18

Group IVB (Group 14)*. Carbon, Silicon, Germanium, Tin and Lead

This group includes carbon, silicon, germanium, tin and lead. Carbon is an essential ingredient of all living organism, and carbon compounds play crucial roles in vegetable and animal kingdom. The carbon dioxide and moisture of our atmosphere are worked up by plants through the agency of their green pigment, *chlorophyll* and in the presence of sunlight into carbohydrates $(C_6H_{10}O_5)x$(starch and cellulose). Carbohydrates are then consumed by the vegetable and animal kingdom and transformed into CO_2 and water. Thus CO_2 is fed back into the cycle. Carbon is found in nature as CO_2, as metal carbonates, as decay product of primeval living organism (*eg.* petroleum). Silicon is the second commonest element of the earth's crust after oxygen and occurs in nature in abundant quantities as various silicate minerals and also as silica. The per cent abundances are : C(0.08%) ; Si(27.7%) ; Ge($\sim 10^{-11}$%) ; Sn($\sim 10^{-6}$%) ; Pb($\sim 10^{-5}$%)

18.1. COMPARATIVE STUDY OF THE GROUP IVB (GROUP 14) ELEMENTS

18.1.1. General Considerations : The chemistry of group IVB (group 14) elements follows from their electronic configurations although the differences in properties between carbon and silicon are rather wide. All the elements have an outermost quantum shell composition of s^2p^2 although germanium, tin and lead have underneath these electrons a d or f subshell. The inner shells of carbon and silicon are those of the preceding noble gases (Table 18.1).

The four ionisation potentials (Table 18.1) taken together are exorbitantly high. Just as in group IIIB (group 13), the fall of ionisation potentials along the group is not prominent. This appears to be a consequence of the enhanced deformation of non-noble gas structures of the inner shells. No compound is known in this group with a + 4 cation. Instead of attaining a noble gas or a pseudo-noble gas configuration through an M^{4+} cation the elements attain the desired configurations in most cases with four single covalent bonds. The four covalent bonds are equivalent, tetrahedral and result from sp^3 hybridisation (Chapter 5). Interestingly this hybridisation is not the only way that a noble gas configuration can be attained. Particularly the smallest carbon has a trend to attain octet through multiple covalent

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* IUPAC recommendation

bonds, which trend decreases sharply to silicon and to other members of the group. Carbon forms multiple bonds of the type :
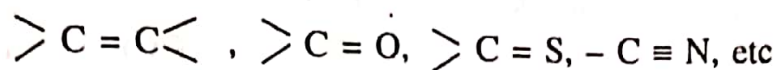
$$> C = C < , \quad > C = O, \quad > C = S, \quad - C \equiv N, \text{ etc}$$

Table 18.1 : Electronic Configurations and Some Properties of Group IVB (Group 14) Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential eV/atom (kJ/mole)	Electro-negativity
C	6	$[He]2s^2 2p^2$	11.25, 24.38, 47.87, 64.48 (1086, 2353, 4618, 6221)	2.50
Si	14	$[Ne]3s^2 3p^2$	8.15, 16.34, 33.46, 45.13 (786, 1576, 3228, 4354)	1.74
Ge	32	$[Ar]3d^{10} 4s^2 4p^2$	7.88, 15.93, 34.23, 45.7 (760, 1537, 3302, 4409)	2.02
Sn	50	$[Kr]4d^{10} 5s^2 5p^2$	7.33, 14.63, 30.6, 39.6 (708, 1411, 2952, 3821)	1.72
Pb	82	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	7.41, 15.03, 32.0, 42.3 (715, 1450, 3087, 4081)	1.55

The electronegativities (Table 18.1) expectedly fall from carbon to lead although not quite regularly. On the whole the electronegativities are low and hence there is not much tendency to form tetranegative anions. If it is at all possible to form a tetranegative anion it should be with carbon. Negative carbon anions are known in Be_2C(i.e. C^{4-}), in sodium alkyls, $NaCH_3$(Na^+ and CH_3^-) and alkali metal carbides Na_2C_2(Na^+ and C_2^{2-} ions). The elctronegativity difference between carbon (2.50) and fluorine (4.0) is not sufficient enough to induce ionic character in the fluorocarbons. As we descend the group the electronegativity difference with halogens increases and ionic character may appear in compounds such as SnF_4 though not in $PbCl_4$ or $SnCl_4$ (Chapter 5). However SnF_4 is now regarded as polymeric covalent (Part I). In essence Fajan's rules hold good.

In general in any group metallic character should increase with increasing atomic number. Unfortunately the charge (+ 4) on the hypothetical cation with the group oxidation state is so very high that even with lead covalence persists. However when the two outer quantum shell s electrons are relatively inert, which effect again increases down the group, we obtain distinct metal character in the heavier elements : Sn(II) and Pb(II). With germanium still not enough basic character appears. Standard potentials of tin and lead are close, – 0.136 and – 0.126 volt respectively (Table 18.2), although not in the expected order. The order however shows, in conformity with experiments, that tin is a better reducing agent than lead.

Table 18.2 : Some More Properties of Group IVB (Group 14) Elements

Element	Atomic Radius (A) (pm)	Ionic (M^{4+}) Radius (A) (pm)	M.P. (°C)	B.P. (°C)	Density (g/ml)	$E°$, volt $M^{2+} + 2e \rightleftharpoons M$
C	0.77 (77)	......	3500	4800	3.52*, 2.25+	—
Si	1.17 (117)	0.39 (39)	1420	3280	2.49	—
Ge	1.22 (122)	0.53 (53)	959	2700	5.36	—
Sn	1.40 (140)	0.71 (71)	232	2360	5.77	– 0.136
Pb	1.54 (154)	0.84 (84)	327	1755	11.34	– 0.126

In contrast to carbon, silicon and the other members of the group have dormant d-orbitals and hence these later elements can accommodate more than eight electrons around them. Whereas in carbon we have a maximum of coordination number four (section 16.2.1) in the others we have six. Carbon-carbon single bond is far stronger than silicon—silicon or germanium—germanium single bonds.

Indeed element-element single bond energies vary in the order :

	C—C	>	Si—Si	>	Ge—Ge	>	Sn—Sn
kcal/mole	83		50-59.7		45.4-50		25-34.6
kJ/mole	347		210-250		190-210		105-145

The strength of carbon-carbon single bonds and carbon-carbon multiple bonds helps carbon to form compounds with long chains of identical atoms. *The property of forming compounds with chains of identical atoms is called catenation.* Catenation in carbon compounds may give rise to long straight chain compounds with C-C links (eg : saturated hydrocarbons called alkanes C_nH_{2n+2}), C = C links (eg : alkenes, C_nH_{2n}), C $\equiv$ C links (alkynes, C_nH_{2n-2}) as also ring compounds (eg : benzene). The tendency to catenation falls off in the order C > Si > Ge $\simeq$ Sn > Pb. It is interesting to note that although a number of silicon hydrides analogous to saturated paraffin hydrocarbons are known there are as yet no reports of silicon analogues of olefines (alkenes), acetylenes (alkynes) or aromatics. This supports the order of catenation among IVB (14) elements. The apathy of Si, Ge, Sn and Pb to catenation is due to the weakness of the M-M/M = M bonds. Compared to the catenated carbon compounds these bonds have to span longer distance and hence the weakness. With increase in atomic number size of the elements increases and hence catenation gets weaker.

According to Fajans' rules the tendency to complexation should be the highest in carbon in + 4(IV) state and least in lead. C^{4+} does not exist and indeed the tetravalent carbon compounds have so strong covalent bonds that usual coordinating ligands cannot break such bonds. In the other elements over and above the s- and p-orbitals, d-orbitals are also available

* = diamond ; + = graphite

and hence they are capable of forming more than four bonds. Thus with later elements adduct formation, such as $SnCl_4 \cdot bpy$, is a common feature. On the whole the tendency to complex formation decreases down the group.

In the + 2(II) state, Fajans' rules predict enhanced tendency to form ions with increasing atomic number. The standard potentials of the M^{4+}/M^{2+} couples are for Sn, + 0.5 volt and for Pb, + 1.8 volt. The values indicate that lead(IV) must be a far stronger oxidant than tin(IV), and conversely tin(II) must be a superior reducing agent than lead(II). This is in complete accord with experimental results. The +2(II) state is the common oxidation state with lead and tin but with the other elements + 4(IV) is the common oxidation state. Remember that the varied oxidation states in this group are due to an *inert pair effect.*

18.1.2. Chemical Behaviour. The chemical behaviour may be examined under the +4(IV) and + 2(II) states.

A. Tetravalent State. Hydrides : All the elements form volatile covalent hydrides. The ease of formation decreases down the group. Due to the strong tendency to catenation (being the result of very strong carbon-carbon bonds) carbon forms a vast array of chain and ring compounds including the *alkanes* (C_nH_{2n+2}), *alkenes* (olefines) (C_nH_{2n}), *alkynes* (acetylenes) (C_nH_{2n-2}) and many aromatic compounds. Silicon forms a few saturated hydrides (Si_nH_{2n+2}) called *silanes.* Acid hydrolysis of magnesium silicide Mg_2Si gives a mixture of SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10} which are then separated and purified by fractional distillation. $SiCl_4$, Si_2Cl_6 react with $LiAlH_4$, NaH or LiH in ether at low temperature to yield silanes :
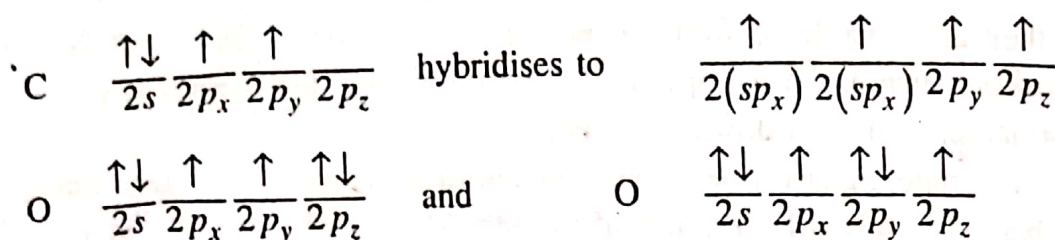
$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_3$$

$$Si_2Cl_6 + 6NaH \rightarrow Si_2H_6 + 6NaCl$$
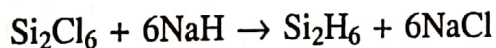
Germanium forms only a few polynuclear hydrides GeH_4, Ge_2H_6, Ge_3H_8 whereas tin and lead form only SnH_4 and PbH_4. The thermal stability of these hydrides decreases down the group. The reducing properties increase down the group. The ease of syntheses also falls off down the group. Thus SnH_4 and PbH_4 are difficult to prepare and are obtained by the action of $LiAlH_4$ on the tetrahalides :

$$SnCl_4 + LiAlH_4 \rightarrow SnH_4 + LiAlCl_4$$
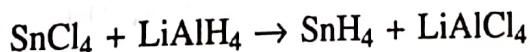
Electrolysis of $SnCl_2$ or $PbCl_2$ with the respective metal as cathode also produces the hydride.

Oxides and Oxoacids : Carbon dioxide is an acidic oxide reacting with alkali to form normal carbonates and hydrogencarbonates. Silicic acid (freshly precipitated from metal silicates) is highly condensed. It is amphoteric, reacting with bases to form silicates, and with acids like HF to form SiF_4 or H_2SiF_6. The other dioxides GeO_2, SnO_2 and PbO_2 have diminished acidic character. GeO_2 is not as strongly acidic as SiO_2, and SnO_2 and PbO_2 are still amphoteric.

Carbon dioxide is a discrete covalent compound, $O = C = O$. Two sp_x hybridised orbitals of carbon (with one unpaired electron on each) overlap with p_x orbitals of two oxygens. The p_y orbital of carbon then overlaps with the p_y orbital of one oxygen (both having one unpaired electron) to give a π-bond. Similar overlap along z-axis gives another carbon-oxygen π-bond. Thus CO_2 is made up of two σ- and two π-bonds.

In. Ch. II—13

C $\quad \underbrace{\uparrow\downarrow}_{2s} \underbrace{\uparrow}_{2p_x} \underbrace{\uparrow}_{2p_y} \underbrace{}_{2p_z}$ hybridises to $\quad \underbrace{\uparrow}_{2(sp_x)} \underbrace{\uparrow}_{2(sp_x)} \underbrace{\uparrow}_{2p_y} \underbrace{\uparrow}_{2p_z}$

O $\quad \underbrace{\uparrow\downarrow}_{2s} \underbrace{\uparrow}_{2p_x} \underbrace{\uparrow}_{2p_y} \underbrace{\uparrow\downarrow}_{2p_z}$ and O $\quad \underbrace{\uparrow\downarrow}_{2s} \underbrace{\uparrow}_{2p_x} \underbrace{\uparrow\downarrow}_{2p_y} \underbrace{\uparrow}_{2p_z}$

An M. O. description of the molecule is given in Chapter 5.

As we come to silicon the available p orbitals, being 3p, are of larger size and a π-type overlap with oxygen 2p orbitals of smaller size becomes less effective.

Multiple bonding over a longer internuclear distance is weak compared to multiple bonding over a shorter internuclear distance. Moreover electronegativity difference between silicon and oxygen is much larger than the difference between carbon and oxygen and hence the bonds in silica have considerable ionic character. All these lead to a three dimensional infinite structure in SiO_2 and silicates. Thus CO_2 is a gas and SiO_2 is a high-melting solid. However it should be noted that there is no difficulty in getting a good overlap of a silicon 3d orbital with a 3p orbital of a halogen or an sp^3 hybrid orbital of H_2O molecule.

It may be mentioned here that SiO_2 exists in two crystalline forms with characteristic range of stability.

Quartz	Cristobalite
(< 870°C)	(> 1470°C)

Basically both the forms have SiO_4 tetrahedra linked up with bridging oxygen (as in the silicates) but the details of tetrahedral arrangement varies. Each of these has an α-form and a β-form—the two forms varying by a slight rotation of the tetrahedra with respect to each other without a change in the overal arrangement of the tetrahedra.

Halides : The tetrahalides are all covalent and tetrahedral (sp^3 hybridisation). Carbon tetrafluoride is very stable and unreactive. Silicon and the other halides are readily hydrolysed. The trend towards hydrolysis decreases down the group. $GeCl_4$ and $GeBr_4$ are less readily hydrolysed than the silicon halides. In order that hydrolysis can occur there must first be a nucleophilic (nucleus seeking a lone pair) attack by H_2O on the parent element of the halide (18-I). Since carbon does not have any d-orbital in its outer quantum shell ($n = 2$) for attack by a nucleophile (H_2O) its halides do not suffer any hydrolysis. CCl_4, CF_4 are also

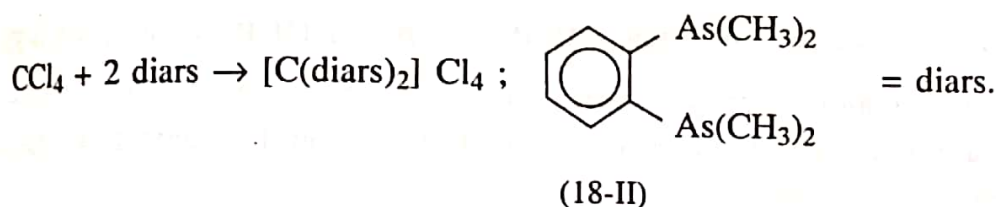$$\xrightarrow{\text{heat}} SiO_2 + 4HCl$$

(18-I)
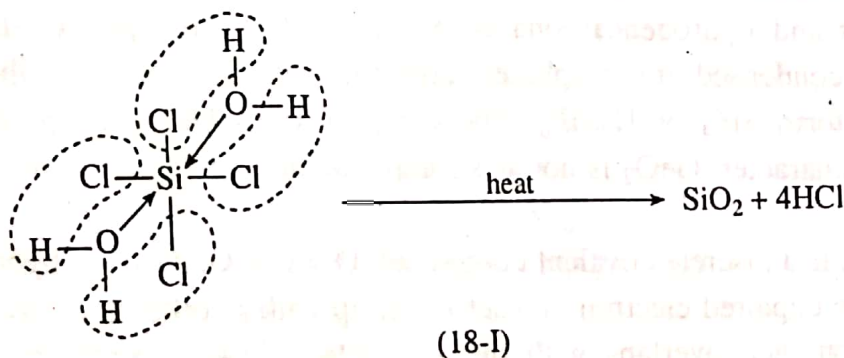
coordinatively saturated but this is not the case with $SiCl_4$, $GeCl_4$ which can go upto a coordination number six. Moreover because of electronegativity difference silicon in $SiCl_4$

has more $\delta+$ charge than carbon in CCl_4. This also facilitates nucleophilic attack by H_2O. The other elements possess vacant d-orbitals to which the aqua molecule can get attached and hence they suffer hydrolysis. Because of the availability of d-orbitals halo complexes with coordination number six, such as $(NH_4)_2[PbCl_6]$, $H_2[SiF_6]$ etc. are also possible.

Lead tetrabromide and lead tetraiodide are not known probably because the highly oxidising lead(IV) cannot survive in the presence of the highly reducing bromide and iodide ions. Compare the standard potentials :

$$Pb^{4+} + 2e = Pb^{2+} ; E° = + 1.8 \text{ volt}$$

$$I_2 + 2e = 2I^- ; E° = + 0.54 \text{ volt}$$
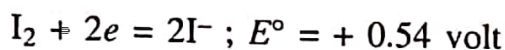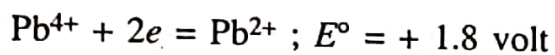
Complexes : Carbon complexes are little known. Nyholm has prepared complexes with o-phenylenebisdimethylarsane (diars) (18-II) by the reaction :

$$CCl_4 + 2 \text{ diars} \rightarrow [C(diars)_2] Cl_4 ;$$

(structure with two $As(CH_3)_2$ groups on benzene ring) = diars.

(18-II)

Metathesis of the chloride salt with other anions (X^-) produced other salts : $[C(diars)_2]X_4$. All these were found to be true tetra-univalent electrolytes.

Silicon is tetrahedrally coordinated in the vast majority of its compounds, namely SiO_2, silicates, silanes, silicones etc. Only a limited few examples of six coordinate complexes of silicon, germanium, tin and lead are known :

$$[Si(acac)_3]^+, [SiCl_4 (N(CH_3)_3)_2]; [SnCl_4 \text{ bpy}];$$

$$[M(C_2O_4)_3]^{2-} (M = Si, Ge, Sn, Pb) ; [SiI_2py_4]I_2;$$

$$[GeCl_6]^{2-} ; trans [GeCl_4L_2] (L = \text{tertiary amine})$$
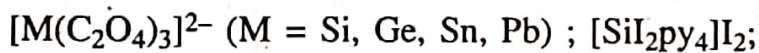
Availability of d-orbitals with silicon, tin, lead doubtless facilitates the formation of the above six-coordinate complexes. Carbon halides are clearly incapable of forming such six-coordinate complexes.

B. Bivalent State : Carbon monoxide is an electron deficient molecule and hence functions as an excellent π-acid (electron acceptor) in metal carbonyls. More on metal carbonyls appears in Chapter 24. Germanium(II) oxide is acidic and is a stronger acid than $Sn(OH)_2$. But $Sn(OH)_2$ is amphoteric reacting with acids to form salts and with alkalies to give stannites M_2SnO_2. But lead hydroxide is more basic than is acidic ($K_A \sim 8 \times 10^{-12}$ and $K_b \sim 1 \times 10^{-13}$). Bivalent tin and lead expectedly give rise to cationic properties. Tin(II) is a strong reducing agent though lead(II) is not.

A lone pair is left on the metal ions in their + 2(II) state. While it is possible to prepare complexes of these metal ions with donor ligands (eg : $SnCl_2$ reacts with donor solvents L to give $SnCl_2.L$) it is also possible to use $SnCl_2$ or $SnCl_3^-$ as donors to other metal ions. Thus

the interaction of platinum group metal salts with $SnCl_2$ leads to the formation of complex anions of Ru(II), Rh(I), Pt(II) which have been isolated as salts of large cations. The anions are formulated as $[RuCl_2(SnCl_3)_2]^{2-}$, $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ and cis/trans $[PtCl_2(SnCl_3)_2]^{2-}$. $SnCl_3^-$

$$[PtCl_4]^{2-} + 2SnCl_3^- \longrightarrow [PtCl_2(SnCl_3)_2]^{2-} + 2Cl^-$$
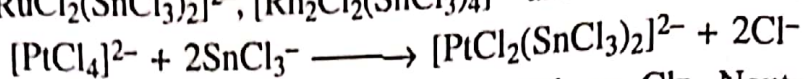
anion is considered to be of the same donor strength as Cl^-. Neutral complexes like $[F_3B \leftarrow SnX_2(NMe_3)]$ (X = Cl, Br, I), $[PtCl(SnCl_3)(Ph_3P)_2]$ have also been synthesised. The lone pair left on tin(II) also generates interesting stereochemical features. In $SnCl_2.2H_2O$ one H_2O is loosely bound as it is lost at 80°C. Sn(II) has thus two coordinated Cl^-, one coordinated H_2O and the lone pair occupying the fourth point of the tetrahedron. This pyramidal structure is often called as ψ-tetrahedral (ψ here indicating that a lone pair takes up a coordination site of the metal ion). $SnCl_3^-$ is also ψ-tetrahedral. Similar ψ-tetrahedral behaviour for Ge(II) and Pb(II) has not yet been exposed.

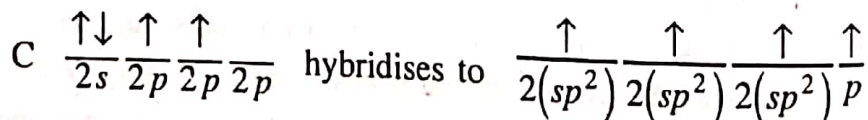## 18.2. ELEMENTARY FORMS OF THE GROUP IVB (GROUP 14) ELEMENTS

Carbon exhibits two major allotropic forms (diamond and graphite). These forms are manifestations of attaining a stable noble gas configuration even in the elementary state, and this can be achieved in two ways.

18.2.1. Diamond : Hybridisation of carbon 2s orbital and the three 2p orbitals gives four equivalent sp^3 orbitals each of which contains one unpaired electron. If all the carbons are assumed to have this hybridisation then overlap of these hybrid orbitals of neighbouring

$$\text{C} \quad \underset{2s}{\uparrow\downarrow} \ \underset{2p}{\uparrow} \ \underset{2p}{\uparrow} \ \underset{2p}{\quad} \quad \text{hybridises to} \quad \underset{2(sp^3)}{\uparrow} \ \underset{2(sp^3)}{\uparrow} \ \underset{2(sp^3)}{\uparrow} \ \underset{2(sp^3)}{\uparrow}$$
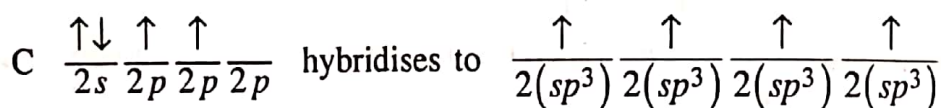
carbon atoms will lead to a non-ending tetrahedral structure (Fig. 18.1a). This is what obtains in diamond. Diamond thus has covalent bonds but these bonds do not end to produce discrete 'molecules', instead three-dimensional 'giant' 'molecules' are formed. Diamond is therefore an extremely hard and high-melting substance. The C—C bonds (length 1.54A) (154 pm) are extraordinarily stable, the non-volatility (sublimes at 3500°C) reflecting the difficulty of breaking these bonds. Diamond scratches all other metals. Tips of cutting tools are often set with diamond.

18.2.2. Graphite : An alternative hybridisation of the 2s and two 2p orbitals gives three equivalent sp^2 hybrid orbitals at 120° to each other on the same plane. The third 2p orbital is perpendicular to the plane of the sp^2 orbitals. If all carbons are assumed to have this

$$\text{C} \quad \underset{2s}{\uparrow\downarrow} \ \underset{2p}{\uparrow} \ \underset{2p}{\uparrow} \ \underset{2p}{\quad} \quad \text{hybridises to} \quad \underset{2(sp^2)}{\uparrow} \ \underset{2(sp^2)}{\uparrow} \ \underset{2(sp^2)}{\uparrow} \ \underset{p}{\uparrow}$$

hybridisation, and if each carbon overlaps with three neighbouring carbon atoms we have a non-ending two dimensional hexagonal planar structure (Fig. 18.1b). The third 2p orbital of each carbon of C_6 hexagonal unit then overlaps with each other to form a π-type molecular orbital. This is equivalent to a resonating alternate double bond on the valence bond model. More than one such layer is possible, and these layers have a weak van der Waals' type

force between them. This structure prevails in graphite. The ability of the planar layers to slip over one another makes graphite a good lubricant. Our 'lead' pencils are really made
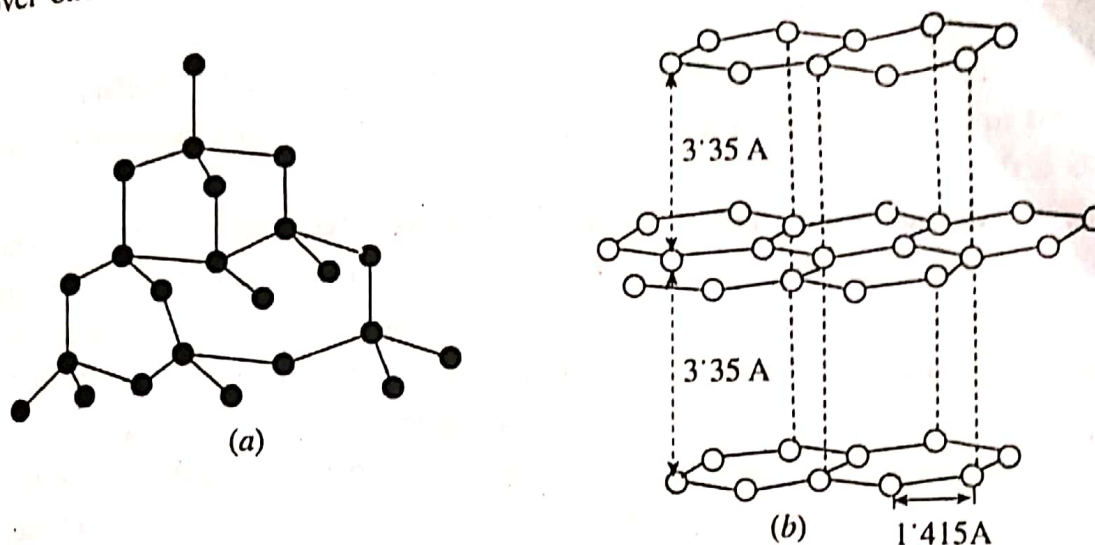

Fig. 18.1.: Models of (a) diamond and (b) graphite

of graphite and their layers of graphite rub off as we write. Graphite too has a high-melting point (~ 3500°C) since the bonds within the polymeric layer is quite tough. Because π-electrons are mobile (not being restricted between two atoms) graphite can conduct electricity but diamond cannot. Graphite is found in nature in mines in several countries. Ceylon graphite is purest. Siberian and Bohemian varieties are used in pencils. Artificial graphite is manufactured by heating (~ 2500°C) electrically a mixture of sand and anthracite or coke for about thirty hours. The presence of sand presumably catalyses the conversion to graphite. Graphite finds extensive use in dry batteries and as electrodes. Graphite can be changed to diamond by the application of high pressure and high temperature (~'3000°C) in presence of a catalyst, such as Cr, Fe or Pt metal. An inspection of the densities of graphite and carbon (Table 18.2) shows that pressure must be applied to enhance the conversion of graphite to diamond. C-C bond length in graphite is 1.41A (141 pm) and inter-layer spacing is 3.35A (335 pm).

Graphite can slow down fast neutrons and hence it is used as a moderator in nuclear reactors (Chapter 12.21.3).

18.2.3. **Amorphous carbon :** Besides diamond and graphite there are several other forms of carbon collectively called as amorphous carbon, such as charcoal, soot, lampblack. These are really inferior, microcrystalline varieties of graphite. The amorphous forms contain only few unit cells of the graphite structure. The physical properties of these varieties depend on their surface areas. The finely divided forms contain vast surface areas and are capable of absorbing large amounts of solutes from solution as also gases. When vegetable substances such as wood, sugar are heated to ~ 300°C in the absence of air a black residue is obtained. This is called *charcoal.* An animal source under similar treatment gives animal charcoal. The absorptive capacity of charcoal can be increased by treatment with steam or with air-steam mixtures for long periods at high temperatures. This treatment increases the porosity and also

removes hydrocarbons. Thus treated, charcoal is called *active charcoal*, Active charcoal is used in adsorption of gases and colouring matter and in decolourising sugar syrup. It also has use as a catalyst.

Carbon black is another finely divided form of carbon. It is usually obtained by heating hydrocarbons in an atmosphere of insufficient oxygen. It finds use as a pigment, in printer's ink and as a filler for rubber materials.

18.2.4. Fullerenes (Buckyballs) : In the two allotropes, diamond and graphite, there are a non-ending (non-finite) number of carbon atoms arranged tetrahedrally and hexagonally respectively. Recently a strange type of allotrope with finite number of carbon atoms with closed caged structure has been identified. Carbon atom clusters with 28, 32, 50, 60, 70, 84 and 90 atoms have been confirmed, the C_{60} cluster being the most dominant.

The structures of these clusters have been determined to be near-spherical, being close to a football. It was not possible to make a closed-cage structure model of C_{60} cluster with hexagons alone. Ultimately it was possible to have a closed structure with 20 hexagons and 12 pentagons. On top of this model there could be seen 60 vertices representing the 60 carbon atoms. These clusters being a strange new form of carbon have been named after the American architect, Buckminster Fuller, who has invented the geodesic dome. These clusters are fondly called "fullerene" or "buckyball" for short.

The discovery of the fullerenes was made by a group of physicists in 1985 at Rice University in Houston under the leadership of Richard Smalley. This group was studying the formation and structures of atomic clusters and large molecules. They developed a vacuum chamber inside which there was a hollowed out steel block. Different elements were placed in the hollow block and heated with intense laser beam. This vapourised the element which was immediately driven by inert helium jet into another chamber. The vapour was allowed to cool and to form atom clusters. These clusters were transferred to a mass spectrometer for identification of the mass. In the case of carbon the mass spectrometer registered signals for several carbon clusters of which C_{60} was the most abundant.

The original attempt by Smalley and coworkers produced only a microscopic amount of C_{60} cluster. Later studies (1989) by Huffman at Arizona and Kratschmer at Munich gave a better yield, the technique being to pass electric arc between two graphite electrodes in a helium environment.

Back home at the Indian Institute of Science, Bangalore scientists have identified C_{60} and C_{70} clusters by burning benzene and leading the resulting soot by argon jet into a water-cooled copper vessel to collect the fullerenes formed. The soot thus obtained can be dissolved in benzene and the C_{60} and C_{70} clusters separated chromatographically, the ratio of the two clusters being 5 and 1 respectively.

Thermal decomposition of naphthalene in an inert atmosphere of argon around $1000^{\circ}C$ also gives these C_{60} and C_{70} clusters.

The structure of C_{60} cluster could not be explained by conventional means. A closed football-like structure ultimately emerged from sewing together of 20 hexagons and 12 pentagons.

Crystal structure studies of the C_{60} fullerene by X-ray and electron diffraction techniques in 1990 confirmed the closed-cage structure.

Every 6-membered hexagon ring is surrounded alternately by hexagons and pentagons of carbon. Every carbon pentagon is connected to five carbon hexagons. Such fusion of pentagons and hexagons force the sturcture to curve. Note that in graphite each hexagon is fused to six hexagons giving a flat structure.

Graphite has a flat two-dimensional layer structure with each carbon making as many as three sp^2 σ-bonds with three neighbouring carbon atoms while the third p_z orbital of each carbon (carrying one electron) makes π-overlap with all the p_z orbitals of the carbon atoms over the flat carbon layers (π M.O's). Because of the presence of both C_6-hexagonal and C_5-pentagonal framework, the fullerenes are not flat two-dimensional but three dimensional in character. Because of the three-dimensional nature the σ-bonds are under strain and the π-bonds are less delocalised than in graphite. Because of these inherent strains in the bonds some fullerenes are less stable than others (C_{60} cluster is quite stable).

Eventually fusion of 60 carbons (C_{60}) gives a dome-like structure curving around itself to a football (soccer ball)-like shape. ^{13}C NMR studies indicate all 60 carbon atoms are equivalent. Although all the atoms are equivalent all the carbon-carbon bonds are not. X-ray studies on C_{60} have revealed that C-C bond length at the fusion of two 6-membered rings is shorter (1.355A ; 135 pm) than C-C bond length at the fusion of 5- and 6-membered rings (1.467A ; 146.7 pm). A greater degree of π-bonding is present at the fusion of the 6-membered rings.

C_{70} cluster has the shape of a rugby ball (somewhat prolate structure) while C_{120} has the shape of a dumb-bell, two C_{60} units being linked through four carbon-carbon bonds.

Air-stable fullerenes are yellow-brown to black-brown and soft like graphite. They are lighter than graphite : d-graphite, 2.25 g/cm^3 ; d-C_{60} fullerene, 1.65 g/cm^3 ; Fullerenes are insoluble in water and only moderately soluble in benzene, cyclohexane, toluene, carbon tetrachloride and carbon disulphide. Dilute solutions of C_{60} in organic solvents are purple to red-violet due to π→π* transition (C_{60}HOMO → C_{60} LUMO). When heated above 1500°C in the absence of air fullerenes are converted exothermically to flat two-dimensional graphite. Fullerenes behave as semiconductors since the π-electron system is limited (not infinite like graphite) because of a finite molecular size.

Since fullerenes possess extended π-system a number of reactions have been conducted on them. Treatment of C_{60} and C_{70} with Zn and conc. HCl gives $C_{60}H_{36}$ and $C_{70}H_{36}/C_{70}H_{38}$.

Fullerenes react with fluorine slowly over a period of two weeks and through several intermediates to give $(CF)_{60}$. All the fluorines project outwards from the buckey ball. All the double bonds are gone and all the carbons are now sp^3 hybridised. Each carbon is connected to three neighbouring carbon and one fluorine. Since the π-bonds of fullerene are all broken the fullerene fluoride has no aromatic character.

In the vapour phase ($\sim 400°C$) alkali metals react to give fulleride anions :

$$C_{60} + mM \longrightarrow (M^+)_m (C_{60}^{m-})$$
$$\text{wine-red}$$
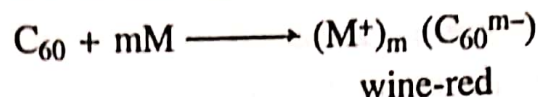
Osmium tetraoxide (OsO_4), a good oxidant, can add across the double bond of fullerene. On reacting OsO_4 with C_{60} and 4-*t*-butylpyridine, a complex of the type :

$$C_{60} \underset{O}{\overset{O}{<}} \hspace{-0.3em} > Os(O)\ (O)\ (4 - t\text{-butylpyridine})_2$$
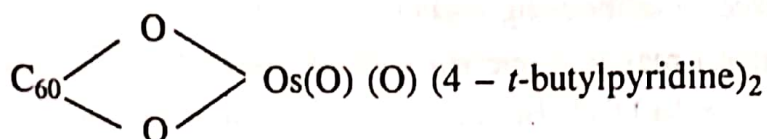
is obtained. Two OsO_4 oxygens serve as a bridge between Os and C_{60}. (Fig 18.2).
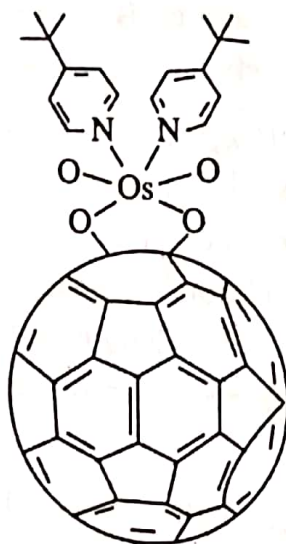
Fig. 18.2 : The complex C_{60} (OsO_4) $(4$-*t*-butylpyridine$)_2$

Possibilities of fullerene getting coordinated to a metal either through the five-membered pentagonal C_5 ring (as in ferrocene) or through the six-membered hexagonal C_6 ring (as in dibenzenechromium (0)) have also been explored. For details see Section 24.10.

Smalley has been awarded the Nobel Prize for Chemistry in 1996.

18.2.5. Silicon and Germanium : Silicon and germanium occur in one structural form that of diamond. With increasing atomic number metallic bonding predominates. Since the heavier elements cannot participate in strong multiple bonding the graphite structure does not appear beyond carbon. Table 18.3 gives a summary of the crystal structures of the group IVB (group 14) elements.

Table 18.3 : Crystal Structures of Group IVB (Group 14) Elements

| Structure Type	Carbon	Silicon	Germanium	Tin	Lead
Diamond	Yes	Yes	Yes	Yes (<13°C)	No
Graphite	Yes	No	No	No	No
Metallic	No	No	No	Yes (>13°C)	Yes

18.3. INTERCALATION* COMPOUNDS OF GRAPHITE

Graphite has a non-ending hexagonal structure with planar three-coordinate sp^2 carbon. In between the successive layers there are open interlayer spacings of 3.35A (335 pm). A variety of compounds have now been authenticated where a second element such as halogens, alkalies has been inserted inside the inter-layer spacing.

Intercalation of graphite leads to two situations :

1. Intercalation destroys the π-bonding in the graphite layer resulting in loss of conductivity eg. : CF_4, C_8Br etc.

2. Intercalation maintains the π-bonding, thus retaining the electrical conductivity eg. C_8Rb, C_8Cs.

1. At 400-500°C graphite reacts with fluorine to give a monoflouride CF_x ($x \sim 0.68$-0.99), the colour of the product changing with changing fluorine content : black ($x \sim 0.7$); grey ($x \sim 0.8$) ; silvery ($x \sim 0.9$) and transparent white ($x \sim 0.99$). At higher temperature (~ 600°C) a mixture of CF_4, C_2F_6 and C_5F_{12} is obtained. Other halogens behave differently. Liquid chlorine gives C_8Cl while bromine gives C_8Br, $C_{12}Br$, $C_{16}Br$ and $C_{20}Br$. Iodine alone does not seem to intercalate, although C_8ICl and $C_{36}ICl$ have been prepared.

In $(CF)_x$ all the $C = C$ double bonds of graphite are broken and one additional fluorine is added to each carbon (Fig. 18.3). All the carbons are now sp^3 hybridised (tetrahedral) : $C - C$ bond length, 1.47A ; $C - F$ bond length, 1.4A. One carbon has its fluorine pointing up while the next carbon has its fluorine pointing below. The interlayer spacing varies in different samples from 5.8A to 6.15A and is thus considerably larger than in graphite.
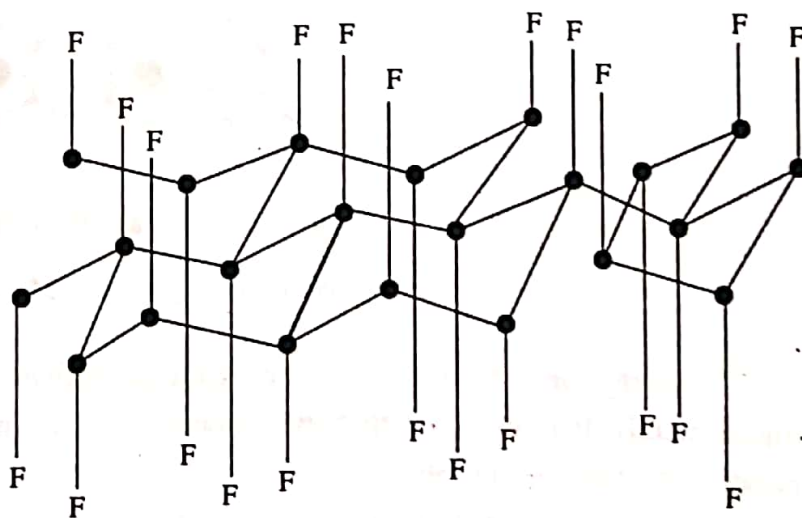
Fig. 18.3 : The structure of graphite fluoride $(CF)_x$.

* Intercalation means insertion of an element in interlayer spacing.

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The π-system is more or less destroyed as indicated by increased resistance. C_8Cl and C_8Br are more conducting than graphite, indicating that the graphite layer has donated electrons to bromine and chlorine. The layer character of C_8Br has been established by X-ray crystallography.

2. Potassium as also Rb and Cs vapour react with graphite at 300°C to give MC_8. Heating at 300°C under reduced pressure gives several products : MC_8 (bronze red) ; MC_{24} (steel blue), MC_{36} (dark blue) ; MC_{48} and MC_{60} (black). Some of these compounds have also been prepared by (1) the reaction of graphite with liquid ammonia solutions of the alkali metals and (2) by electrolysing fused alkalies with graphite electrodes.

In MC_8 (M = K, Rb, Cs but not Na) the carbon atoms of one layer are exactly above the carbon atoms of the next layer. This is distinct from that in pure graphite. The interlayer spacing in MC_8 is ~ 5.4A (K), 5.61A (Rb), 5.75A (Cs) compared to 3.35A in graphite. At the centre of the hexagonal carbon rings is positioned the alkali metals (Fig. 18.4). Since the composition is MC_8 only, the number of M is few and far between to have all the hexagonal spacings occupied. Potassium graphite KC_8 is increasingly finding use as a reducing agent in preparative studies.
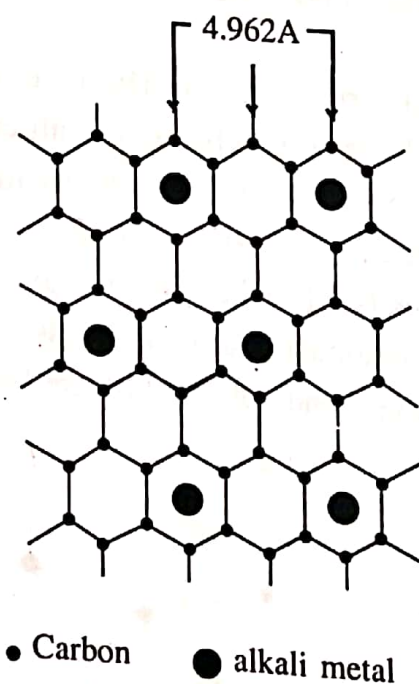
Fig. 18.4 : Alkali metal graphites MC_8 (M = K, Rb, Cs)

The compounds have a very small paramagnetism (much below the odd electron of the alkali metal). It is believed that the valence electron of the alkali metal atom moves to the conduction band of graphite.

In general, the alkali metal-graphite intercalation compounds are intensely coloured and show significant electrical conductivity. On heating strongly the alkali metals volatilise out of interspace between graphite layers.

A wide array of metal halides ($FeCl_3$, $MoCl_5$, $CuBr_2$, $AlBr_3$, $NiCl_2$, $CuCl_2$, $MnCl_2$, $ZrCl_4$ etc.) also form intercalation compounds with graphite. $C_{6.69} FeCl_3$ is an example. The structures are not fully understood yet.

18.4. BINARY CARBIDES

Binary carbides have some superficial resemblance with the binary hydrides in regard to classification : I. salt-like carbides ; II. covalent carbides and III. metallic or interstitial carbides. As with the hydrides, this classification of carbides based on the type of bonding may not be ideal but will certainly serve our purpose.

Three general methods of syntheses are : (1) combination of the elements at or above 1500°C ; (2) reaction of metal oxide with carbon at elevated temperature ; (3) reaction of acetylene or methane with metals or solutions of metal salts.

18.4.1. Salt-like Carbides. These carbides are ionic and expectedly formed by strong electropositive elements of groups IA, IIA and IIIA (groups 1, 2 and 3).

These carbides can be clasified as (a) methanides and (b) acetylides. Methanides contain C^{4-} anion and the acetylides C_2^{2-} i.e. $^-C \equiv C^-$ anion. Salt-like carbides possess ionic crystal lattice. They are easily decomposed by water or dilute acids liberating CH_4 or C_2H_2. Carbides of beryllium (Be_2C) and aluminium (Al_4C_3) are colourless and crystalline with ionic crystal structures. These compounds contain the tetranegative C^{4-} ions and are easily hydrolysed in water giving CH_4.

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4 \; ; \; Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$
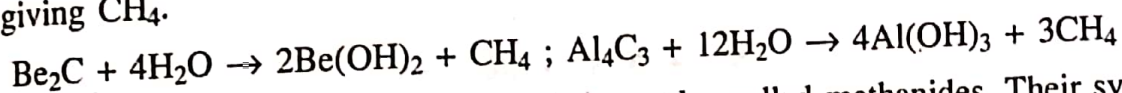
Due to this hydrolysis behaviour these carbides are also called methanides. Their synthesis involves combination of the elements at ~ 1500°C.

The commonly called acetylides have two carbon atoms inside the anion which is dinegative. The acetylides are a large group of carbides formed mainly by elements of groups IA, IIA and IIIA (groups 1, 2 and 3) and to some extent by the lanthanides and by thorium and uranium. Some examples are :

Group IA (group 1) : Na_2C_2, K_2C_2 etc ; Cu_2C_2, Ag_2C_2

Group IIA and IIB (groups 2 and 12) : BeC_2, MgC_2, CaC_2, ZnC_2

Group IIIA and IIIB (groups 3 and 13) : LaC_2, ThC_2, UC_2, Al_2C_6

Calcium acetylide, commonly known as calcium carbide, is obtained by heating a mixture of CaO and coke to ~ 2250°C in an electric furnace : $CaO + 3C \rightarrow CaC_2 + CO$. Calcium acetylide collects at the bottom and is tapped off from time to time (Chapter 16). It finds use in the preparation of acetylene and calcium cyanamide—a nitrogenous fertiliser :

$$CaC_2 + 2HCl \rightarrow CaCl_2 + C_2H_2 \; ; \; CaC_2 + N_2 \rightarrow CaN.CN + C$$
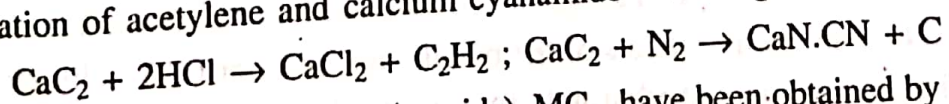
The carbides of the lanthanides (lanthanoids), MC_2, have been obtained by heating M_2O_3 with carbon in an electric furnace in an inert atmosphere. They are mainly acetylides and

hydrolyse to give acetylene and other hydrocarbons. The acetylides of Cu, Ag, Zn, Mg are prepared by passing acetylene through solutions of the metal salts. Ammoniacal solutions of copper(I) and silver(I) are used for the synthesis of Cu_2C_2 and Ag_2C_2 while petrol solutions of dialkyl zinc and dialkyl magnesium are used for ZnC_2 and MgC_2. The compounds react with water and produce acetylene :

$$MgC_2 + 2H_2O \rightarrow Mg(OH)_2 + C_2H_2$$
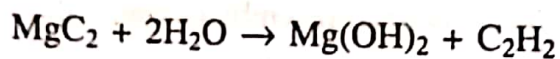
All acetylides have ionic sodium chloride structure. Positions of sodium and chlorine in NaCl are taken up by Ca^{2+} and C_2^{2-} ions of calcium carbide.

In CaC_2 the C—C distance is 1.19A (119 pm) whereas in the trivalent metal acetylides the C—C distance is 1.24 – 1.28A (124-128 pm). Note the $C \equiv C$ distance is 1.2A (120 pm).

18.4.2. Covalent Carbides. Depending on volatility these covalent carbides can be sub-divided into two classes. The first class consists of small discrete molecules, formed especially by hydrogen and the elements of groups VIB and VIIB (groups 16 and 17). Examples are CH_4, CO_2, CS_2, CCl_4 etc. The second class forms giant molecules although the bonding is still covalent. The most known compound is *carborundum* (SiC) which is a very hard solid decomposing above 2200°C and has a diamond like lattice. This is made by reducing SiO_2 with carbon in an electric furnace (at ~ 2000°C).

$$SiO_2 + 2C \rightarrow Si + 2CO ; Si + C \rightarrow SiC$$
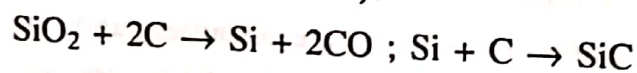
It is quite resistant to chemical reactions. However it can be decomposed by chlorine or alkali in presence of oxygen :

$$SiC + 2Cl_2 \rightarrow SiCl_4 + C$$
$$SiC + 2NaOH + 2O_2 \rightarrow Na_2SiO_3 + CO_2 + H_2O$$
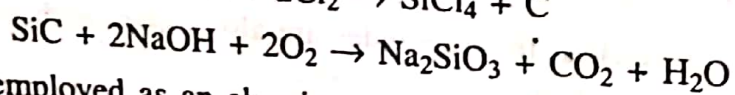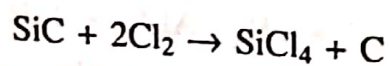
This is widely employed as an abrasive and a refractory material. Its crystal structure reveals that each of the carbon (or silicon) is tetrahedrally surrounded by atoms of the other element.

18.4.3. Interstitial Carbides. Close packed structures of metals have holes in the lattice. These holes are of two kinds : octahedral holes created by close packng of six metal atoms in octahedral positions and tetrahedral holes created by some metals positioned in tetrahedral points. The small carbon atoms can sometimes be fitted into holes of suitable sizes (which are dependent on the size of the metal atoms) and naturally the radius ratio rules (Chapter 6) will dictate the formula of such interstitial carbides. From our discussion in Chapter 6 it can be inferred that carbon/metal radii ratios should be ~ 0.4 to 0.7 for octahedral holes (NaCl structures). Investigations on the structures of several interstitial carbides show that critical radius ratio is ~ 0.6. Taking the covalent radius of carbon as 0.77A (77 pm) it can be inferred that the atomic radius of the metal must be from 1.3A (130 pm) to 1.9A (190 pm) so as to have such an octahedral hole fitting. Metals like Cr, Mn, Fe, Co, Ni have their atomic radii less than 1.3A (130 pm) and hence do not form carbides of this type. On the

other hand Ti, Hf, W, Nb, have their radii larger than 1.3A (130 pm) and hence form interstitial carbides : TiC, HfC, W_2C, NbC etc. The octahedral holes (interstices) of the transition metal M in MC type carbides (eg. TiC, NbC etc.) are occupied by the small carbon atoms, leading to an NaCl type structure.

Such compounds have conductivity, metallic lustre like metallic alloys and the forces between the metal atoms are very much like those in the metal itself. The insertion of carbon atoms results in an increase in volume (~ 9%).

Many of these carbides have very high melting points :

Carbides	TiC	ZrC	TaC	NbC	MoC
M.P. (°C)	3150	3500	3800	3500	2965

These are very hard, their hardness being in between those of diamond and topaz. Interstitial carbides are formed by heating the metal or its oxide with carbon.

$$TiO + 2C \rightarrow TiC + CO$$

$$MoO_2 + 4C \rightarrow MoC + 3CO$$
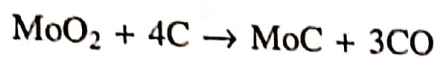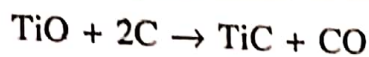
Some carbides have been prepared by heating the metal in CH_4 :

$$Mo + CH_4 \rightarrow MoC + 2H_2$$
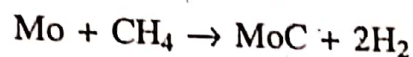
Because of the formation of very stable interstitial carbides, carbon reduction of metal oxides is not preferred for extraction of titanium, zirconium, tungsten etc.

TaC and WC are used in making high-speed cutting tools. SiC is used as a refractory and abrasive material.

Interstitial Carbides as Catalysts : Some interstitial carbides namely WC and Mo_2C, are very effective as catalysts—as much effective as platinum group metals and additionally far less costly.

1. They are very useful as catalysts in Fischer-Tropsch process of converting water gas $(CO + H_2)$ to gasolene (B. P. 90° – 200°C ; C_6H_{14} to $C_{11}H_{24}$ hydrocarbons). Water gas and hydrogen mixture (in the ratio : $CO : H_2 = 1 : 2$) is first passed over an iron oxide catalyst to remove H_2S and any other sulphur compounds. The purified mixture is then passed over heated cobalt oxide catalyst (at ~ 200°C). The resulting product is condensed and unconverted gases and crude gasolene is fractionated and gasolene (C_6H_{14} to $C_{11}H_{24}$) is separated from heavier Diesel fraction (B.P > 300°C ; C_{13} to C_{18} hydrocarbons) the reactions presumably are :

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$
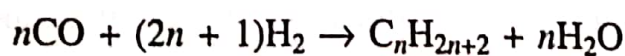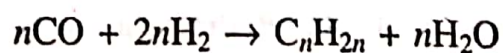
It is supposed that the cobalt catalyst is partially converted to cobalt carbide. Replacement of the traditional cobalt catalyst by the interstitial carbides WC/Mo_2C provides good conversion.

2. WC/Mo_2C are also useful catalysts in cracking of petroleum to light hydrocarbons.

3. They are also useful in forcing isomerisation of straight-chain hydrocarbons to branched-chain products, thus giving high-octane fuel.

The carbides, WC and Mo_2C, and the nitrides W_2N and Mo_2N which latter are useful catalysts in the conversion of $N_2 + 3H_2$ to NH_3, are called *Magic Catalysts.*

18.5. SILICATES

18.5.1. General Considerations. Silicates are the most abundant components of the earth's crust. Silicon and oxygen together make up almost 75% by weight of the earth's crust. The unique feature of all silicate minerals is the tetrahedral coordination of silicon by oxygen. The difference in electronegativities of silicon (1.8) and oxygen (3.5) is 1.7 and this large difference suggests considerable ionic character of the bond. Silicon-oxygen bond must be considered therefore to have both ionic and covalent characters. The following two extreme structures (18-III and 18-IV) must be considered to contribute to the real structure:
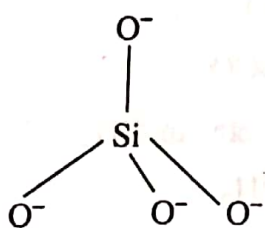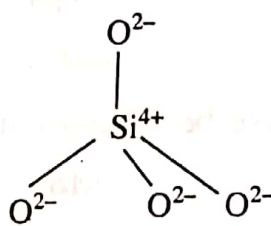
(18-III)   (18-IV)

A silicate, say Mg_2SiO_4, can then be viewed as a salt made up of Mg^{2+} and covalent SiO_4^{4-} or as a complex oxide made up of Mg^{2+}, Si^{4+} and O^{2-} ions. It then follows that isomorphous replacement of cations by other cations of comparable size and charge will be a common feature of silicate composition and structure. The metal ions are so arranged in the silicate crystal lattice that they have their preferred coordination numbers and stereochemistry. The metal ions are surrounded by requisite number of silicate oxygens in suitable positions. Within some wide limits metal ions of comparable size and coordination number, which are interchangeable are : Mg^{2+} (coordination number 6, ionic radius 0.65A, 65 pm) ; Fe^{2+} (6, 0.8A, 80 pm) ; Na^+(6, 0.95A, 95 pm) ; Ca^{2+} (6, 0.99A, 99 pm) etc. Furthermore the Al^{3+} : O^{2-} radius (0.52A, 52 pm ; 1.4A, 140 pm) ratio (0.36) is close to the critical value for transition from coordination number 6 to 4 (Chapter 6) and hence Al^{3+} can even replace Si^{4+} (0.39A, 39 pm) in addition to replacing other cations in octahedral sites. For every aluminium so introducd into the silicate tetrahedra a corresponding substitution of Ca^{2+} for Na^+, Al^{3+} for Mg^{2+} etc. must occur in order to maintain electroneutrality.

Tetrahedral SiO_4^{4-} units may be linked together by sharing corners but not edges or faces. Thus discrete SiO_4^{4-} units as also infinite chains, rings, sheets and three-dimensional framework structures are possible.

18.5.2. Classification and Structure of Silicates. Some possible closed silicon-oxygen groupings in silicates are shown in Fig. 18.5. These include (a) isolated tetrahedra SiO_4^{4-} (orthosilicates, Mg_2SiO_4), (b) tetrahedra sharing one oxygen atom $Si_2O_7^{6-}$ (thortveitite, $Sc_2Si_2O_7$), (c) tetrahedra sharing two oxygen atoms to form a three-membered (Si) ring structure $Si_3O_9^{6-}$ (benitoite, $BaTiSi_3O_9$) and (d) tetrahedra sharing two oxygen atoms forming a six-membered (Si) ring $Si_6O_{18}^{12-}$ (beryl, $Be_3Al_2Si_6O_{18}$). Note that the silicon-oxygen links of Fig. 18.5 are not wholly covalent. They possess substantial ionic character. It is necessary to point out that these structures are not the only possible ones for silicates. For example,

(a)   (b)   (c)   (d)
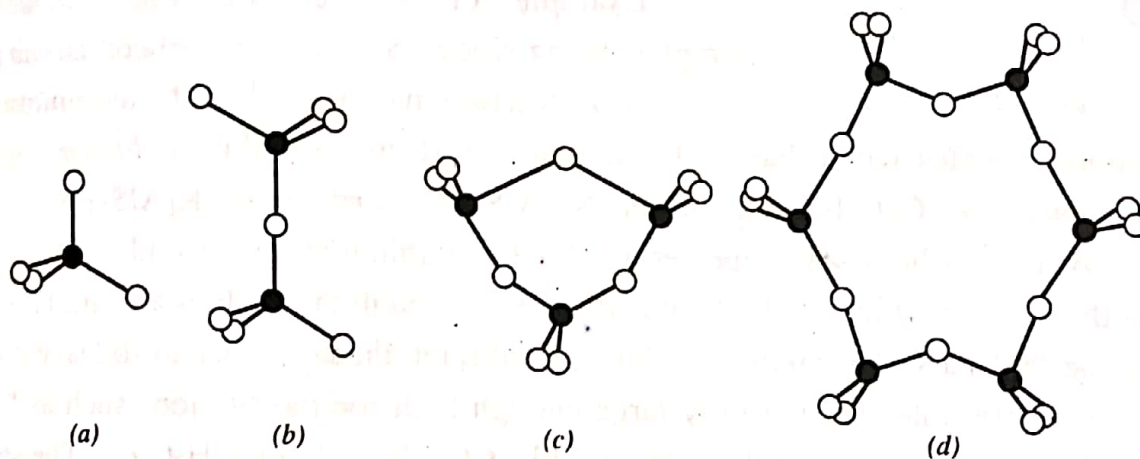
Fig. 18.5. : Some possible closed silicon-oxygen groupings in silicates :

(a) SiO_4^{4-} (b) $Si_2O_7^{6-}$ (c) $Si_3O_9^{6-}$ (d) $Si_6O_{18}^{12-}$

an open chain linear polymeric structure is possible if the SiO_4^{4-} tetrahedra share two oxygen atoms (18-V). This structure is found in *pyroxenes* (enstatite $MgSiO_3$, diopside $Ca(Mg)(SiO_3)_2$, spodumene $LiAl(SiO_3)_2$. The second compound is an example of isomorphous replacement

$$= [\,SiO_3^{2-}\,]n$$

(18-V)
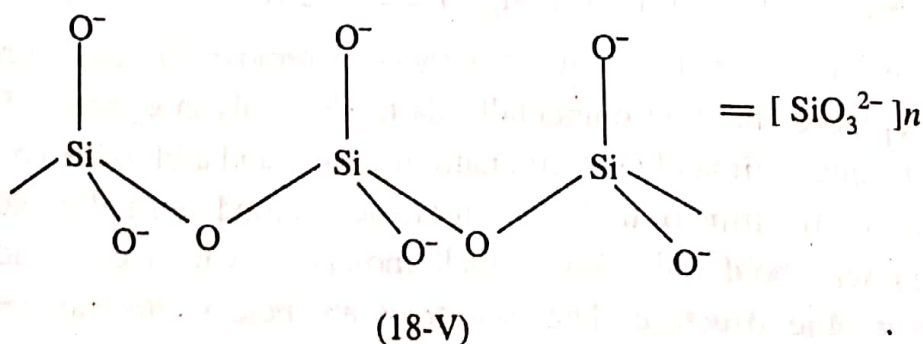
of two divalent cations, and the third illustrates replacement of two divalent ions in the second compound by mono- and trivalent cations. A linear net structure is attained in $(Si_4O_{11})_n^{6-}$ when SiO_4^{4-} tetrahedra share alternately two and three oxygen atoms (18-VI) : *Amphiboles* (tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$) belong to this class (18-VI), the hydroxy groups being associated with the cations in the crystal. Isomorphous replacement of the cationic metal ions such as Fe for Mg, Na and Al for two Mg, and also of Al for Si in the SiO_4^{4-} tetrahedra is very common in this series.

Fire bricks can withstand high temperature and are used in the linings of furnaces. They are made by firing clay with strongly fired temperature-resistant clay at ~ 1450°C. Roughly they correspond to $Al_2O_3.2SiO_2$; softening point is ~ 1700°C. Higher Al_2O_3 content provides firebricks with higher softening temperature.

Ceramics, in general, are thermally stable inorganic solids which are made by high temperature treatment of suitable raw materials (such as metal silicates and metal aluminosilicates). Stonewares ceramics are made by mixing stoneware clay (with low iron oxide content) with silica/quartz and kaolin with flux (calcite or feldspar) and firing the mixture at ~ 1100–1300°C. Useful household construction products thus obtained are sinks, bathtubs, commodes etc. Porcelains are translucent (i.e partly transparent) while stonewares are opaque. The raw materials for the making of porcelain are kaolin, quartz and feldspar (as flux). Firing of 50% kaolin, 25% quartz and 25% feldspar at ~ 1400–1500°C gives hard porcelain, while firing of 25% kaolin, 45% quartz and 30% feldspar at ~ 1200–1300°C gives soft porcelain. Brightly coloured porcelain dishes are made of soft porcelain because the paints used in their decorations can withstand the comparatively lower firing temperature.

While concluding this section it is pointed out that the quality of the raw materials, nature of the fillers and fluxes used, their proportions and finally the firing temperature make all the difference in various earthenwares, bricks, stonewares and porcelain articles.

18.6. COMPOUNDS OF THE GROUP IVB (GROUP 14) ELEMENTS

18.6.1. Halides. All the four tetrahalides of carbon, silicon, germanium and tin are known. With lead only the tetrachloride is known. SnF_4 appears to have a polymeric six-coordinate structure with four bridging equatorial fluorines and two non-bridging axial fluorines (cf : Chapter 5, Part I). All others are covalent as revealed by their volatility and non-conducting behaviour. There are a few interesting points of comparison : (1) The carbon halides are highly resistant to hydrolysis, this being due to the non-availability of a d-orbital for nucleophilic attack by H_2O (18.1.2), (2) CBr_4 and CI_4 decompose below their boiling points whereas $SiBr_4$, SiI_4, $GeBr_4$ do not. This is presumably due to larger halogens clustering around a small carbon atom, (3) Contrary to usual behaviour of covalent compounds $SiCl_4$ has a lower B.P. than CCl_4.

	CCl₄	SiCl₄	GeCl₄	SnCl₄	PbCl₄
B.P. (°C)	76.4	57.6	83	114.1	105

	B.P(°C)		B.P(°C)
CF₄	– 128	SiF₄	– 86
CCl₄	76.4	SiCl₄	57.6
CBr₄	190	SiBr₄	153
GeF₄	– 37	SnF₄	subl. 704
GeCl₄	83	SnCl₄	114.1
		SnBr₄	293
		SnI₄	340

This anomaly has been explained on the assumption of multiple bonding between silicon d-orbital and filled p-orbital of chlorine (Fig. 18.6) so that there is an effective decrease in the intermolecular van der Waals' forces in silicon halides compared. to that in carbon halides. For the other halides boiling points are normal. Syntheses of the important halides appear in subsequent sections.
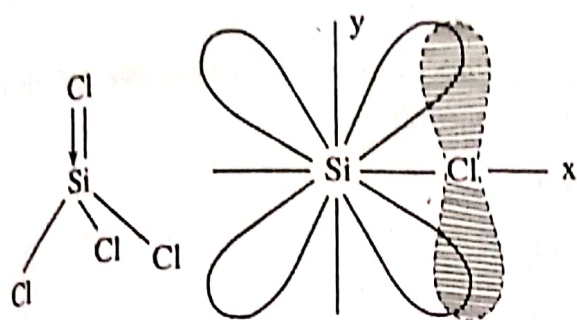
Fig. 18.6. : Bonding in $SiCl_4$ showing overlap of a vacant silicon d orbital (d_{xy}) with a filled chlorine p-orbital (p_y).

18.6.2. Freons. Mixed chloride fluorides of carbon are today valuable refrigerants. Engineers were searching a refrigerant chemical which will be non-toxic, odourless, volatile, non-inflammable, non-corrosive and of course less expensive. Midgley, an American engineer, noted that elements on the right hand side of the Periodic Table were the only ones that formed sufficiently volatile compounds. Inflammablity of the compounds also showed a decreasing trend from left to right of the Table, and toxicity increased in a group from top to bottom. A combination of all these ideas led to the discovery of a series of mixed chloride fluorides of carbon, which has the right properties as refrigerant chemicals. These chloride fluorides are called *freons*. These are conveniently made by passing CCl_4 over CoF_3 at 150—200°C when a mixture of CCl_3F, CCl_2F_2, $CClF_3$ and CF_4 is obtained.

$$CCl_4 + 4CoF_3 \rightarrow CF_4 + 4CoF_2 + 2Cl_2$$

$$2CCl_4 + 2CoF_3 \rightarrow 2CCl_3F + 2CoF_2 + Cl_2$$

These can be separated by making use of the difference in their volatility. CCl_2F_2 has also been obtained by the action of HF on CCl_4 in the

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$CCl_3F + HF \xrightarrow{SbCl_5} CCl_2F_2 + HCl$$
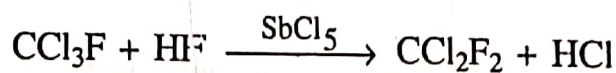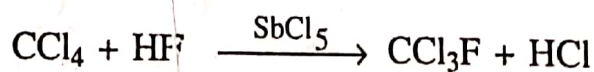
presence of $SbCl_5$. $CHClF_2$ is also considered as a freon and is obtained by the reaction of $CHCl_3$ and HF in the presence of $SbCl_5$ as a catalyst :

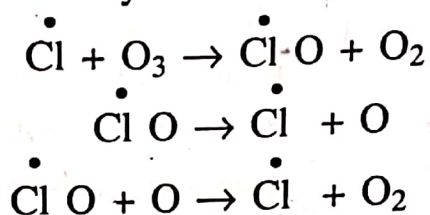$$CHCl_3 + 2HF \xrightarrow{SbCl_5} CHClF_2 + 2HCl$$
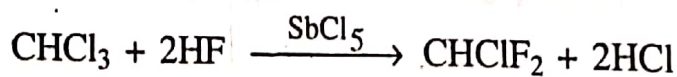
CCl_2F_2 is the most commonly used freon. These freons possess all the properties expected of ideal refrigerants. They have low boiling points, low viscosity, low surface tension, high density and they are odourless, non-inflammable, non-toxic, chemically inert and thermally stable.

Recall that carbon has no d-orbitals; and that in tetravalent state it has attained noble gas configuration. There is no scope for further reaction. Since fluorine is the most electronegative element the polarity of C-F bonds is such that we may conceive carbon to have undergone

some slight oxidation ($C^{\delta+} - F^{\delta-}$). All these explai· the inertness of freons to chemic reagents like H_2O, O_2 etc.

The freons escaping into the atmosphere undergo decomposition giving particularly atoms which damage the ozone layer in the upper atmosphere :

$$\overset{\bullet}{Cl} + O_3 \rightarrow \overset{\bullet}{Cl}\text{-}O + O_2$$

$$\overset{\bullet}{Cl}\,O \rightarrow \overset{\bullet}{Cl} + O$$

$$\overset{\bullet}{Cl}\,O + O \rightarrow \overset{\bullet}{Cl} + O_2$$

The ozone layer serves as a shield and protects the earth from harmful ultraviolet radiatio

18.6.3. Teflon : This is polytetrafluoro ethylene, $(C_2F_4)_n$. This is obtained by the pyroly of the freon $CHClF_2$ at 250°C to give first the monomer C_2F_4 which is then polymeris

$$2CHClF_2 \xrightarrow{\quad 250°C \quad} CF_2 = CF_2 + 2HCl$$
$$(B.P. - 76°C)$$
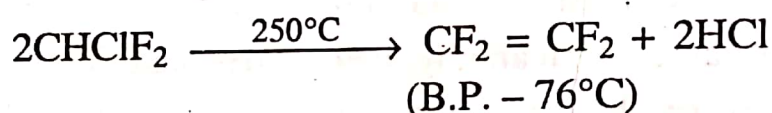
in contact with an aqueous solution of a peroxodisulphate or oil-soluble peroxides un moderate pressure and low temperature.
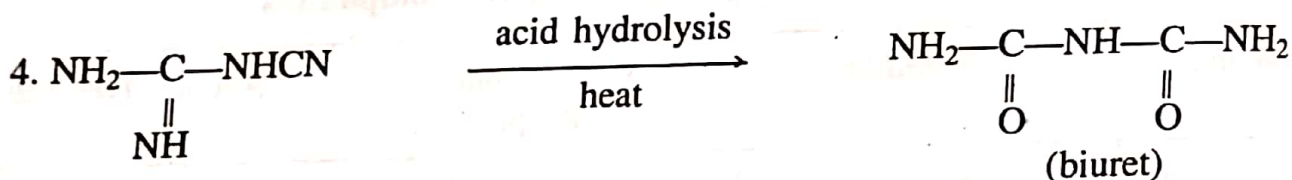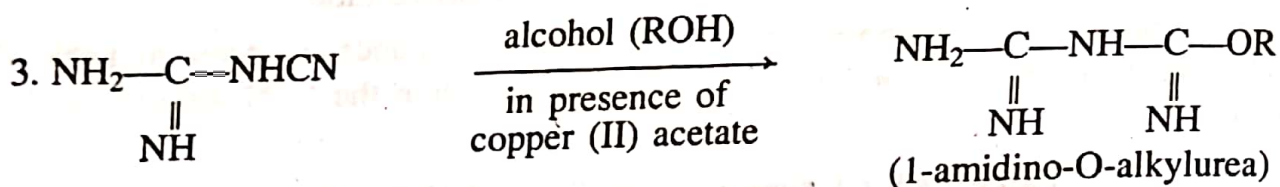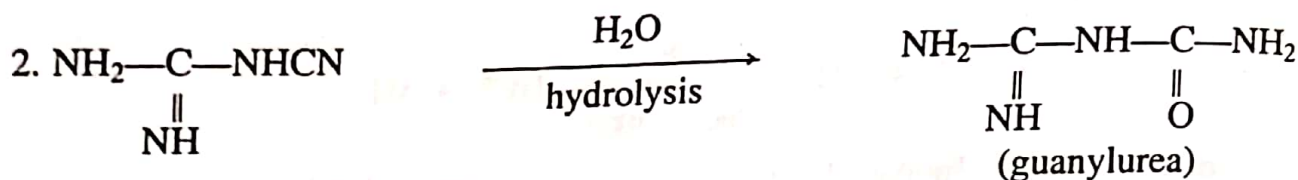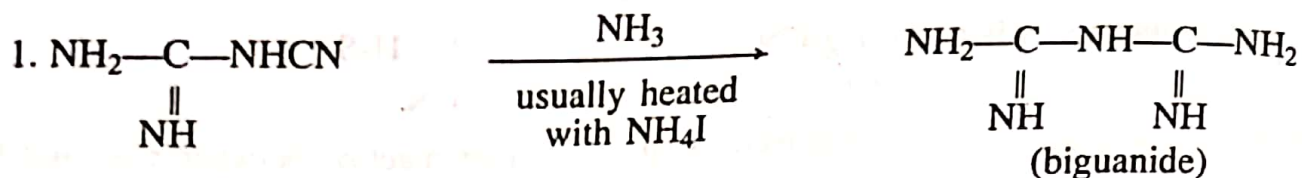
$$n(CF_2 = CF_2) \rightarrow [CF_2\text{---}CF_2]_n$$
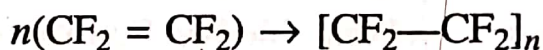
This is a white solid with good electrical insulting properties and exceptional resistance chemical attack. It is insoluble in any solvent.

The polymer comprises a straight backbone of carbon atoms symmetrically surround by fluorine atoms :
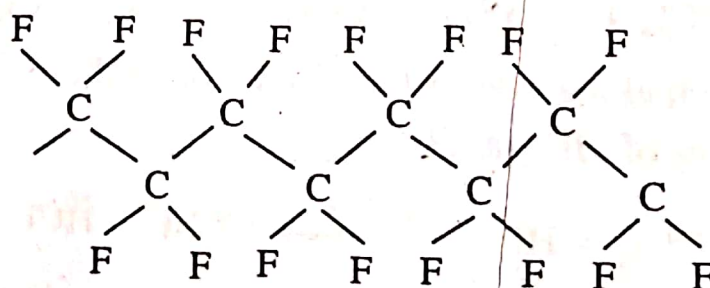
It is now extensively used in electrical insulation, high-temperature industrial plasti non-stick cooking utensils, razor blades, chemical equipments etc.

Dicyandiamide is the starting material for the syntheses of a series of formidable didentate (N, N) donors :

1.
$$NH_2—C—NHCN$$
(with NH below the first C)
$\xrightarrow[\text{usually heated with } NH_4I]{NH_3}$
$NH_2—C—NH—C—NH_2$ (with NH below both C's)
(biguanide)

2.
$$NH_2—C—NHCN$$
(with NH below the C)
$\xrightarrow[\text{hydrolysis}]{H_2O}$
$NH_2—C—NH—C—NH_2$ (with NH below first C, O below second C)
(guanylurea)

3.
$$NH_2—C—NHCN$$
(with NH below the C)
$\xrightarrow[\substack{\text{in presence of} \\ \text{copper (II) acetate}}]{\text{alcohol (ROH)}}$
$NH_2—C—NH—C—OR$ (with NH below both C's)
(1-amidino-O-alkylurea)

4.
$$NH_2—C—NHCN$$
(with NH below the C)
$\xrightarrow[\text{heat}]{\text{acid hydrolysis}}$
$NH_2—C—NH—C—NH_2$ (with O below both C's)
(biuret)

Dicyandiamide, on heating in NH_3 gives *melamine*, a cyclic trimer $(H_2NCN)_3$ (18-VII) :
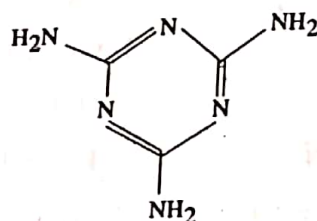
(18-VII)

It is also made from urea at 300°C and at 100 atm pressure :

$$6NH_2CONH_2 \longrightarrow (H_2NCN)_3 + 6NH_3 + 3CO_2$$
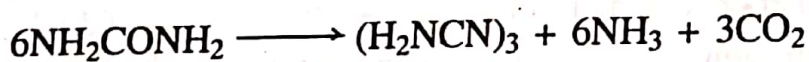
Melamine is used in plastics.

18.6.10. Silicones : These are some polymeric organosilicon compounds with carbon-silicon and silicon-oxygen bonds. Complete hydrolysis of silicon tetrachloride leads to polymeric SiO_2. But alkyl substituted chlorosilanes respond differently to hydrolysis. For
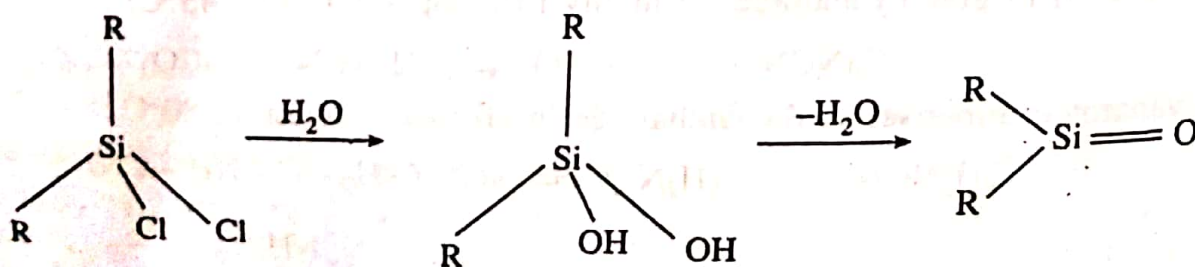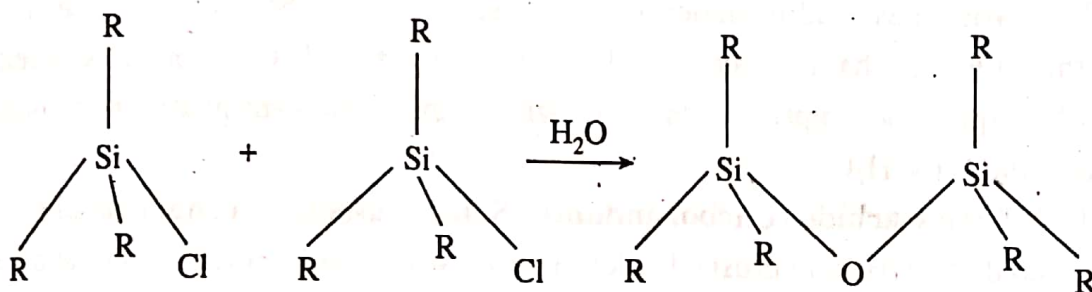
example, dialkyl dichlorosilanes do not give dialkyl silicon oxide but polymeric compounds called silicones (18-VIII) :
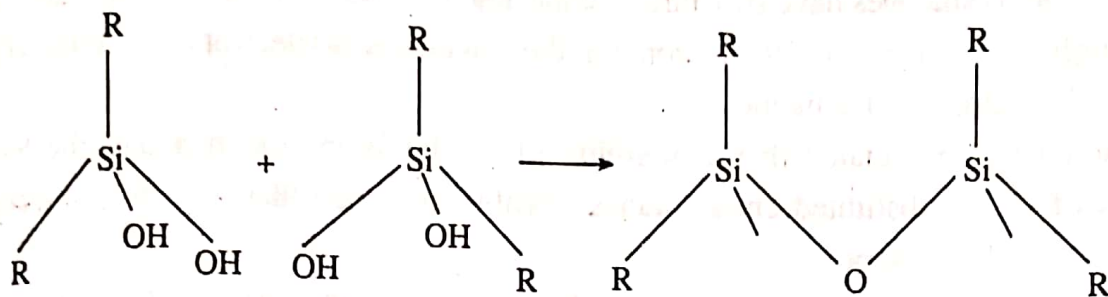

(18-VIII)

Trialkyl monochlorosilanes R_3SiCl produce hexaalkyl disiloxanes (18-IX) :

(18-IX)

Hydrolysis of alkyl trichlorosilanes, $RSiCl_3$, gives a complex cross-linked polymer (18-X). The degree of cross linking and the nature of the products depends not only on the substituents but also on the condition of hydrolysis. Polymers of varying molecular weights can be obtained by changing the reaction conditions. The intermediate, alkyl/aryl chlorosilanes, necessary for the manufacture of the above silicones have been obtanied by a variety of methods :
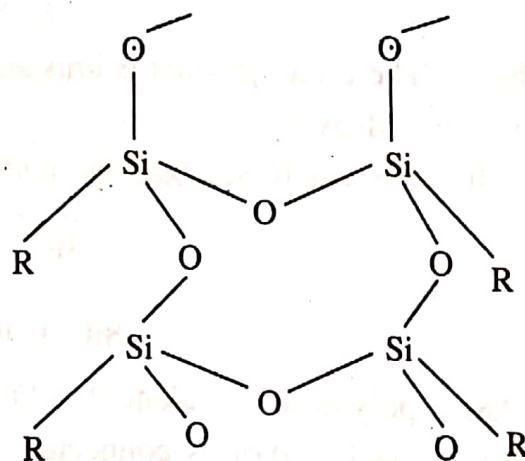
(1) Reaction of $SiCl_4$ with suitable Grignard reagents :

(18-X)

$$SiCl_4 + CH_3MgI \rightarrow SiCH_3Cl_3 \text{ (also } Si(CH_3)_2Cl_2 \text{ and } Si(CH_3)_3Cl) + MgClI$$
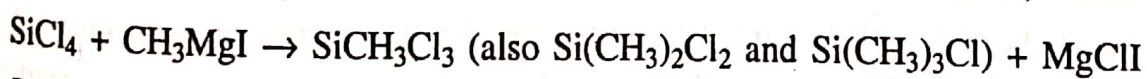
(2) Reaction of silicon and alkyl halides with zinc or aluminium which functions as halogen acceptors :

$$SiCl_4 + 3CH_3Cl + 2Al \rightarrow SiCH_3Cl_3 + (CH_3)_2AlCl + AlCl_3$$

(3) Reaction of methyl chloride with copper-activated silicon at 300°C :

$$CH_3Cl + Si(Cu) \rightarrow Si(CH_3)_nCl_{4-n} \ (n = 1 \text{ and } 2)$$