LiAl}(\text{SiO}_3)_2$ , jodeite  $\text{NaAl}(\text{SiO}_3)_2$ , enstatite  $\text{MgSiO}_3$  and diopside  $\text{CaMg}(\text{SiO}_3)_2$ .



- (iv) **Double chains** - Here two simple chains are held together by shared oxygen atoms. The discrete unit is  $(\text{Si}_4\text{O}_{11}^{6-})_n$ . Example mineral tremolite  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ . Double chain silicates are also called amphibole.
- (v) **Cyclic silicates** - Here two oxygen atoms per  $\text{SiO}_4^{4-}$  tetrahedra are shared giving discrete unit  $\text{Si}_3\text{O}_9^{6-}$  and  $\text{Si}_6\text{O}_{18}^{12-}$ . Example Beryl  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ .
- (vi) **Sheet-silicates** - Here three oxygen atoms per tetrahedra are shared giving two dimensional sheet having discrete unit  $(\text{Si}_2\text{O}_5^{2-})_n$ . Example Talc  $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ , Kaolin  $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)_2$ .
- (vii) **Frame work silicates** - Here all four oxygen atoms of each tetrahedra are shared. Example are quartz, zeolites, tridymite and cristobalite.

### Some important terms:

- **Quartz or rock crystal** - It is purest form of silica. It is optically active.
- **Flint** - It is amorphous silica associated with quartz.
- **Kieselguhr** - Siliceous rock composed of the remains of sea organisms. Used as absorbent for nitroglycerine.
- **Silica gel** - Transparent gel of bluish white colour  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ .
- **Water glass or sodium silicate** - Sodium silicate containing excess of  $\text{SiO}_2$ .
- **Silica garden** - Aqueous solution of sodium silicate containing crystals of various coloured salts e.g. copper sulphate, cobalt nitrate, manganese chloride, nickel chloride etc.
- **Permutit** - Artificially prepared sodium aluminium silicate containing varying composition of sodium, aluminium and silica  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ . Used for softening hard water.
- **Zeolites** - They have honey comb like structure and have the general formula  $\frac{M_x}{n}(\text{AlO}_2)_x \cdot (\text{SiO}_2)_y \cdot z\text{H}_2\text{O}$   

$$M = \text{Na}^+, \text{K}^+ \text{ or } \text{Ca}^{++}$$

$$n = \text{Charge on metal}$$

They act as ion exchanger and molecular sieves. They can be artificially prepared by heating **China clay, Silica** and  **$\text{Na}_2\text{CO}_3$** .
- **Ultramarines** - Zeolite type silicates, containing ions like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$  and not water, are known as ultramarines e.g.  $\text{Na}_2(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S}_2$ . Many of them are coloured and used as pigments and calicoprinting.



- **Carborundum** - silicon carbide . It is nearly as hard as diamond  

$$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$$

$$\text{Si} + \text{C} \rightarrow \text{SiC}$$
- **Tin cry** - It produces a peculiar cracking sound on bending which is known as tin cry.
- **Tin plague** - It is the conversion of white tin to grey tin at low temperature which crumbles into powder.
- **Tinning** - Since tin is not attacked by organic acids the utensils are protected by thin layer of tin .A pinch of  $\text{NH}_4\text{Cl}$  is sprinkled over hot and clean surface, when  $\text{HCl}$  liberated removes the oxide film.Tin then rubbed over the clean surface with the help of rag dipped in  $\text{NH}_4\text{Cl}$  powder. The utensil is immediately dipped in water to avoid oxide formation .
- **Tin plating** - It involves the depositing of thin protective layer of tin over sheets of iron electrolytically.
- **Butter of tin** -  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  used as mordant in dyeing.
- **Purple of cassius** - Colloidal particles of gold absorbed by stannic acid  $\text{Sn}(\text{OH})_4$  is known as purple of cassius. It is used for colouring glass and pottery.
- **Plumbo Solvancy** - Formation of lead hydroxide with  $\text{H}_2\text{O}$  in presence of air is known as plumbo solvancy.  

$$2\text{Pb} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Pb}(\text{OH})_2$$

Hence lead is readily corroded hard water has no action on lead which forms a protective layer of  $\text{PbCO}_3$  and  $\text{PbSO}_4$   
Hence hard water can be conveyed through lead pipes.