

density is  $1.50 \text{ g cm}^{-3}$

**Unique Character of Carbon.** Carbon with smallest atomic radius and lowest molar volume is most compact of all the elements in this group. It has highest melting and boiling points. It has the highest ionisation energy and is the most electronegative element in this group. Also because of the absence of  $d$  orbitals, it has least tendency to form complex compounds. Its maximum covalency remains 4.

Carbon can form multiple bonds, *i.e.*, double bonds and triple bonds, in a number of its compounds. The most remarkable property of carbon, however, lies in its property of catenation as a result of which it forms thousands of compounds in which carbon atoms are bonded to one another through covalent bonds.

**Comparison of Carbon with Silicon.** Carbon and silicon, the first two elements of this group, have a number of properties in common. Due to similar electronic configurations, they form similar hydrides (*e.g.*,  $\text{CH}_4$ ,  $\text{SiH}_4$  and  $\text{C}_2\text{H}_6$  and  $\text{Si}_2\text{H}_6$ ), similar halides (*e.g.*,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ), similar oxides (*e.g.*,  $\text{CO}_2$ ,  $\text{SiO}_2$ ) and similar oxyacids (*e.g.*,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SiO}_3$ ), etc. In spite of these similarities, the two elements and their compounds differ appreciably from one another in several respects. Most of these differences, though not all, arise from the following factors : 1. Difference in sizes of carbon and silicon atoms, carbon atom being much smaller than silicon atom. 2. Non-availability of  $d$  orbitals in carbon atom. 3. Carbon having high capacity for catenation, as pointed out above.

Some of the important differences between the two elements are summed up below :

1. Carbon is harder and has higher melting and boiling points than silicon.
2. Carbon in the form of graphite is a good conductor of electricity while silicon is a poor conductor of electricity.

3. Carbon, due to its small atomic size, can form pi bonds with oxygen involving  $p$  orbitals while silicon due to its large atomic size cannot do so.

4. Due to its high capacity for catenation, carbon forms thousands of compounds. Silicon has much lower capacity for catenation. The number of its compounds is, therefore, limited.

5. Carbon is an essential constituent of living organisms belonging to animal or vegetable kingdom. Silicon is an essential constituent of most of the non-living materials including rocks, hills, clays, soils, ores, etc.

The compounds of carbon and silicon also differ in several respects as illustrated below.

**1. Hydrides.** The hydrides of carbon are numerous (e.g.,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{CH}_3$  and a host of others). Many of these are highly stable. Silicon hydrides ( $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ , etc.) are only a few in number and are not as stable.

**2. Oxides.** Carbon forms two similar oxides,  $\text{CO}$  and  $\text{CO}_2$ , both being *gases* at ordinary temperatures. Silicon forms only one oxide,  $\text{SiO}_2$ , which is a *solid* with high melting and boiling points. The reason why  $\text{CO}_2$  is a gas while  $\text{SiO}_2$  is a highly stable solid has been discussed in details in a subsequent section in this chapter dealing with the **structure of silica**.

**3. Halides.** Carbon tetrachloride does not undergo hydrolysis in water. It also does not form addition compounds. Silicon tetrachloride, however, gets hydrolysed in water and forms addition compounds with ammonia. This is due to the presence of  $d$  orbitals in silicon. Carbon does not form dihalides while silicon does.

**4. Silicones.** Silicon is capable of forming cross-linked silicones through hydrolysis of its halides. These compounds are used as lubricants, water repellents and insulators, etc. No such compounds are formed by carbon.

## PROPERTIES OF ELEMENTS OF GROUP 14

**Properties of Carbon. Physical Properties.** Carbon exists in various allotropic forms, of which *diamond* and *graphite* are crystalline while *coal*, *wood charcoal*, *animal charcoal*, *lamp black*, *coke* and *gas carbon* are amorphous. The X-ray analysis has revealed, however, that the so-called amorphous carbons are in reality crystalline in structure. However, they consist of extremely fine crystals. These carbons are, therefore, termed as **microcrystalline carbons**. Diamond and graphite are, however, structurally very much different from each other. While diamond has a *three-dimensional tetrahedral structure*, graphite has a *two-dimensional layer structure*, as discussed below.

**Structure of diamond.** Diamond is a big *three-dimensional polymer* comprising of a large number of carbon atoms arranged *tetrahedrally* by utilising their  $sp^3$  hybrid orbitals. The structure is shown in Fig. 1.



The C – C bond distance is 1.54 Å. It will be seen that each carbon atom lies at the centre of a regular tetrahedron and is linked to four surrounding carbon atoms lying at the corners of the tetrahedron by strong covalent bonds through sharing of their valency electrons. The result is a very big, three-dimensional polymer. Due to high strength of covalent bonds holding numerous carbon atoms together, diamond is very hard and has high density. Since melting of diamond requires breaking of the strong covalent bonds, the melting point of diamond is unusually high, being close to 3500°C. Diamond is the purest form of carbon and is the hardest substance known. It has a very high refractive index (2.417) and a very high density (3.51 g cm<sup>-3</sup> at 25°C). It is transparent to X-rays and is a bad conductor of heat and electricity.

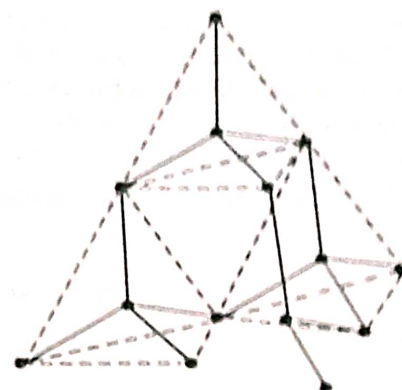


Fig. 1. Structure of diamond.

**Structure of graphite.** Graphite, unlike diamond, has a *two-dimensional* structure. In this case, only three of the four valency electrons of each carbon atom are involved in bonding. Thus, each carbon atom makes use of its three  $sp^2$  hybrid orbitals forming three covalent bonds with three other carbon atoms in the same plane (unlike the structure of diamond in which each carbon atom is linked to four other carbon atoms through  $sp^3$  hybrid bonds). Thus, the structure of graphite is two-dimensional sheet-like consisting of a number of benzene rings fused together (Fig. 2a), unlike that of diamond which is three-dimensional. The sheets or layers are held together by relatively weak van der Waals forces. The C – C covalent bond distance is 1.42 Å. The distance between the two successive layers is 3.36 Å (Fig. 2b). This large distance rules out the possibility of covalent bonding, i.e., the fourth valency electron remains unpaired or free. This free electron can easily move from one carbon atom to another under the influence of applied potential. This permits the passage of electricity through graphite and makes graphite a good conductor of electricity.

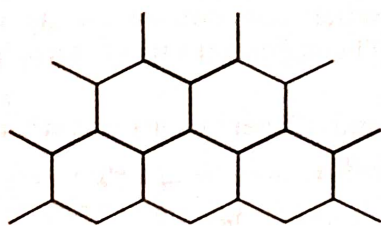
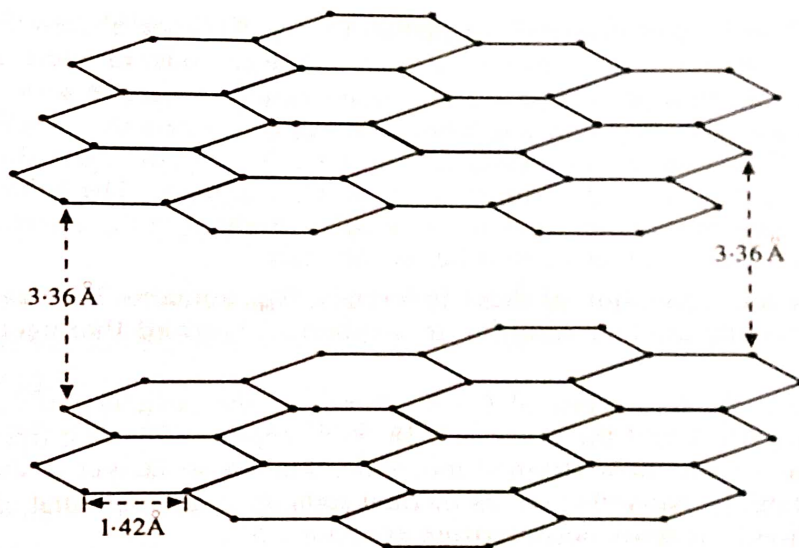


Fig. 2. (a) Hexagonal layer structure of graphite



(b) Bonding in graphite.

The above layer structure of graphite is less compact than that of diamond. Further, since the bonding between the layers involving only van der Waals forces is weak, these layers can slide over each other. This gives softness, greasiness and lubricating character to graphite.