Group - 14 (Carbon Family)

* Members :- C, Si, Ge, Sn, Pb

* Anamalous behaviour of carbon :- Due to the high E.N, small size, high I.E, no d-orbitals. It shows catenation property

* Allotropes of carbon :-

(a) Diamond :- Crystalline lattice, sp^3 hybridisation, 3D network of carbon atoms, directional covalent bonds are present, hardest natural substance on earth

(b) Graphite :- Layered structure, Vanderwall's force between the two layers, sp^2 hybridisation, one free e^-, thermo-dynamically more stable than diamond, good conductor of electricity

(c) Fullerenes :- Smooth structure, 20 six membered rings, 12 five membered rings, sp^2 hybridisation. eg.- C_{60} molecule.

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* Carbon Monoxide (CO) :-

(a) Preparation :- (i) $C_{(s)} + CO_2(g) \longrightarrow 2CO(g)$

(ii) $H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{\Delta} CO(g) + H_2O$

(iii) $HO-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{\Delta} H_2O + CO + CO_2$

(iv) $C(s) + H_2O(g) \xrightarrow{\Delta} CO(g) + H_2(g)$ [Water gas]

$C(s) + O_2(g) + 4N_2(g) \xrightarrow{\Delta} 2CO + 4N_2(g)$ [Producer gas]

(v) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \xrightarrow{\Delta} K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$

(b) Properties :- (i) Colourless, odourless gas; burns with a blue flame, neutral oxide, toxic, forms carboxyhaemoglobin with blood which can lead to death.

(ii) CO is a powerful reducing agent in the extraction of Fe and Ni.

$Fe_2O_3(s) + CO(g) \longrightarrow 2Fe(s) + 2CO_2(g)$

$NiO(s) + CO(g) \longrightarrow Ni(s) + CO_2(g)$

(iii) Mond's process :- $Ni(s) + 4CO(g) \xrightarrow{28^\circ C} Ni(CO)_4 \xrightarrow{180^\circ C} Ni + 4CO$

(iv) $CO + Cl_2 \longrightarrow COCl_2$ (Phosgene)

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* Carbon dioxide (CO_2) :-

$CO_3^{-2}(aq.) + 2H^+(aq.) \longrightarrow CO_2(g) + H_2O(l)$

(i) Colourless, odourless gas; used in fire extinguishers.

(ii) H_2CO_3/HCO_3^- is a buffer solution

(iii) Lime Water Test :- $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3(s) + H_2O$

$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2(aq.)$

* Carbon suboxide (C_3O_2):-

($O=C=C=C=O$)

(i) $CH_2(COOH)_2 + P_4O_{10} \longrightarrow 3\,C_3O_2 + 4\,H_5PO_4$

[Malonic acid]

(ii) $C_3O_2 \xrightarrow{\Delta} CO_2 + 2C$

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* Carbides :-

(a) Ionic carbides:-

(i) Methanides:- (C^{4-}). It gives methane on hydrolysis.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(ii) Acetylides :- (C_2^{-2}) gives acetylene on hydrolysis.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_2(C_2)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3\,C_2H_2$$

(iii) Allylides :- (C_3^{-4}) gives propyne on hydrolysis.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3-C\equiv CH$$

(b) Covalent carbides :-

CH_4, CO_2, CS_2, SiC, B_4C etc.

(c) Interstitial carbides :- These are formed by transition metals; carbon atoms occupy octahedral voids, very hard in nature ; they have high M.P., conduct electricity.
eg.- $-\overset{\oplus}{N}\equiv C^{\ominus}$

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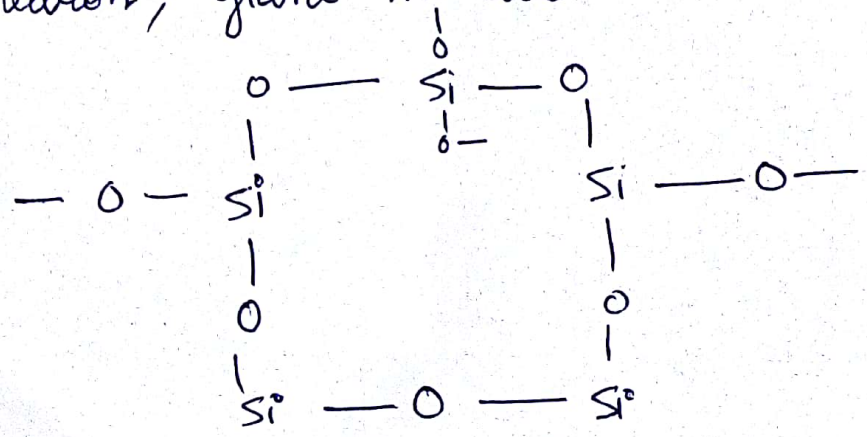
* Silicon (Si°) :-

$$SiO_2 + 2Mg \xrightarrow{\Delta} 2MgO + Si^{\circ}$$

* Silicon Dioxide (SiO_2) :-

(a) Silica is a covalent, 3D network solid.

(b) Each Si atom is tetrahedrally bonded to the four 'O' atoms ; each corner is shared by another tetrahedron ; giant molecule with 8-membered rings.



(c) $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

* **Silicates** :- Co-ordination no. of 'Si' is four; sp^3 hyb.

(a) Orthosilicates :- Discrete $[SiO_4]^{-4}$ units; no sharing of corners with other atoms.
eg.- $Zr SiO_4$, $Mg_2 SiO_4$, $Zn_2 SiO_4$.

(b) Pyrosilicates :- $[Si_2O_7]^{-6}$ units; 2 tetrahedral units share 'one' corner oxygen atom
eg.- $Sc_2 Si_2O_7$

(c) Cyclic Silicates :- $[SiO_3]_n^{2n-}$ unit, two oxygen atoms per tetrahedron are shared; eg.- Emerald.

(d) Chain silicates :- Pyroxenes :- Simple chain $(SiO_3)_n^{2n-}$
Amphibales :- Double chain $(Si_4O_{11})_n^{6n-}$.

(e) 2-D sheet silicates :- 3 oxygen atoms per tetrahedron are shared. $(Si_2O_5)_n^{2n-}$ unit.

(f) 3-D sheet silicates :- All four oxygen atoms are shared. SiO_4^{4-} unit.

Trick :- Decrease the oxygen atom by 0.5 and charge by 1 on going bottom.

Remember :- Amphibales gen. formula:
$(Si_4O_{11})^{6-}$

* Silicate	No. of 'O' atoms shared per unit	Gen. Formula
Ortho	0	SiO_4^{-4}
Pyro	1	$(SiO_{3.5})^{-3}$
Cyclic / Single chain	2	$(SiO_3)^{-2}$
2-D	3	$(SiO_{2.5})^{-}$
3-D	4	SiO_2

* Silicones :- (i) Synthetic organosilicon compounds having R_2SiO units held by $Si-O-Si$ linkages.

(ii) General formula:- $[R_2(SiO)]_n$

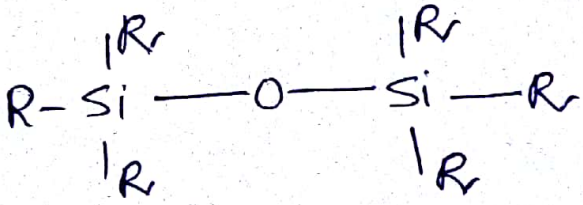
(iii) Silicones are ~~held~~ formed by alkyl and aryl structures (substituted chlorosilanes) and their subsequent polymerisation.

$$RCl + Si^{\circ} \xrightarrow[300^{\circ}C]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$$

(a) Silicones from R_3SiCl :-

$$R_3SiCl + H_2O \longrightarrow R_3Si(OH)$$

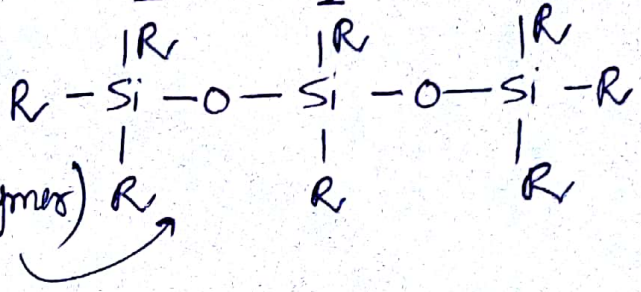
$$2R_3SiOH \xrightarrow{\text{condensation}}$$



(linear polymer)

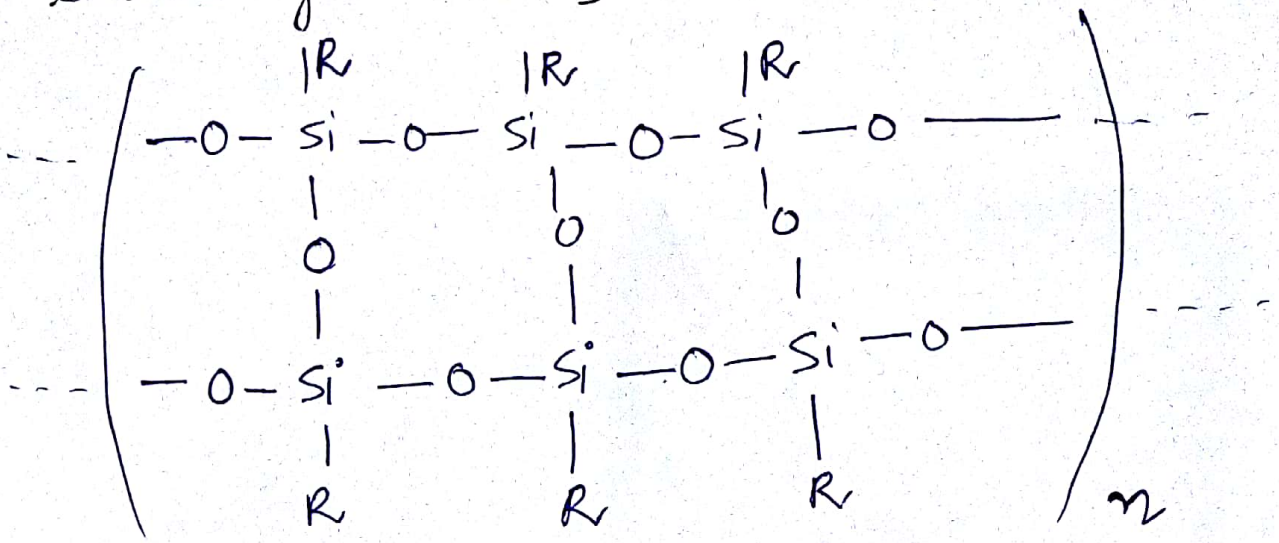
(b) Silicones from R_2SiCl_2 :-

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2$$

$R_2Si(OH)_2 \xrightarrow{\text{Polymerise}}$ 

(long chain polymer)

(c) Silicones from $RSiCl_3$:-



cross-linked polymer.

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* Litharge (PbO) :-

$$2Pb + O_2 \xrightarrow{\Delta} 2PbO \text{ (Amphoteric oxide)}$$

* Lead oxide (PbO_2) :-

(i) $PbO + NaOCl \xrightarrow{\Delta} PbO_2 + NaCl$

(ii) $Pb_3O_4 + 4HNO_3 (dil.) \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

↳ Chocolate brown (solid)

(iii) $2PbO_2 \xrightarrow{\Delta} 2PbO + O_2$

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(iv) PbO_2 is an oxidising agent. ($Pb^{+4} > Pb^{+2}$) → O.A.

(v) $PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + \frac{1}{2}O_2 + H_2O$

✱ Red lead (Pb_3O_4) :-

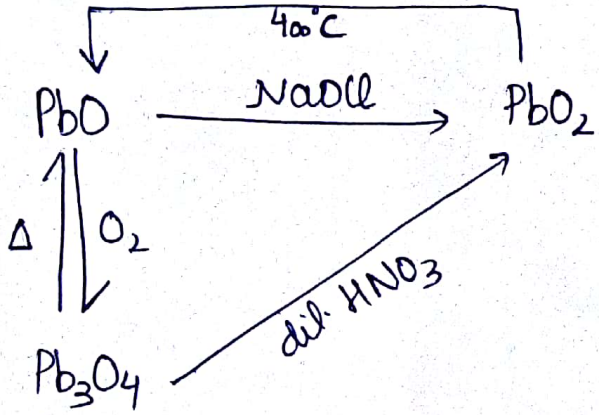
(i) $6PbO + O_2 \xrightarrow{\Delta} 2Pb_3O_4$ (Red powder)

(ii) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 \downarrow + 6H_2O$

(iii) $Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2\uparrow$

(iv) $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2\uparrow$

(v) $2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2\uparrow$



* PbO_2 } $\xrightarrow{H_2SO_4}$ $PbSO_4 + O_2\uparrow$
  Pb_3O_4 } $\xrightarrow{HCl}$ $PbCl_2 + Cl_2\uparrow$

* $PbO_2 \xrightarrow{HNO_3} Pb(NO_3)_2 + O_2\uparrow$

* $Pb_3O_4 \xrightarrow{HNO_3}$ No oxygen.