TDC Part I
Paper I, Group B
Inorganic Chemistry

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TOPIC:-
Group-14,Carbides,Hydrides,Halides

Carbides

Compounds of carbon with a less electronegative element are called carbides. This excludes binary compounds of carbon with N, P, O, S and halogens. Depending on the bond – type carbides are classified as – ionic, interstitial or covalent.

Ionic (salt – like) carbides

These are formed with electropositive metals and may contain different carbide anions. The bonding is predominantly ionic with some covalent character. The most well characterized carbide ions are C^{4-} and C_2^{2-}. Species containing C^{4-} are represented by Al_4C_3 and Be_2C. These are called methanides as they hydrolyze to give methane.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

The C_2^{2-} ion is found in CaC_2, carbides of Cu, Ag, Au and some lanthanides. The most important carbide is CaC_2, which is obtained by strongly heating lime with coke. It is structurally similar to NaCl (Fig.13).

$$\mathbf{CaO + 3C \longrightarrow CaC_2 + CO}$$

It is called acetylide as it yields ethyne on hydrolyses

$$\mathbf{CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2}$$

The C_3^{4-} ion is found in Mg_2C_3, which yields propyne ($H_3C - C{\equiv}CH$) on hydrolysis.

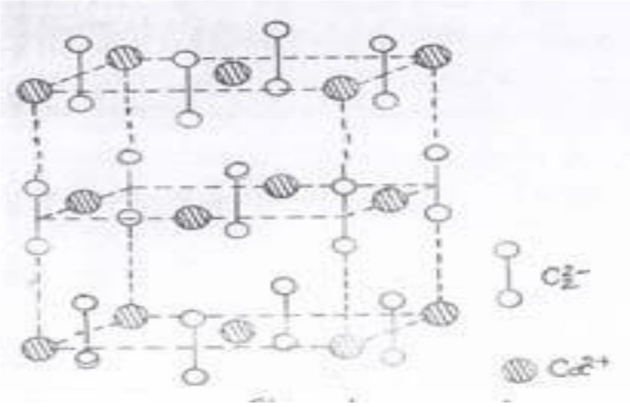


Fig. 13: Structure of Calcium carbide

(a) Interstitial carbides

They are formed with transition metals like Cr, Mn, Fe, Co, Ti and W and with some lanthanides. They are generally high melting and hard. The C atoms occupy octahedral voids in the metal lattice and do not affect the conductivity of the metal. The ability of carbon atoms to enter the metal lattice without distortion indicates that the interstices should be fairly large (possible if atomic radius of metal > 135 pm). For smaller metals i.e. those of the 3d series, inclusion of carbon results in distortion of the lattice, giving rise to complicated structures.

(b) Covalent carbides

These are formed when carbon combines with an element of comparable electro-negativity e.g. SiC and B_4C SiC (Carborundum) is very hard, un-reactive and a good refractory material. B_4C is better represented as $B_{12}C_3$. They are hard, infusible and inert macromolecules.

Hydrides

All the elements form covalent hydrides but the number of hydrides formed, their stability and ease of formation decreases down the group. Carbon forms a large number of hydrides involving chains, rings and multiple bonds between carbon atoms. These hydrides form the basis of organic chemistry.

Silicon forms a limited number of hydrides, the silanes (represented by the formula $Si_n H_{2n+2}$). Monosilane, SiH_4, is the most stable and is tetrahedral, like methane. Silanes containing up to eight silicon atoms have been synthesized but their stability decreases with increase in chain – length. The hydrides are prepared as a mixture when magnesium silicide is treated with dilute acids.

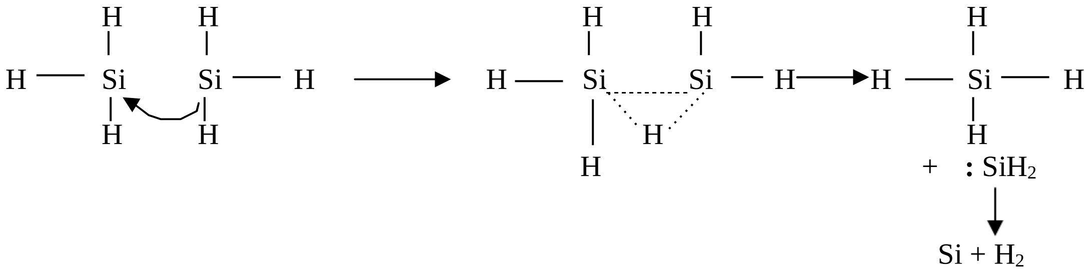
$$Mg_2Si + H_2SO_4 \longrightarrow SiH_4 + \text{higher silanes}$$

Monosilane can be prepared by reaction of $SiCl_4$ with lithium aluminium hydride or sodium hydride

$$SiCl_4 + Li[AlH_4] \longrightarrow SiH_4 + LiCl + AlCl_3$$

$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4\,NaCl$$

Silanes are more reactive than the corresponding alkanes. Various reasons are attributed to this. The Si –Si bond is slightly weaker than the C-C bond (bond energies are 340 & 368 $KJmol^{-1}$ respectively). The Si-H bond is weaker than the C-H bond (bond energies 393 & 435 $KJmol^{-1}$). The electronegativity values of Si, C and H are 1.8, 2.5 and 2.1 respectively so the polarity of Si-H and C-H bonds differ and are depicted as Si – H and C-H. Silicon is more susceptible to nucleophilic attack than carbon as the larger size of silicon provides greater surface area for the nucleophile to attack. Silicon has vacant low- lying d orbitals, which can accept electron pairs from nucleophiles and form reactive intermediates. Silanes decompose to give silicon of high purity by elimination of SiH_2. The following mechanism has been suggested.



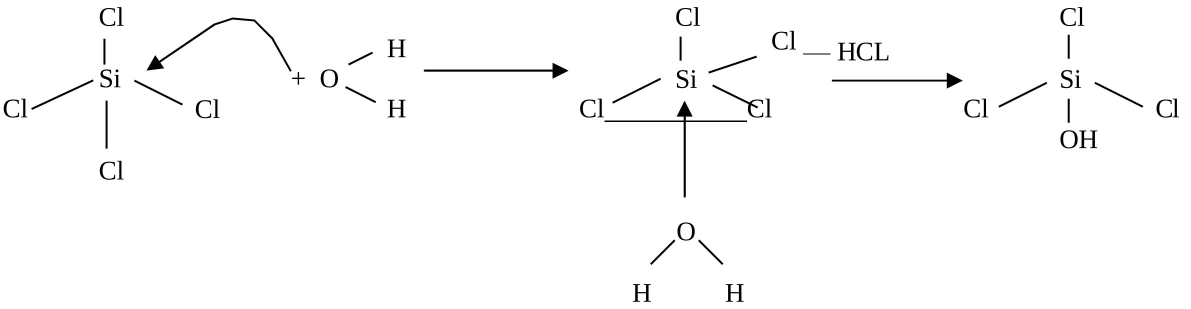
Germanes containing unto five germanium atoms and represented by the formula $Ge_n\ H_{2n+2}$ are known. They are less stable than the silanes. Tin forms only two hydrides SnH_4 and Sn_2H_6 while lead form the unstable PbH_4.

Halides

Tetra-halides (MX_4) of all elements are known; but Pb (IV) readily oxidizes iodide and hence the compound PbI_4 is not known. The stability of the tetra-halides decreases down the group. The fluorides, by virtue of high electronegativity of fluorine, are the most ionic. SnF_4 and PbF_4 are high melting solids; the others are covalent, tetrahedral and volatile. The halides of carbon are inert towards water, however the halides of silicon readily hydrolyze.

$$\mathbf{SiCl_4 + 4H_2O \longrightarrow Si(OH)_4}$$

The hydrolysis proceeds via an intermediate where silicon has a coordination number of five.



This process continues till Si-OH bonds replace all the Si-Cl bonds. Since carbon does not have d orbitals it cannot form such an intermediate and therefore tetra-halides of carbon do not hydrolyze.

Germanium, tin and lead form both tetra-halides and di-halides. The tetra-halides have a tendency to hydrolyze, but the hydrolysis can be suppressed by adding the appropriate halogen acid

$$SnCl_4 \xrightleftharpoons[HCl]{H_2O} Sn\,(OH)_4$$

The halides of Si, Ge, Sn and Pb can increase the coordination number to 6 by forming complexes like $[SiF_6]^{2-}$, $[SnCl_6]^{2-}$ etc where the vacant d orbitals are used.

There is an increase in stability of dihalides on moving down the group

$$SiX_2 << GeX_2 < SnX_2 < PbX_2$$

SiF_2 can be made at high temperature by the reaction

$$SiF_4 + Si \rightleftharpoons 2SiF_2$$

Divalent germanium halides are stable. GeF_2 is polymeric having fluorine bridges. Tin (II) halides are well – characterized and the most important one is $SnCl_2$. it undergoes partial hydrolysis and is soluble in organic solvents. It is a mild reducing agent as shown by the following reactions:

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCL_4$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$