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TOPIC:- Group 14
Physical properties
Allotropy of Carbon

Group 14

The elements in this group range from a non-metal, carbon to the metals tin and lead, with the intervening element – germanium showing semi metallic behaviour. Carbon has been known from pre history as the charcoal resulting from partial combustion of organic matter. Carbon is an essential constituent of all living matter. Silicon is the second most abundant element in the earth's crust; tools made of flint (a form of SiO_2) were used in the Stone Age. Tin and lead have also been known since ancient times Germanium was a "missing element" in Mendeleev's periodic table. He named this element as "ekasilicon" and predicted its properties that later matched with those of germanium. All the elements have an outer electronic configuration of ns^2 np^2 and some important physical constants are summarized in Table 7.

Table 7 : Physical properties of Group 14 elements

Property	C	Si	Ge	Sn	Pb
Electronic Configuration	$[He]2s^22p^2$	$[Ne]3s^23p^2$	$[Ar]3d^{10}$ $4s^24p^2$	$[Kr]4d^{10}$ $5s^25p^2$	$[Xe]4f^{14}$ $5d^{10}6s^26p^2$
Covalent radius (pm)	77	118	122	140	146
Ionization Energy (I) ($KJmol^{-1}$)	1086	786	762	709	716
Electronegativity	2.54	1.92	1.99	1.82	1.85
Melting Point (^0C)	4100	1420	945	232	327
Boiling Point (^0C)	Sublimes	3280	2850	2623	1751
M – M bond energy ($KJmol^{-1}$)	348	297	260	240	-

The general trends observed in size and ionization energy follow the same order as in group 13.

The main isotope of carbon present in the earth is ^{12}C (in the modern system of atomic mass this is taken as the standard), two other isotopes ^{13}C and ^{14}C are also known. ^{13}C NMR spectroscopy is common for characterization of organic compounds.

^{14}C is obtained from nitrogen in the atmosphere by thermal neutrons in presence of cosmic radiation.

$$^{14}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

The ^{14}C produced is oxidized to $^{14}CO_2$ which is radioactive and this alongwith non- radioactive CO_2 is incorporated into plants by photosynthesis. The ratio of ^{14}C to ^{12}C in a living plant is the same as that in the atmosphere. When the plant dies the amount of ^{14}C diminishes by radioactive decay and this loss is not compensated by assimilation of $^{14}CO_2$ from the atmosphere. The ratio of ^{14}C to ^{12}C decreases. The half-life of ^{14}C is 5730 years and by measuring the remaining amount of ^{14}C it is possible to know the age of the substance (i.e. time of its death). This is called "radiocarbon dating'.

Allotropy of Carbon

Until 1985, only two allotropes of carbon were known – diamond and graphite. Diamond is the hardest substance known, having a very rigid structure. Each carbon atom is sp^3 hybridized and linked to four other atoms. Graphite has a layer – structure in which weak van der Waal's forces hold individual layers of fused six membered rings together. The carbon atoms are sp^2 hybridized and out of four valence electrons, three are involved in σ -bond formation the fourth electron is involved in delocalized π-bonding. The layers slide over one another and the π electrons move within each layer making graphite a conductor of electricity and conferring lubricating properties. The structures of diamond and graphite are show in fig 12 and some physical properties in table 8.

Table 8 : Physical properties of Diamond and Graphite

Property	Diamond	Graphite
Density (gcm^{-3})	3.51	2.26
Electrical Resistivity (Ωm)	$1X\ 10^{11}$	$1.3X10^{-5}$
C-C distance (pm)	154.4	141.5 (Intra Layer) 335.4 (Inter Layer)

At room temperature graphite is thermodynamically more stable and can be converted to diamond at high pressure and temperature. Artificial diamonds are prepared from graphite.

A fascinating discovery was the synthesis of spheroid carbon-cage molecules called fullerenes. These were first prepared by evaporation of graphite using laser. A more practical method is to heat graphite in an electric are in an inert atmosphere (helium or argon). A sooty material so formed consists of C_{60} with smaller amounts of C_{70} and other fullerenes containing even number of carbon atoms. Unlike diamond and graphite fullerenes dissolve in organic solvents like toluene. C_{60} is the most stable fullerene containing twenty six- membered rings and twelve five-membered rings. The six- membered rings are fused to other six membered and five- membered rings while five- membered rings and connected to only six- membered rings. (Fig.12). Two types of bond lengths are noted, the C-C bond lengths at fusion of two six membered rings is 135.5 pm while the C-C distances at fusion of five and six membered rings is 146.7 pm. Thus there is greater π character in the bonds obtained by fusion of six membered rings.

The smallest known fullerene is C_{20} obtained from the hydrocarbon $C_{20}H_{20}$ by a two- step reaction. First, the hydrogens are replaced by bromine, this is followed by debromination. The Nobel Prize for Chemistry (1996) was shared by R.F. Curl, H. Kroto and R.E. Smalley for the discovery of fullerenes.

Silicon and germanium predominantly crystallize in diamond structure and both are semiconductors. Tin exists in a diamond form (α) and metallic form (β) while lead is metallic.

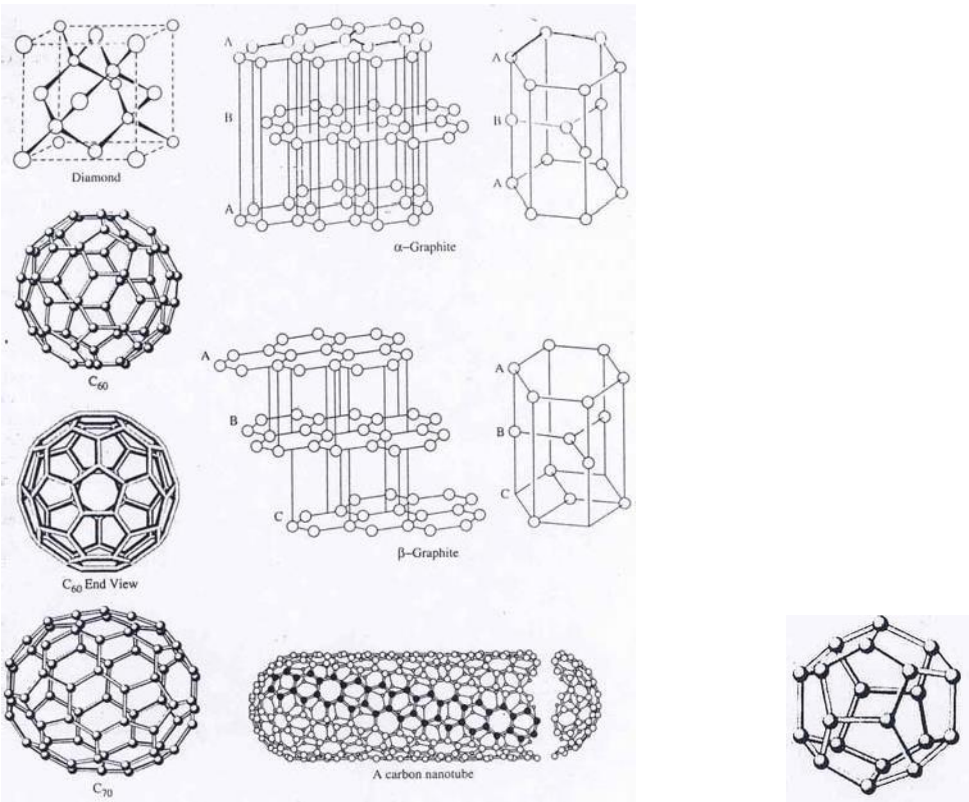

Fig. 12: Diamond, Graphite, Fullerenes