Group 14 – Carbon Family

① C 6
Si 14
Ge 32
Sn 50
Pb 82

→ Carbon is essential constituent of all living organisms. → 17th most abundant.

→ Isotope ^{12}C, ^{13}C (Stable), ^{14}C (Radioactive, $t_{1/2}$ = 5770 years) used for radiocarbon dating.

→ Si is second abundant (27.7%) element on the earth's crust.

→ Present in form of silica and silicates. Used in ceramics, glass and cement.

→ Ge exists in traces.

→ Tin occurs only as Cassiterite (SnO_2)

Lead ⇒ Galena (PbS)

→ Ultrapure form of Ge and Si used in transistors and semiconductor devices.

② EC :- $ns^2 np^2$

③ Covalent Radius

C Si Ge Sn Pb
77 118 122 140 146

Small increase

Due to presence of completely filled d- orbitals and f- orbitals

④ IE :-

	C	Si	Ge	Sn	Pb
ΔH_i	1086	786	761	708	715

Slight dec. — Inc. ★

Due to poor shielding of d and f- orbitals and dec in size of atom.

⑤ EN :-

More EN than Group 13.

C	Si	Ge	Sn	Pb
2.5	1.8	1.8	1.8	1.9

Almost same

⑥ Physical Properties

→ All solids

→ C, Si → Non-Metals
Ge → Metalloid
Sn, Pb → Soft metal, with low MP.

→ BP and MP are much higher than Group 13.

⑦ Chemical Properties

Oxidation States :-

→ Common OS +4 and +2

→ Carbon also exhibit –ve OS

→ Compounds in +4 OS are pure covalent [Sum of first four IE is very high].

→ Heavier elements show +2 OS

Tendency :- Ge < Sn < Pb

Due to inability of ns^2 e⁻ to participate in bond formation.

→ C, Si → Mostly +4 OS
Ge → Stable +4 OS, few comp. in +2 OS.
Sn → +4, +2
★ Sn in +2 is reducing agent.
Pb → +2 OS stable
★ +4 strong OA

⇒ Electron precise compounds

Carbon cannot expand its covalence beyond +4.

⇒ Other elements have vacant d- orbital → can expand covalence.

↳ Halides undergo hydrolysis

→ form complexes [SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$]

↳ Hybridisation sp^3d^2

Reactivity with :-

(i) Oxygen.

→ when heated in O_2 form oxide

→ Type MO, MO_2.

→ SiO only exist at high T.

→ Oxide in higher OS are more acidic.

→ CO_2, SiO_2, GeO_2 } Acidic

SnO_2, PbO_2 } Amphoteric.

→ CO → neutral
GeO → acidic
SnO, PbO → Amphoteric

(ii) Water

→ C, Si, Ge ⇒ Not affected by water.

→ $Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$ (steam)

→ Pb is unaffected by H_2O because of a protective oxide film formation.

(iii) Halogen

→ form MX_2, MX_4.

→ except C, all other member react directly with X_2.

→ MX_4 are covalent (most) ⇒ sp^3, tetrahedral

→ SnF_4 and PbF_4 are ionic.

→ PbI_4 does not exist.

cause Pb-I initially formed does not release enough energy to unpair $6s^2$ e⁻ to make available 4 unpaired e⁻ around Pb atom

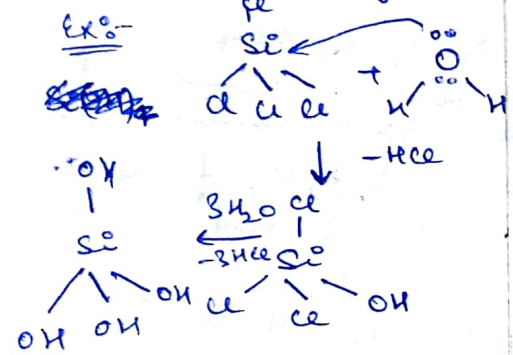
→ Higher elements Ge to Pb form MX_2

Stability of MX_2 & MX_4 inc. ↓ group.

→ $GeX_4 > GeX_2$ } stable
$PbX_2 > PbX_4$ }

→ Except CCl_4, others MX_4 are hydrolysed by water.

Ex:-



* $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not.

→ 6 Cl^- cannot be accommodated around Si^{4+}

→ Interaction b/w lone pair of Cl^- and Si^{4+} is not very strong.

(8) Anomalous Behaviour of Carbon :-

(i) Small size
(ii) High EN
(iii) High IE
(iv) Unavailibity of d- orbitals.

=> Carbon has unique ability to form $p\pi$-$p\pi$ multiple bonds with itself and with other small size and high EN elements.

Ex: C=C, C≡C, C=O, C=S, C≡N

→ Heavier elements do not form $p\pi$-$p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

→ Carbon ⇒ tendency to link and form chains / rings.
↳ Catenation.

↓
Because C-C bonds are very strong.

↓ group, size ↑, EN ↓
Catenation ↓

C >> Si > Ge ≃ Sn

(9) Allotropes

Crystalline ↔ Amorphous

↳ Due to ability to form $p\pi$-$p\pi$ bond formation and catenation.

Diamond, Graphite } → Crystalline

Diamond

→ Crystalline lattice.
→ Each C → sp^3 hybridised.
→ C-C BL → 154 pm
→ 3D structure
→ Dir. Covalent bonds are present.
→ Hardest substance.
[diff. to breakdown extended covalent bond].
→ Used as abrasive for sharpening hard tools, in making dyes, in manufacture of tungsten filaments.

Graphite

→ Layered structure
→ Held by Van der Waals forces.
→ Dist. b/w two layers 340 pm.
→ C-C BL → 141.5 pm
↳ sp^2 hybridisation → 3σ, 1π

→ e⁻ delocalised over the whole sheet.
↳ mobile → conducts electricity.

→ Very soft and slippery
Dry lubricant in machines which run at high T where oil cannot be used.

Fullerenes

→ Made by heating graphite in electric arc with inert gas (He, Ne).
→ Sooty material formed by condensation of vaporised C atoms consists C_{60} (mainly) with small quantity C_{70} and traces of fullerene with even C atoms upto 270 or above.
→ Only pure form of C because they have smooth structure without having dangling bonds.
→ Cage like mol., C_{60} have soccer like shape, called Buckminsterfullerene.
↳ 20 6M-rings
12 5M-ring
↳ fuse with 6 or 8 M ring
↓ fuse with only 6M ring.
→ 3σ bonds, 4th e⁻ delocalised in molecular orbitals. which gives aromatic character to it.
→ Single Bond → 143.5 pm
Double Bond → 138.3 pm
Spherical fullerenes ↳ called buckyballs.

* Thermodynamically, graphite is most stable.

$\Rightarrow \Delta H^\circ_{f(graphite)} = 0$

$(\Delta H^\circ_f)_{Diamond} = 1.90$ kJ/mol

$(\Delta H^\circ_f)_{fullerene} = 38.1$ kJ/mol

=> Carbon black, coke, charcoal → all impure forms of graphite / fullerenes.

- burning hydrocarbons → limited air
- burning wood / coal (charcoal) (coke) in absence of air.

(10) Uses :-

- → Graphite fibres embedded in plastic materials [form high strength, lightweight composites]
- → Composites used in tennis rackets, fishing rods, aircrafts, canoes.
- → Graphite => Electrodes
- → Crucibles are inert to (dil. acids and alkalies. → made of graphite.
- → Activated charcoal (porous) → adsorb poisonous gases, remove organic contaminators from water, control odour in airconditioning systems.
- → Carbon black => black ink and filler in automobile tyres.
- → Coke is used as fuel, RA in metallurgy.
- → Diamond => precious stone (Measured in 1 carat, 1 carat = 200 mg)

(11) Carbon Monoxide (CO) :-

→ $2C + O_2 \longrightarrow 2CO$ (limited supply)

→ on small scale,

$HCOOH \xrightarrow[373K]{Conc.\ H_2SO_4} CO + H_2O$

→ Commercial Scale,

$C + H_2O \xrightarrow{473K-1273K} CO + H_2$ (Steam)

Water gas / Synthesis gas

$C + O_2 + N_2 \xrightarrow{1273K} CO + N_2$

Producer gas

Important Industrial fuels.

→ colourless, odourless.

→ water insoluble.

→ Powerful RA. Reduce all MO except that alkali, alkaline earth metals, Al and a few transition metals

Ex :-

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$ZnO + CO \rightarrow Zn + CO_2$

→ $:C \equiv O:$ Act as Donor

form metal carbonyls.

→ forms stable complex with haemoglobin [300 more than O-H complex].

Poisonous

(12) Carbon Dioxide

→ $C + O_2 \xrightarrow{\Delta} CO_2$

$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$

→ Laboratory,

$CaCO_3 + HCl \rightarrow CaCl_2 + CO_2 + H_2O$

→ on commercial scale, obtained by heating limestone.

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$.

→ Colourless, odourless

→ low solubility in water

immense biochemical and geochemical imp.

→ With H_2O, forms carbonic acid [Weak dibasic acid]

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

H_2CO_3 / HCO_3^- buffer sys. maintains pH of blood b/w 7.26 – 7.42

→ Being acidic in nature, forms metal carbonates with alkalies.

→ In atmosphere, 0.03% (normally) by vol. Used in photosynthesis.

$6CO_2 + 12H_2O \xrightarrow[\text{chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$

→ Not poisonous.

→ Inc. combustion of fuels and decomposition of $CaCO_3$ in cement industry inc. CO_2 content which leads to green house effect and raise temp. of the atmosphere.

CO_2 in solid form
↓
dry ice

formed by allowing CO_2 (liq.) to expand rapidly

→ Used as :-

→ Refrigerant for ice-cream and frozen food.

→ Gaseous CO_2 is extensively used to carbonate soft drinks.

→ CO_2 ⇒ Heavy, used in fire extinguishers
→ non-supporter of combustion.

→ CO_2 is used in manufacture of urea.

→

$$:\overset{-}{\ddot{O}}-C\equiv\overset{+}{O}: \leftrightarrow :\ddot{O}=C=\ddot{O}: \leftrightarrow :\overset{+}{O}\equiv C-\overset{-}{\ddot{O}}:$$

sp hybridised

BL = 115 pm, no dipole moment

C ⇒ form two pπ-pπ bonds and two σ bonds.

(12) Silicon Dioxide (SiO_2) :-

→ 95% Earth crust ⇒ silica and silicates.

→ Commonly silica.

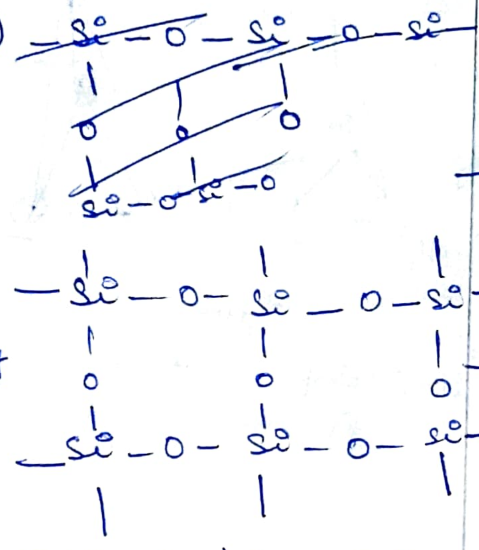
→ Occurs in many crystallographic forms —

→ Quartz
→ Cristobalite
→ Tridymite

} → Crystalline forms.

Interconvertible at suitable temp.

→ SiO_2 ⇒ covalent, 3D network solid



Entire crystal ⇒ giant molecule with 8M rings with alternate Si, O atoms.

→ In normal form, SiO_2 is non-reactive because of high Si–O bond enthalpy.

→ Resists attack by halogen, dihydrogen, most acids and metals even at elevated T.

But HF and NaOH react as follows :-

$$SiO_2 + HF \rightarrow SiF_4 + H_2O$$

$$SiO_2 + NaOH \rightarrow Na_2SiO_3 + H_2O$$

→ Quartz ⇒ Piezoelectric material.
↓
Made possible to develop extremely accurate clocks, television broadcasting, modern radio, mobile radio communications.

→ Silica gel is used as an drying agent and as a support for chromatographic materials and catalysts.

→ Kieselghur
Amorphous form
Used in filtration plants

(13) Silicones :-

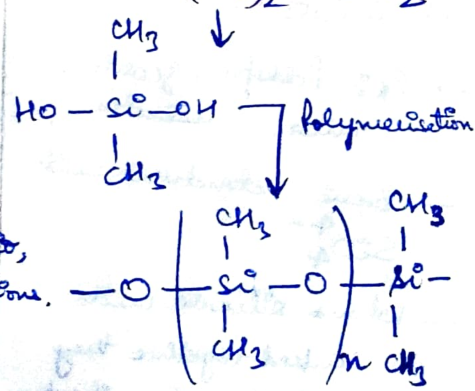
→ Organosilicon polymers $-(R_2SiO)-$ as repeating units.

→ Starting materials for manufacture are alkyl / aryl substituted silicon chlorides $R_nSiCl_{(4-n)}$.

→ When CH_3Cl reacts with Si in presence of Cu at 573K, following chlorosilanes of formula $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl, Me_4Si (small amount) are formed.

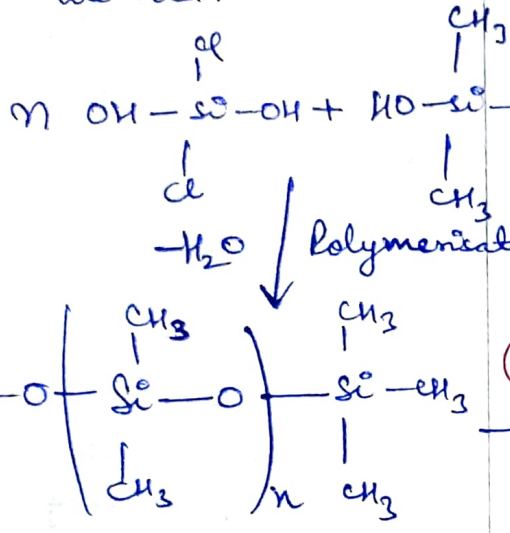
→ Hydrolysis of Me_2SiCl_2 followed by condensation polymerisation yields straight chain polymers.

$$CH_3Cl + Si \xrightarrow[573K]{Cu\ Powder} (CH_3)_2SiCl_2 \xrightarrow{H_2O} (CH_3)_2Si(OH)_2$$



Silicone

⇒ Chain length of polymer can be controlled using $(CH_3)_3SiCl$ which blocks the end.



Silicone

→ Water repelling (non-polar alkyl groups)

→ High thermal stability, high dielectric strength, resistance to oxidn and chemicals.

→ Used as sealant, greases, electrical insulators and for water proofing of fabrics.

Being biocompatible, used in surgical / cosmetic parts.

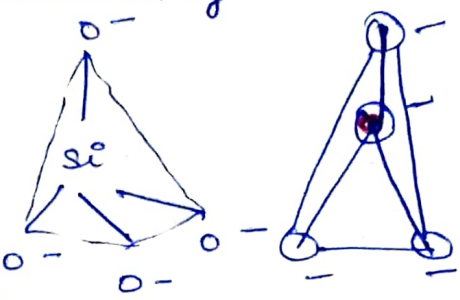
(14) Silicates :-

→ Ex :- feldspar, zeolites, mica, asbestos.

→ basic structural unit SiO_4^{4-}

→ When silicate units are linked together they form chain, ring, sheet or 3-D structures.

→ Negative charge on silicates is neutralised by metal cation



O → oxygen • → Si

→ Imp. silicates are :- glass and cement.

(15) Zeolites :-

→ When Al atoms replace some Si atoms in SiO_2 struct, new struct. aluminosilicates is formed.

→ Negative charge is balanced by Na^+, K^+ or Ca^{2+}.

→ Ex :- Feldspar, Zeolites

→ Zeolites ⇒ Used in cracking of hydrocarbons [petrochemical industry] and isomerisation.

Ex :- ZSM-5 → Used to convert alcohol directly into gasoline.

⇒ Hydrated zeolites are used as ion exchangers in softening of hard water.

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① BF_3 on hydrolysis give $HBF_4^- + B(OH)_3$

② SF_6 is inert towards hydrolysis.

↓

Ineert ⇒ Due to steric hindrance of sulphur atoms.

SF_6 does not react with molten Na (Below its BP) but reacts exothermically with Li.

③ PbO_2 → Amphoteric

Part of lead storage battery.

④ $NH_3 + H_2O + CO_2$

↓

$(NH_4)_2CO_3$

$(NH_4)_2CO_3 + H_2O + CO_2$

↓

NH_4HCO_3

$NH_4HCO_3 + NaCl$

↓

$NH_4Cl + NaHCO_3$

⑤ TlI_3 (isomorphous to CsF_3)

Metal has +1 OS.

due to inert pair effect.