

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

Subject - Chemistry

Paper - V1th

Group - C

Dr. Kumud Kumari
H.D. Jain college, Agra.

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 of with each other is known as catenation. All the elements of group 14 have i.e C, Si, Ge, Sn ~~and~~ P 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 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 decreases from carbon to tin. Bond energy of C-C is maximum

[2]

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 decrease 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 Si 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.

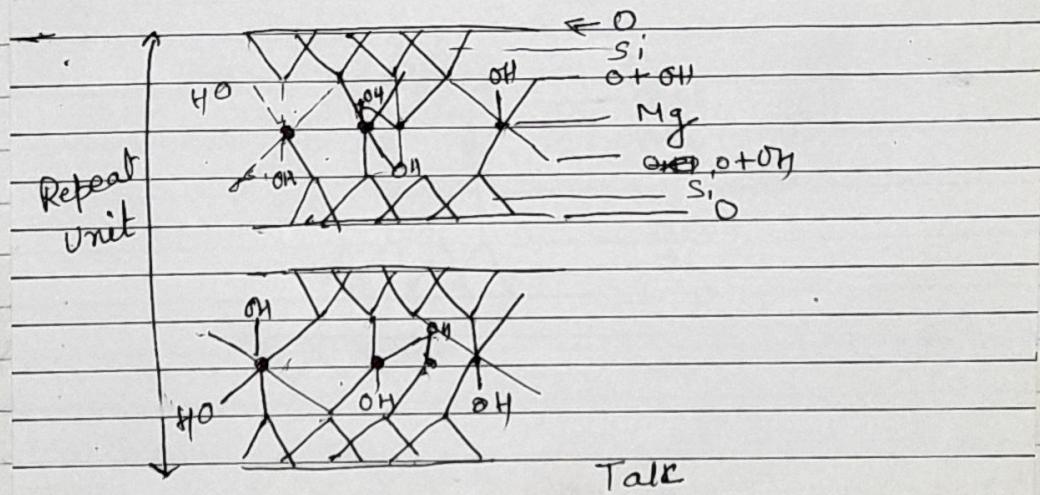
Carbon form a number of catenated halides, the best known being Teflon or Polytetrafluoroethylene. The polymers formed have chain length of several hundred carbon atom.

Silicon forms $(SiF_2)_n$ and $(SiCl_2)_n$, polymers, which decompose on heating into low molecular weight polymers of formula Si_nX_{2n+2} , the longest chains known are Si_6F_{14} , $Si_{16}F_{34}$ and Si_4Br_{10} .

Germium forms the dimer Gr_2Cl_6 but Sn and Pb don't 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.

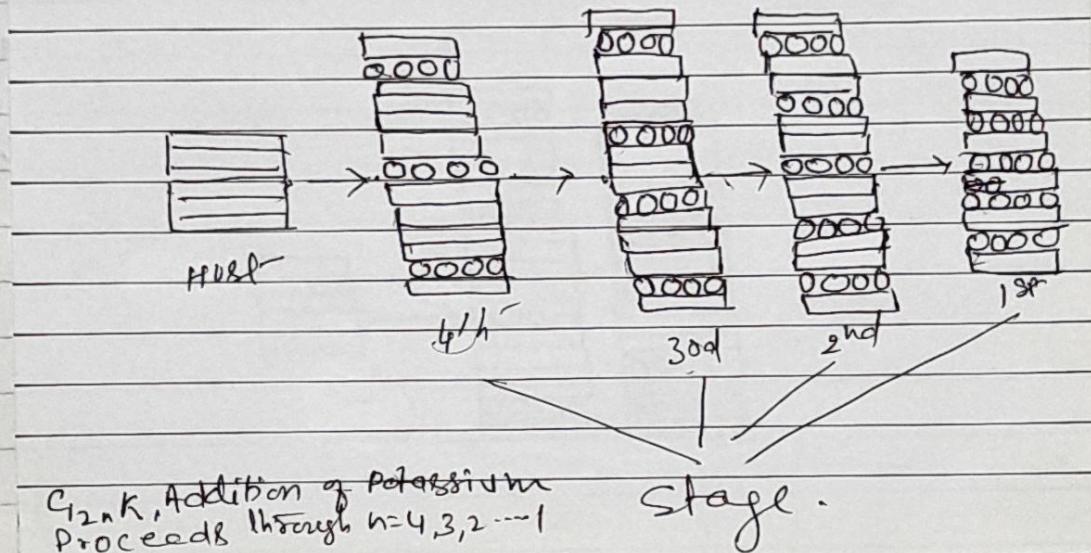


Another example sodium beta alumina where the sodium ions are free to move between the spinel layer. The sodium ions can be replaced by any +1 cations such as Li^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , H_3O^+ etc. The conductivity of these materials varies with the size of the ions mainly between the fixed distance ($\text{Al}-\text{O}-\text{Al}$) layers.

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

[4]

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



HETEROPOLY ANIONS — Heteropoly anions where two or more different types of anion condensed together - for example molybdate or tungstate 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 around 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 oxoanions such as PO_4^{3-} , SiO_4^{4-} and BO_4^{3-} but other elements including Al, Ge, Sn, As, Sb, Se, Te, I and many

[5]

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 acids.