Chapter 5: Carbon and silicon

The elements of group IV_A: the crystallogens

Group of elements corresponding to the 14th column of the T.P, comprising 5 elements.

element	Z	Symbol	Oxidation degree	Natural form
Carbon	6	С	-4, +2, +4	nonmetal - black for graphite
				nonmetal - transparent for diamond
Silicon	14	Si	+1 → +4	metalloid - gray
Germanium	32	Ge	+2, +4	metalloid - gray-white
Tin	50	Sn	+2, +4	metal - bright white (amphoteric)
Lead	82	Pb	+2, +4	bright blue-white metal

- The crystallogenic family, also called the carbon family, is very heterogeneous because it is made up of non-metals (C), metalloids (Si and Ge) and metals (Sn and Pb).
- Electronic configuration (valence shell): ns2np2

Carbon

Carbon at the head of the group \rightarrow properties different from those of the other elements: non-metal.

Carbon: the oldest known and used fossil fuel. It is the central element of all organic chemistry: that of the inert world (oil, plastics, etc.) or that of the living world (plants and animals).

Carbon Isotopes: Carbon has two stable isotopes in nature:

 12 C (abundance = 98.93%) and 13 C (abundance = 1.07%).

R: ¹²C was chosen as the single reference nuclide for atomic mass 12.

¹⁴C and ¹¹C are radioisotopes.

Industrial preparation:

- Under the influence of an intense electric current: Coke bars \rightarrow C (graphite)
- From oil: cracking of hydrocarbons: $CH_4(g) \rightarrow C(s) + 2H_2(g)$

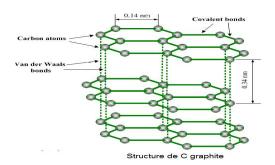
☐ For DIAMOND:

- o Rare natural sources, but prepared at high pressure and temperature or by thermal decomposition of CH4 which gives a deposit of diamond and graphite. The latter reacts on H2 to give volatile hydrocarbons → deposit enriched in diamond.
 - o Conversion of graphite to diamond at high pressure: C (graphite)→C (diamond)

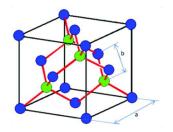
Structures and properties

carbon exists in three crystalline forms:

a) C graphite (the most stable form under normal conditions): black solid, soft, C sp² sheets, hexagonal network (structure), electrically conductive (electrons delocalized in the π network), used in liquid chromatography as a separation substrate.



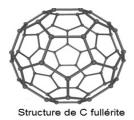
b) C diamond: rigid solid (the hardest known), transparent, face-centered cubic (f.c.c.) lattice, best conductor of heat (five times more than Cu), ideal abrasive (can scratch all other substances and quickly evacuate heat caused by friction), insulator (electrons located in the σ bond).



c) C fullerite: Recently identified (in 1985), football shape, molecular structure.

Fullerene: family of molecules identical to C60 containing more than 60 atoms.

More abundant molecule than graphite and diamond.



- R: 1- Cgr and Cdia are insoluble in liquid solvents while Cfull of molecular structure is soluble in benzene for example
 - 1- Study of fullerenes \rightarrow new forms of $C\rightarrow$: nanotubes, conductive and resistant fibers.

d) Other microcrystalline and amorphous forms:

☐ Carbon black: small graphite crystals. Black is obtained by heating gaseous hydrocarbons to 1000°C, used as printing ink and as a pigment to reinforce rubber.

$$CH4(g) + O2(g) \rightarrow C(s) + 2H2O(g)$$

☐ Activated carbon (or activated charcoal): obtained by heating charcoal in the absence of air, used as a reducing agent.

Carbon oxides:

a) Carbon monoxide CO: Carbon monoxide is a gas (under normal conditions of pressure and temperature).

Physicochemical properties of CO: colorless, odorless, flammable gas (burns in air with a blue flame giving CO₂), very toxic, slightly soluble in water, quite difficult to liquefy. Melting point: -205.1 °C, boiling point: -191.5 °C.

Preparation and use:

- industrially, CO can be obtained by the reduction of CO_2 or $H_2O(g)$ by carbon:

$$C + CO_2 \leftrightarrow 2CO$$

- in the laboratory, CO can be obtained by dehydration of formic acid with H₂SO₄.

$$HCOOH \longrightarrow CO + H_2O$$

- The synthesis of methanol, one of the most important industrial raw materials for synthesis, illustrates this type of process:

$$CO + 2H_2 \rightarrow CH_3OH$$

b) Carbon dioxide CO₂: also called carbonic gas (under normal conditions of temperature and pressure). It is present naturally in the atmosphere (0.03- 0.06% by volume). the molecule having a linear structure of the form O=C=O.

Physicochemical properties of CO₂: colorless, odorless gas, with a pungent taste, heavier than air, is not toxic and does not ignite. Its melting point is $T^{\circ}f = -56.6 \,^{\circ}C$ at 5.185 bar.

Preparation and use:

CO₂ can be obtained by various techniques:

- Complete combustion of organic matter:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
 $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

- Action of acids on carbonates:

$$CaCO_3$$
 (aq) + $2HCl(aq) \rightarrow CO_2$ (g)+ $CaCl_2$ (aq) + $H_2O(l)$

- decomposition of carbonates = commercial source of CaO:

$$CaCO_3(s) \rightarrow 2CO_2(g) + CaO(s)$$

Carbon dioxide has many uses. It is mainly used in the food industry (preservation and carbonation of beverages, cooling and freezing of foodstuffs).