Name of the Teacher- Sutapa Chakrabarty

Subject: Chemistry

Class: Semester-4

Paper: C9T: Inorganic Chemistry

Topic: Chemistry of p Block elements

Part 1

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**]**

Group-IV A

C, Si, Ge, Sn and Pb are the five members of group-IVA of the Periodic table. They have the general valency shell electronic configuration ns^2np^2 and so they have been included in group-IV. Their electronic configuration and oxidation states are given below.

Element	Atomic Number	Electronic configuration	oxidation state	valency
C	6	He$[2s^2 2p^2]$	4	4
Si	14	$[Ne]3s^2 3p^2$	4	4
Ge	32	$[Ar]\,3d^{10}4s^2 4p^2$	2, 4	2, 4
Sn	50	$[Kr]\,4d^{10}5s^2 5p^2$	2, 4	2, 4
Pb	82	$[Xe]4f^{14}5d^{10}6s^2 6p^2$	2, 4	2, 4

The elements can exibit a valency of 4 by using all the valency shell ns^2np^2 electrons or may exibit valency of two using only np^2. On descending the group the ns^2 electron pair gradualy becomes inert and so as a result of inert pair effect, there is a decrease in stability of the +4 oxidation state and an increase in stability of the +2 state on discending the group. Thus Ge(II) is a strong reducing agent where as Ge(IV) is a stable. Sn(II) exits as simple ion which are strongly reducing but Sn(IV) is co-valent and stable. Pb(II) is ionic, stable and more common than Pb(IV) which is oxidising agent.

Q. BCl$_3$ has $p_\pi - p_\pi$ back-bonding, no such bonding exists in CCl$_4$ - Explain.

In BCl$_3$, 'B' atom is sp^2 hybridised to give a tri-angular planer structure. The empty 2p orbital on 'B' atom which is not involved in the hybridisation, is parpendicular to the tri-angular plane. This 2p orbital overlaps with a filled 'p' orbital of any of the three 'cl' atoms forming a $p_\pi - p_\pi$ back bond.

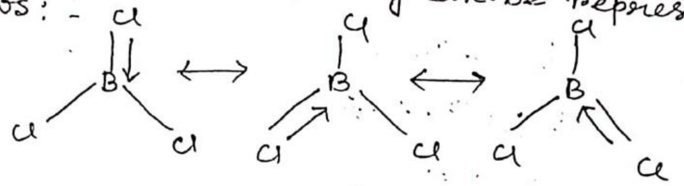
'B' atom in G.S :- $\overset{2s}{\boxed{\uparrow\downarrow}}\quad\boxed{\uparrow\,|\quad|\quad}$

B atom in E.S :- $\underbrace{\boxed{\uparrow}\quad\boxed{\uparrow\,|\,\uparrow\,|\quad}}_{sp^2\text{ hybridised}}$

B atom in sp² hybridisation :- $\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}\quad\overset{P_z}{\boxed{}}$

BCl_3 molecule :- $\underset{\substack{|\sigma\\ Cl}}{\boxed{\uparrow}}\underset{\substack{|\sigma\\ Cl}}{\boxed{\uparrow}}\underset{\substack{|\sigma\\ Cl}}{\boxed{\uparrow}}\ \overset{P_z}{\boxed{}}$

The back-bonding can be represented as follows :-



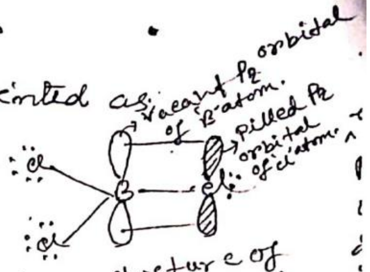


fig:- structure of BCl_3 molecule.

In CCl_4, 'c' atom is sp³ hybridised to give a tetrahedral shape of the molecule. 'c' atom has no vacent orbital for acceptance of electron pair, so $P_\pi - P_\pi$ back-bonding between 'c' and 'cl' does not occur.

'c' atom in G.S :- $\overset{2s}{\boxed{\uparrow\downarrow}}\quad\overset{2p}{\boxed{\uparrow\,|\,\uparrow\,|\quad}}$

'c' atm in E.S :- $\underbrace{\boxed{\uparrow}\quad\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}}_{sp3\text{ hybridisation}}$

C atom in sp³ hybridisation :- $\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow\,|\,\uparrow}$

CCl_4 molecule :- $\underset{\substack{|\sigma\\ cl}}{\boxed{\uparrow}}\underset{\substack{|\sigma\\ cl}}{\boxed{\uparrow}}\underset{\substack{|\sigma\\ cl}}{\boxed{\uparrow}}\underset{\substack{|\sigma\\ cl}}{\boxed{\uparrow}}$

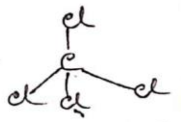


Fig:- Tetrahedral structure of CCl_4 molecule

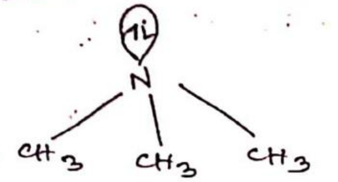
Q. $(CH_3)_3N$ acts as a Lewis base but $(SiH_3)_3N$ has no basic proparties. Explain.

The outer electronic configuration of 'N' atom is $2s^2 2p^3$

$\underbrace{\boxed{\uparrow\downarrow}\quad\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}}_{sp^3\text{ hybridised.}}$

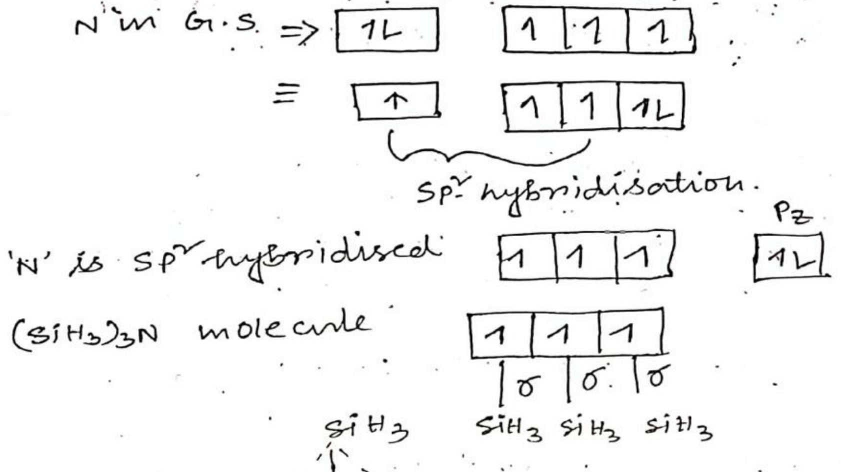
In $(CH_3)_3N$. these three unpaired electrons form bonds ~~whi~~ with three $-CH_3$ groups i.e tetrahedral arrangement of three bond pairs and one lone pair. So its structure is pyramidal.

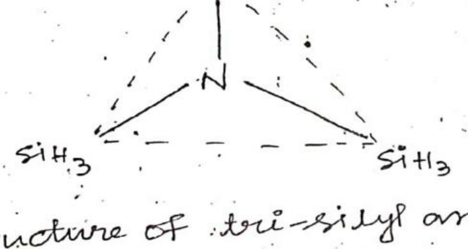
or the presence of lone pair in one sp^3 hybrid orbital, $(CH_3)_3N$. acts as a Lewis base.



Pyramidal (structure of tri-methyl amin) Shape.

But in case of tri silyl-amin N uses sp^2 hybrid orbitals for bonding with silicon, giving a planer tri-angular structure. The lone pair of electrons occupy a p-orbital at right angles to the tri-angular plane. This overlaps with empty 'd' orbitals on each of the three 'si' atoms results in $p\pi$-$d\pi$ back-bonding. Due to this back bonding the lone pair on 'N' is not free for protonation that is why $(SiH_3)_3N$ has no basic properties.

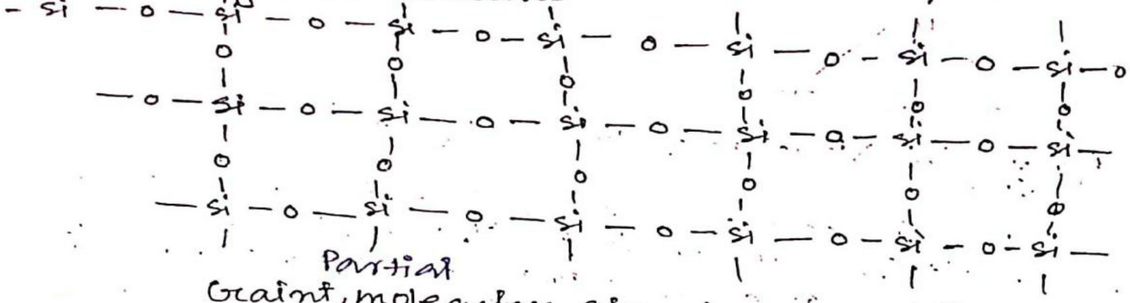




Structure of tri-silyl amine (Planer shape)

Q. SiO_2 is a high melting solid but CO_2 is a gas at room tempr — Explain.

Silicon (Si) being a third period element it has a large atomic volume and can not fulfill octet by forming $p_\pi - p_\pi$ bond with 'o' atom. To fulfil the octel larger number of SiO_2 molecules combined tetrahedraly with σ- bonds only to form a gaint molecule.



Partial Graint molecular structure of SiO_2

Large number of co-valent bonds binds the side molecules tightly. So it is a high melting solid.

'c' is a second period element. It can form strong $p_\pi - p_\pi$ bond with 'o' atom. For due to this p_π-p_π bond 'c' and 'o' get their octet fulfill.

$$:\ddot{O} \underset{\sigma}{\overset{\pi}{=}} C \underset{\sigma}{\overset{\pi}{=}} \ddot{O}:$$

co-valent CO_2 molecules attract each other by weak vanderwaals' force. The intermolecular distance is greater in CO_2 molecules. For that reason CO_2 is a gas at ordinary tempr.

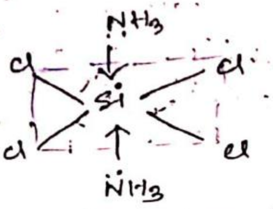
Q. $SiCl_4$ forms adduct with NH_3 but CCl_4 does not. — Explain.

NH_3 can form adduct by acting as a nucleophile i.e by donating the lone pair to an empty orbital. In CCl_4, 'c' has no empty orbital and 'cl' atom prevants the nucleophilic attack for its partial negative charge which gains from the polarity of C-Cl bond. So CCl_4 does not form adduct with NH_3.

In $SiCl_4$, 'si' has empty '3d' orbital and also it creats positive charge due to the polarity of Si-Cl bond, which accelarates nucleophitic attack .. So $SiCl_4$ forms adduct with H_3 by accepting of electron pair.

$CCl_4 + NH_3 \xrightarrow{\times}$

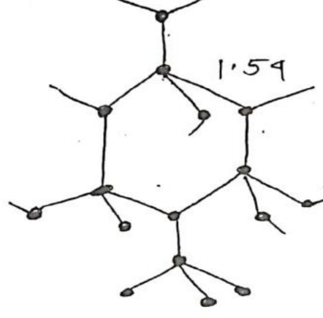
$SiCl_4 + 2NH_3 \longrightarrow$



* $\boxed{\text{Maximum co-valency}}$ → 2nd explanation.

Q. Diamond is a non-conductor of electricity but graphite is a good conductor of electricity. — Explain.

Diamond and graphite are the two allotropes of 'c'. But they differ widely in structure. In diamond 'c' atoms are arrenged tetrahedraly and equidistance with a c–c bond of 1·54 A°. The diamond consists of gaint molecule in which each 'c' atom is sp^3 hybridised and linked with four other 'c' atoms by four equivalent σ-bonds. The presence of a large number of σ-bonds binds the 'c' atom very strongly as a consiquence diamond becomes very hard with high melting point.

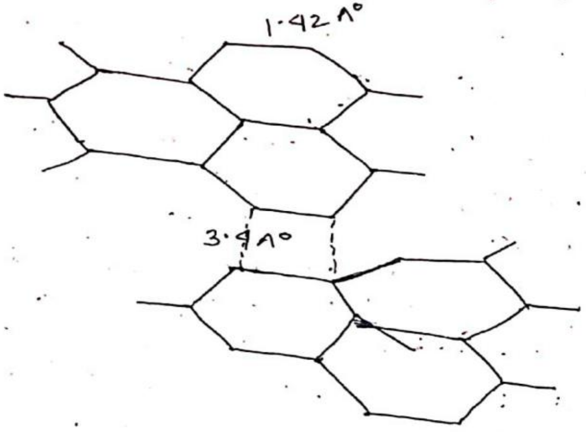


Graint molecular structure of diamond.

Diamond structure shows there is no free electron or ions. So diamond is a non-conductor of electricity. ~~So~~

In graphait the layers of 'c' atom form a regular hexagonal network with a c-c-bond length 1·42 A°. The different layers being 3·4 A° apart, the layers are held together by weak vanderwaals' forces. Each 'c' atom in graphite is linked with three neighbouring 'c' atoms ~~to~~ by σ bond only.

one unhybridised p-orbital on each 'c' atom combined to form a delocalised to molecular orbital containing mobile electrons. Presence of mobile electrons in graphite accounts for its good electrical conductivity. The wide separation of the layers makes graphite soft.



Partial layer structure of graphite.

SILICONES

Q. Silicones :

Silicones are organo silicon polymers containing —O—Si—O—linkages. These may be linear silicones, cyclic silicones and cross linked silicones.

* Preparation :-

These are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$ and polymerisation of alkyl or aryl hydroxy derivatives. Thus this method consist of the following steps -

* a) To prepare alkyl or aryl derivatives of $SiCl_4$:

These derivatives are prepared by the following ways :

i) Alkyl chloro silanes can be obtained by the action of grignard reagent on $SiCl_4$.

$R\text{-}Mg\text{-}Cl + SiCl_4 \longrightarrow R\text{-}SiCl_3 + MgCl_2$

$2R\text{-}Mg\text{-}Cl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$

$3RMg\text{-}Cl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$

ii) Phenyl chloro silane is obtained by heating C_6H_6 with $SiHCl_3$ at 200-300°c in presence of a catalyst like BF_3, BCl_3 etc.

$$C_6H_6 + SiHCl_3 \xrightarrow[\text{catalyst}]{\Delta} C_6H_5SiCl_3 + H_2$$

b) To prepare silanoles :-

The silanols are obtained by the hydrolysis of $RSiCl_3$, R_2SiCl_2 and R_3SiCl respectively.

$RSiCl_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HCl$

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

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

chloro. silanes silanoles

c) To allow the silanols to undergo polymerisation:-

Polymerisation process involves removal of some H_2O molecules and leads to the formation of different types of silicones. The type of siliconeobtained depends on the nature of alkyl or aryl hydroxy derivative.

e.g; A) when many molecules of alkyl tri- hydroxy silane undergoes polymerisation, a cross linked two dimensional silicon is obtained.

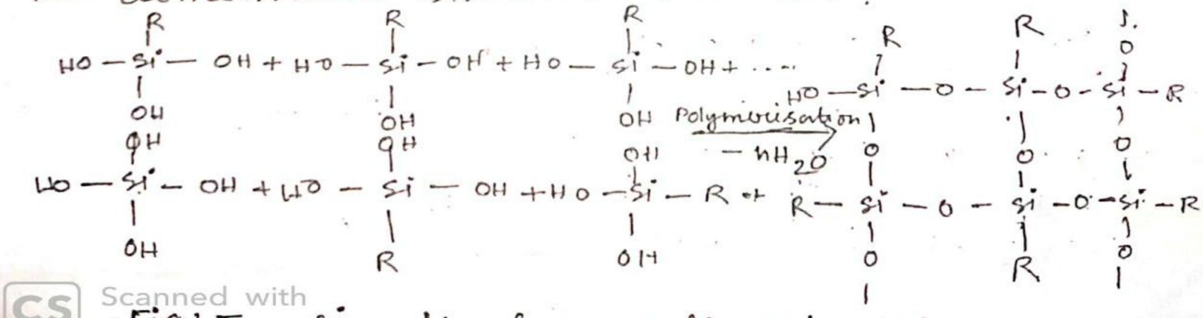
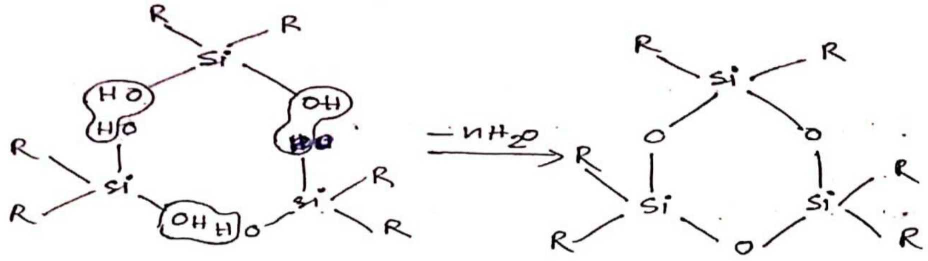
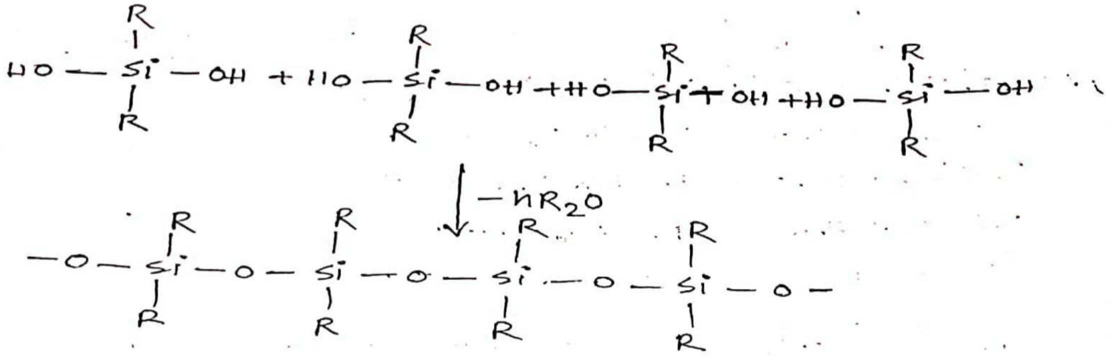


Fig: Two dimentional cross linked silicon.

B) When many molecules of dialkyl dihydroxy silane undergo polymerisation, a straight chain or cyclic silicon is obtained.





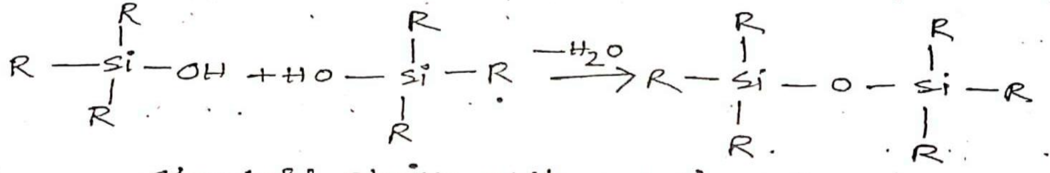
$$HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH \;\cdots$$

$$\downarrow -nR_2O$$

$$-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-$$

Linear or straight chain silicone.

c) When two molecules of tri-alkyl mono-hydroxy ~~silico~~ silane undergo polymerisation, a straight chain silicon is obtained.



$$R-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-R \xrightarrow{-H_2O} R-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-R$$

Straight chain silicon (dimer)

Q. Proparties and uses of silicons :-

The following proparties and uses are common to all types of silicones;

i) They have high thermal stability in the absence of air upto 250−300°c.

) 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.