**Name of the Teacher- Sutapa Chakrabarty**

**Subject: Chemistry**

**Class: Semester-4**

**Paper: C9T: Inorganic Chemistry**

# Topic: Chemistry of p Block elements

## Part 2

**Comments-** Study the whole lesson thoroughly.

**[N.B. -** Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

They remain uneffected by most of the chemical reagents such as weak acids, alkalies and salt solutions i.e, silicones are chemically inert.

iii) They are water repellent (जलविकर्षी) i.e, they are not wetted and are used in making water proof cloth and paper.

iv) All sillicones have good insulating proparties. Due to these proparties they are used as insulating materials for electric motors and other electric substances/instruments.

v) They are non-toxic.

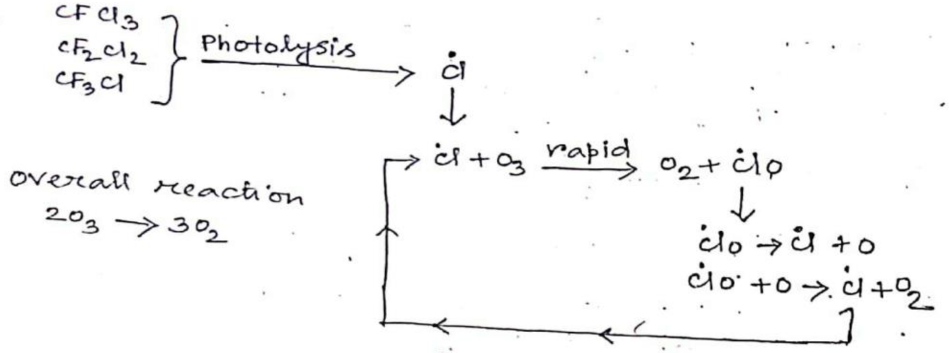
## *** Freons (C.F.C) [Chloro fluro carbon]

Mixed chloro fluro carbons such as $CFCl_3$, $CF_2Cl_2$, $CF_3Cl$ are known as freons. They are unreactive and non-toxic and are widely used as refrigeration fluids and for washing computer boards etc. Despite being inert they cause environmental damage.

Freons are very much more effective green house gases in the atmosphere than $CO_2$, though the amount of freons present is extremely small. Much more seriously the freons have penitrated the upper atmosphere and are causing damage to the ozone layer. A hole in the ozone layer has appeared over the southpole and a similar hole seems to be developing over the north pole. The ozone layer is important as it filters the radiation from the sun and prevents most of the harmful UV radiation from reaching the earth. Excessive exposer to UV radiation should be avoided as it cause skin-cancer in humanes.

In the upper atmosphere freons undergo a photolytic reaction and produce free chlorine atoms, (radicals). These react readily with ozone. The ClO radicals from decomposed slowly.

reforming cl radicals, which react with more ozone and so on. There is no effective ~~skin~~ sink for cl radicals. once formed, they are used again and again. so a small number of radicals make a very effective scavenger (transfor) for ozone.



Q: Tetra-ethyl lead:

Tetra-ethyl ~~taste~~ lead is commercially the most important organo lead compound. It can be made by the action of ethyl halides on sodium lead alloy. Actually it is made by the action of ethyl chloride on an alloy of lead with 10% Na. Piridine being used as a catalyst. A temperature of 40-60°c is usually maintained.

$$4C_2H_5Cl + 4Na/Pb \rightarrow Pb(C_2H_5)_4 + 4NaCl + 3Pb$$

Nacl and excess Na are removed by washing with water and tetra ethyl lead is prepared by steam distillation.

It is insoluble and unaffected in $H_2O$. It is used as antiknock agents in petrol. A small percentage of tetra ethyl lade in petrol can prevent knocking in internal combustion engines, whereby it is possible to have a higher compression in the cylinders and hence a higher efficiency. About 2-3 ml of $Pb(C_2H_5)_4$ is used per galon of petrol. It decomposes to produce ethyl radicals.

$$Pb(C_2H_5)_4 \longrightarrow Pb + 4\dot{C}_2H_5$$

These ethyl radicals prevent explosive combustion responsible for knocking.

Pb is poisonous to man. During the burning of petrol lead from $Pb(C_2H_5)_4$ pollutes the atmosphere; since the finely divided Pb. Particles released through the exhaust. U.S.A. has introduced ~~lead~~ free petrol to avoid pollution.

## Hydro. fluo silicic Acid ($H_2SiF_6$) or Fluorosilicic acid :-

It is a complex halide of silicon in which 'si' atom shows hexa covalency.

**Preparation :-**

(i) It is made in solution by dissolving $SiO_2$ in aquous HF.

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

(ii) An aqueus solution of $H_2SiF_6$ is obtained by passing $SiF_4$ into $H_2O$.

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6$$

**Proparties :-**

(i) The anhydrous acid is unknown. on concentrating an aquous solution, the acid decomposses to $SiF_4$ and HF.

$$H_2SiF_6 \rightleftharpoons SiF_4 + 2HF$$

The mono, di, tri and tetra hydrates can be crystallised from the aqous solution.

(ii) The pure acid does not corriode (अपरं क्षरण) glass, but in evaporat it decomposes, liberating HF ($H_2SiF_6 \rightleftharpoons SiF_4 + 2HF$), which attacks glass or porcelain. It is a strong acid and it is highly ionised in solution as is $H_2SO_4$.

$$H_2SiF_6 \rightleftharpoons 2H^+ + SiF_6^{=}$$

(iii) It reacts with alkalies, forming fluo. silicates which are decomposed by excess of alkali.

$$H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O$$

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O$$

(iv) when $H_2SiF_6$ reacts with $KClO_3$, $HClO_3$ is obtained.

$$2KClO_3 + H_2SiF_6 = K_2SiF_6\downarrow + 2HClO_3$$

## Uses :-

This acid is used —

(i) As an antiseptic in medicines :

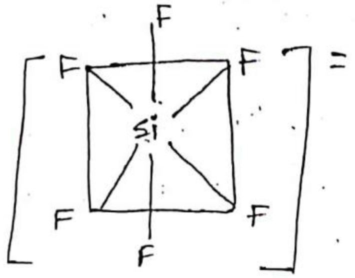
ii) For estimatling potassium.

iii) For testing Ba-salts :

iv) For the preparation of $HClO_3$ etc.

## Structure :-

The fluo silicate ion ($SiF_6^{=}$) is perfectly octahedral.



## Silicon carbide : (SiC) / carborundum

Silicon carbide is a covalent carbide.

## Preparation :-

It is prepared by heating a mixture of coke and $SiO_2$ in an electric furnace at 2000°c by the following reaction.

$$SiO_2 + 3C \overset{2000^\circ c}{=} SiC + 2CO$$

A mixture of sand and crushed coke (5:3) with some common salt and sawdust is heated electrically to 1500-2200°c by a carbon rod passing through the mass. The salt is used to make the mass fusible and the sawdust to make the mass porous. At this high temperature the above reaction occurs resulting in the formation of SiC.

## Proparties (Physical) :-

It is a colourless crystalline solid in pure form. The commercial sample is yellow, green or blue. It is nearly as hard as diamond. It is insoluble in $H_2O$ and alcohol.

i) chemically, SiC is extremely inert and even at high temperature it is not attacked by HF, HCl, $O_2$ or S. Even a mixture of fuming $HNO_3$ and HF has no action on SiC.

ii) It is slightly oxidised by air at about 1000°C. Sillica formed during oxidation forms a protective layer on the surface of SiC. This layer of $SiO_2$ stops further oxidation of SiC.

iii) It reacts with molten NaOH, in presence of $O_2$ to form $Na_2SiO_3$.

$$SiC + 2NaOH + 2O_2 \xrightarrow{fuse} Na_2SiO_3 + H_2O + CO_2.$$

iv) when SiC reacts with $Cl_2$, $SiCl_4$ and $CCl_4$ are obtained.

$$SiC + 2Cl_2 \overset{100°C}{=} SiCl_4 + C$$
$$SiC + 4Cl_2 \overset{1000°C}{=} SiCl_4 + CCl_4.$$

Uses :-

i) Due to its extreme hardness, it is used as an aborasive for cutting and grinding glasses.

ii) It is used in atomic reactor. since it serves as an excellent container for fuel at high temperatures.

iii) It has very high thermal and chemical stability. It also has high thermal conductivity. Due to these properties, it is used as a refractory ([illegible]) material for making crusibles, which are used for melting metals.

Structure:-

SiC has infinite three dimensional structure of silicon and carbon atom in which each 'C' atom is tetrahedrally surrounded by four Si atoms and each Si atom is sorrounded tetrahedrally by four carbon atoms. A simplified partial structure of SiC is shown below-

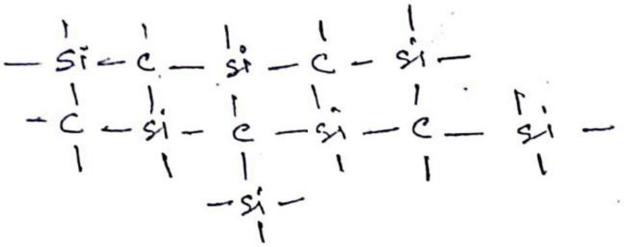


Fig: Partial structure of SiC.

8. Catenation of the elements of group IVA : (14)

All the elements of Gr IV A have a tendency to link with each other and thus form long chains of identical atoms ~~(M-M chains, M= element)~~. Such long chains of identical atoms are called homochains. This type of linking of identical atoms with each other is called ~~concentration~~ Catenation or selflinkage.

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 will be the tendency of M atom to show the proparty of catenation. Thus since the ~~valence~~ values of M-M bond energies decrease from C → Si → Ge → Sn → Pb, 'C' atom shows maximum tendency for catenation. 'C' atom by unity with other 'C' atom can form long C-C chains of any length. These chains may be straight chains, branch chains and cyclic chains. C-C bonds are highly stable in the compounds ~~are~~ containing C-C long chains. The proparty of catenanation show by other elements of this group decreases as ~~the~~ the moving down the group from C to Pb. ~~Thus~~ It ~~is~~ is due to maximum property of catenation of 'C' atom that it is easy to prepare compounds containing C-C chains upto twenty 'C' atoms, while for silicon and Germenium, ~~it~~ it not possible. The silicon and germenium compounds containing six Si or Ge atoms can be prepared. For 'Sn' and 'Pb' it is not possible. The compounds containing two units of 'Sn' and 'Pb' can be prepared.

## Q. Hydrides of Group IVA elements :-

All the elements form volatile covalent hydrides, the ease of formation decreases down the group. Due to the strong tendency of catenation carbon forms a vast no. of chain and ring compounds including the alkanes ($C_nH_{2n+2}$), alkenes ($C_nH_{2n}$), alkynes ($C_nH_{2n-2}$), and many aromatic compounds.

Silicon forms a few saturated hydrides ($Si_nH_{2n+2}$) called silanes, analogous to alkanes. Silanes prepared in a mixture by the following reactions.

$$2Mg + Si \xrightarrow[\text{in absence of air}]{\text{heat}} \underset{\text{Magnesium silicide}}{Mg_2Si}$$

$$Mg_2Si + 2H_2SO_4 \rightarrow \underset{\text{silane}}{SiH_4} + 2MgSO_4$$

$SiH_4$ is purified by fractional distillation.

Pure mono silane has been prepared by reducing $SiCl_4$ with $LiAlH_4$.

$$SiCl_4 + LiAlH_4 \xrightarrow[\text{solution}]{\text{ether}} SiH_4 + LiCl + AlCl_3$$

The silanes are much more reactive than alkanes. The silanes are strong reducing agent, ignites ([illegible]) in air and explode in chlorine, Hydrolised readily in alkaline solution.

$$Si_2H_6 + H_2O \xrightarrow[\text{or alkali}]{\text{trace}} SiO_2 \cdot nH_2O + H_2$$

Several germanium hydrides (germenes) are known with formula $Ge_nH_{2n+2}$ upto n=5, They are similar to silane but less volatile, less reactive, less inflammable and are unaffected by water.

Stannane is much less stable. $Sn_2H_6$ is known and is even less stable. $SnH_4$ and $PbH_4$ are difficult to preparid and are obtained by the action of $LiAlH_4$. ~~on tetrahalides~~.

$$SnCl_4 + LiAlH_4 \rightarrow SnH_4 + LiAlCl_4$$
$$PbCl_4 + LiAlH_4 \rightarrow PbH_4 + LiAlCl_4$$

Q. $SiH_4$ has a higher boiling point than $CH_4$ while the boiling point of $SiCl_4$ is lower than $CCl_4$ – Explain.

'C' and Si are the group IV A elements of the periodic-table. The tetrahydride of 'C' is $CH_4$ and tetrahydride of Si is $SiH_4$. The molecular weight of $SiH_4$ is higher than the molecular weight of $CH_4$. We know that the molecular weight is directly proportional to the inter-molecular forces (vanderwaals' force) among the molecules. Hence the intermolecular forces among the $SiH_4$ molecules are greater than $CH_4$ molecules. That is why $SiH_4$ has higher boiling point than $CH_4$.

The tetrahalide of carbon is $CCl_4$ and the tetra halide of silicon is $SiCl_4$. $SiCl_4$ has higher molecular weight than $CCl_4$. Hence $SiCl_4$ should have higher boiling point than $CCl_4$. But actually the boiling point of $SiCl_4$ is lower than that of $CCl_4$.

This anomaly (বৈপরীত্য) has been explained on the assumption of multiple bonding between vacent 'd' orbital of silicon and filled 'p' orbital of 'cl', so that there is an effective decrease in the inter molecular vanderwaals' forces in si halides compare to that in carbon halides.

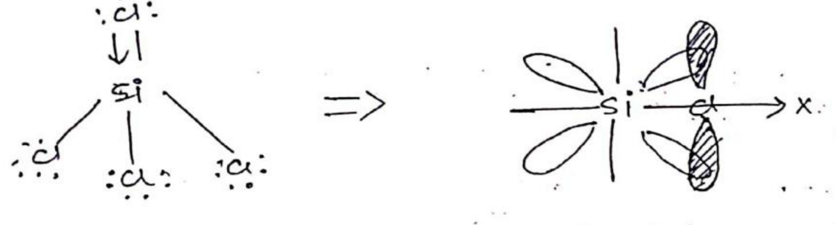
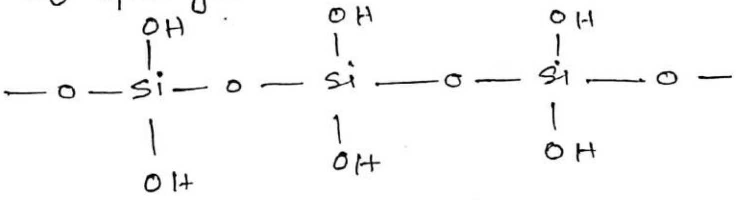


Fig: bonding in $SiCl_4$ showing overlap of a vacant silicon 'd'-orbital (dxy) with a filled 'cl' p orbital (Py)

**Q. Silica gel: (amorphous silica, $SiO_2 , nH_2O$) :-**

silica gel is a completely dehydrated silicic acid containing about 4% moisture. when a concentrated sodium silicate solution is acidified, a gel of polymeric silicic acid molecules results.



$$-O-\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{Si}}}}-O-\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{Si}}}}-O-\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{Si}}}}-O-$$

The gel contains much water held in the cage link structure of the polysilisic acid molecules. on heating in vacuum at 300°c, the water is driven off and the poly silisic acid itself dehydrates and converts to a hard transparent material. It is broken up, washed and dride. The end product is called silica gel.

Silica gel is a substance with a very large surface area and is used—