

Class - B. Sc. part-III (Hons)

Subject - Chemistry

Paper - V<sup>th</sup>

Group - C

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## INORGANIC CHAINS, RINGS, CAGES AND CLUSTERS

Catenation — The properties of self linking of atoms of an element to form straight or branched chains and ring of different size by covalent bond with each other is known as catenation. All the elements of group 14 i.e. C, Si, Ge, Sn and Pb have a tendency to link with each other and thus form a long chain of identical atom.

The tendency of an element M towards catenation is related with the magnitude of M-M bond energy. Greater is the magnitude of M-M bond energy, greater is the instability associated with M-M bond and hence greater will be the tendency of M atom to show the property of catenation. Example — C since the value of bond energies of

$$C-C = 348 \text{ kJ/mole}$$

$$Si-Si = 222 \text{ kJ/mole}$$

$$Ge-Ge = 167 \text{ kJ/mole}$$

$$Sn-Sn = 155 \text{ kJ/mole}$$

Here the bond energies decrease from carbon to tin. Bond energy of C-C is maximum

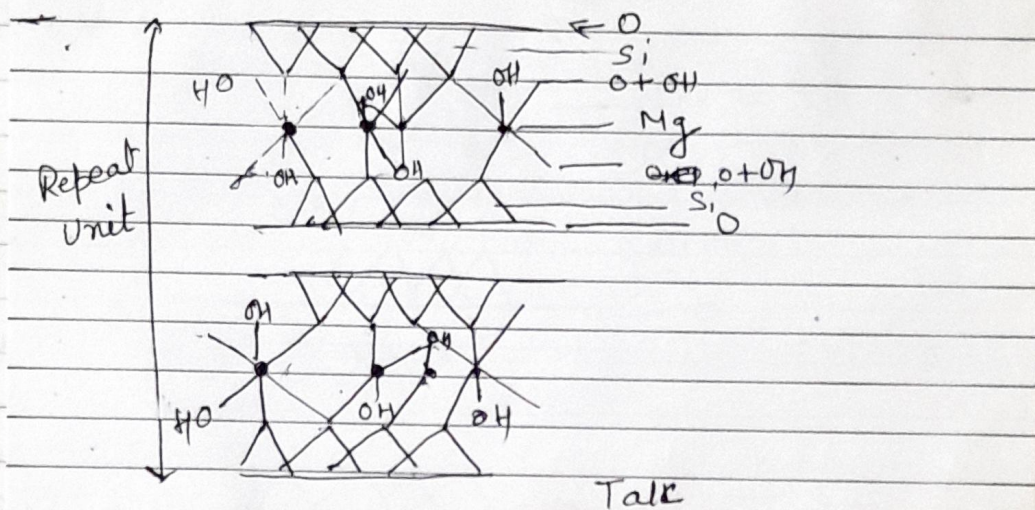
hence C-atom shows maximum tendency for catenation. Carbon atom by uniting with other C-atom can form long C-C chain of any length. These chain may be straight chains, branched chains and cyclic chains. C-C are highly stable in the compounds containing C-C long chains. The property of catenation also shown by Si, Ge and Sn. The property decreases as the value of M-M bond energies decreases from carbon to tin as we moving down the group. The small atomic size of carbon also favour to form long linking chain. Thus it is easy to prepare compounds containing C-C chain upto twenty carbon atom, while Sn and Ge it is not possible to extend the Si-Si or Ge-Ge chain beyond six units where as for Sn and Pb it is not possible to extend the Sn-Sn or Pb-Pb chain even beyond two units.

Carbon form a number of catenated halides, the best known being Teflon or Polytetrafluoroethylene. The polymers formed have chain length of several hundred carbon atom.

Silicon forms  $(SiF_2)_n$  and  $(SiCl_2)_n$  polymers, which decompose on heating into low molecular weight polymers of formula  $Si_n X_{2n+2}$ , the longest chains known are  $Si_6 F_{14}$ ,  $Si_{16} F_{34}$  and  $Si_4 Br_{10}$ . Germanium forms the dimer  $Ge_2 Cl_6$  but Sn and Pb do not form any

catenated halides.

**INTERCALATION CHEMISTRY** — Intercalation compounds consist of layers (sandwiches) of different chemical species. Intercalation compounds has system in which atoms, ions or molecules has inserted between layers of the host material. For example talc and micas form layered structure with ions between the silicate sheets.

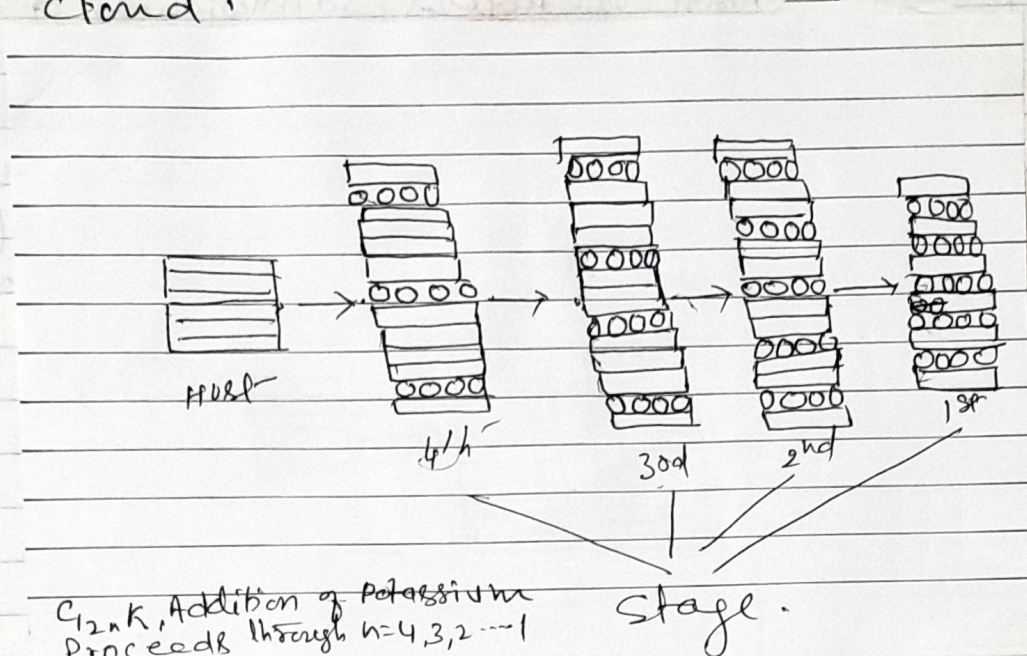


Another example sodium beta alumina where the sodium ions are free to move between the spinel layer. The sodium ions can be replaced by any +1 cations such as  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$  etc. The conductivity of these materials varies with the size of the ions mainly between the fixed distance (Al-O-Al) layers.

Graphite is the simplest layered structure. Many substances can be intercalated between the layers of graphite. The

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potassium ion nests within the hexagonal net carbon net and there is a weak complexing to the carbon  $\pi$  electron cloud.



**HETEROPOLY ANIONS** — Heteropoly anions where two or more different types of anion condensed together — for example molybdate<sup>-</sup> or tungstate<sup>-</sup> groups with phosphate, silicate or borate groups. Heteropoly anions are formed if molybdate or tungstate solution is acidified in the presence of phosphate, silicate or metal ions. The second anion provides a centre round which the  $MoO_6$  or  $WO_6$  octahedra condense, by sharing oxygen atoms with other octahedra and with the central group. The central groups are often oxyanions such as  $PO_4^{3-}$ ,  $SiO_4^{4-}$  and  $BO_3^{3-}$  but other elements including Al, Ge, Sn, As, Sb, Se, Te, I and many

of the transition elements will serve as the second group. The ratio of  $MoO_6$  or  $WO_6$  octahedra to P, Si, B is usually 12:1, 9:1 or 6:1. Between 35 and 40 heteropoly hetero atoms are known to form heteropoly anions and their corresponding acid