

PERIODICITY

Q. What is diagonal Relationship? Give two Similarities b/w Li and Mg.

=> Diagonal Relationship:

Some of the elements of Second period show similarity in their properties with the elements of third period lying diagonally below it which is called diagonal Relationship.

=> Similarities:

Lithium (Li)	Magnesium (Mg)
Size	
1. The atomic radii of the Li = 1.225 \AA .	The atomic radii of the Mg = 1.365 \AA .
Electronegativity	
The electro-negativity of Li = 1.00	The electronegativity of Mg = 1.20.
Decomposition of Water	
It decomposes Water as; $2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2$	It decomposes Water as; $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2$
Thermal Stability	
Li decompose easily $4\text{LiNO}_3 \xrightarrow{\Delta} 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$	It can also decompose easily $2\text{Mg(NO}_2)_3 \xrightarrow{\Delta} 2\text{MgO} + 4\text{NO}_2 + \text{O}_2$
Formation of their Chlorides	
$2\text{Li} + \text{Cl}_2 \rightarrow 2\text{LiCl}$	$\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$

Q: What is inert Pair effect?

=> Definition:

"It is defined as the reluctance of ns electrons to participate in bonding due to higher nuclear charge in post transition metals."

=> Examples:

$ns^2 np^2$ (Group-IV) electronic configuration

→ Pb exists in 2 forms

Pb^{+2}

and

Pb^{+4}

↓

↓

+2

+4

↳ Uses of 2 electrons

↳ Uses of 4 electrons

↳ low polarizing power

↳ High polarizing power

↳ ns^2 doesn't participate

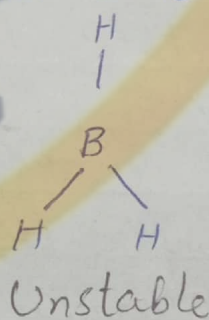
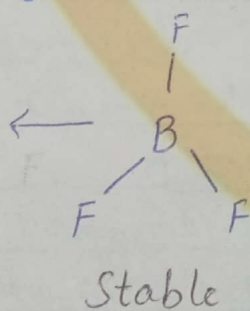
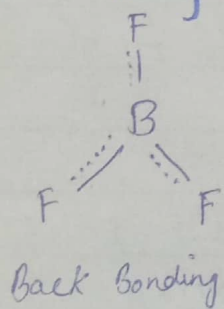
↳ Both ns^2 & np^2 participate

→ Two compounds are formed $PbCl_2$, $PbCl_4$

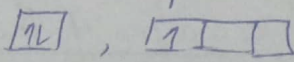
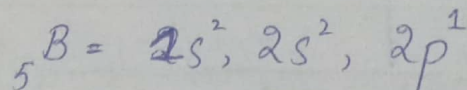
↓
larger size

↓
smaller size

Q: Why BF_3 is more stable than BH_3 ?

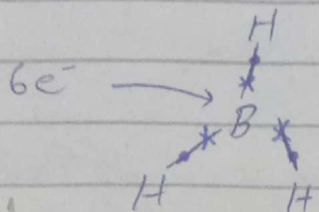


=> Key Point: 'Boron is electron deficient



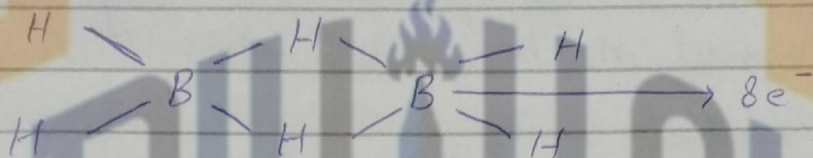
→ vacant orbital

=> In case of BH_3 :



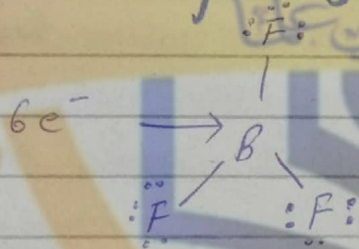
→ Boron have $6e^-$ and needs two more electrons to complete its octet

→ So undergo dimerization and exist as B_2H_6

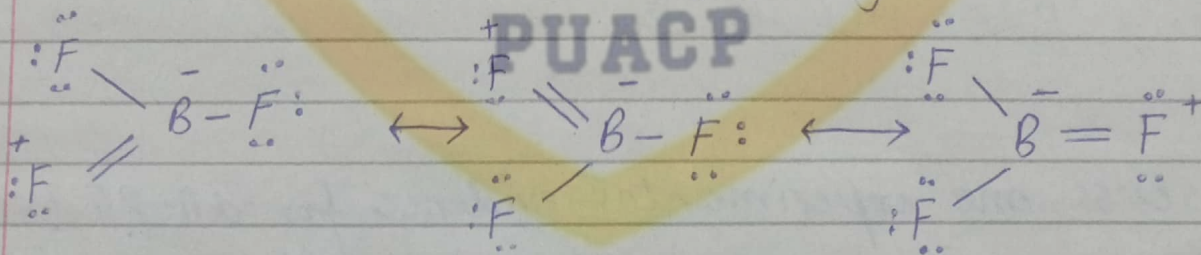


→ Therefore BH_3 never exist, it always exists as B_2H_6

=> In case of BF_3 :

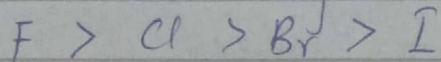


→ F is more electronegative
→ It donates its lone pair to the vacant 'p' orbital of Boron to complete its octet and by forming the "back bonding"



=> Role of Back Bonding:

For the Stability of a Compound back bonding is very important and for Strong back bonding we need more electronegative atom: e.g



→ Trend of ability of back Bonding

Q. Why does fluorine show peculiar behaviour in group VII A?

=> Size:

Fluorine has small size than other halogens.

=> High Electronegative:

↳ Fluorine is highly electronegative having only -1 oxidation state while other halogens show negative as well as positive oxidation states (+1, +3, +5 and +7).

↳ Due to this reason hydrogen bonding is present in HF while it is absent in HCl, HBr, HI.

=> Highly Reactive:

↳ Due to small size, high charge density and high L.P - L.P repulsion ($\ddot{F} \times \ddot{F}$), the bond dissociation energy decreases which cause ease in breakdown of bond making 'F' more reactive than ^{other} halogens.

=> State:

↳ HF is liquid with high boiling point, while HCl, HBr and HI are gaseous.

=> Weak Acid:

↳ HF slightly ionizes in aqueous solution therefore weak acid than HCl, HBr and HI.

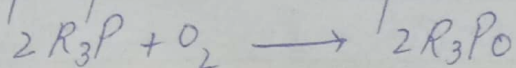
Q. Discuss one experimental evidence for d π -p π ?

=> Comparison of stability of phosphine oxide & amine oxide

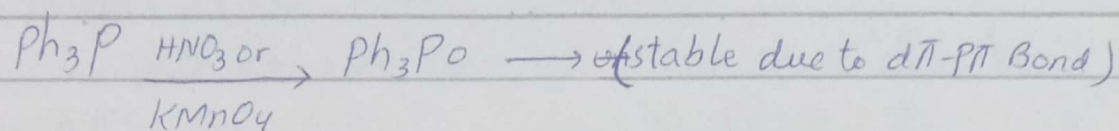
1. Phosphine oxides

↳ R_3PO is more stable than R_3NO because of d π -p π bonding.

↳ Aliphatic phosphine decompose below 700°C

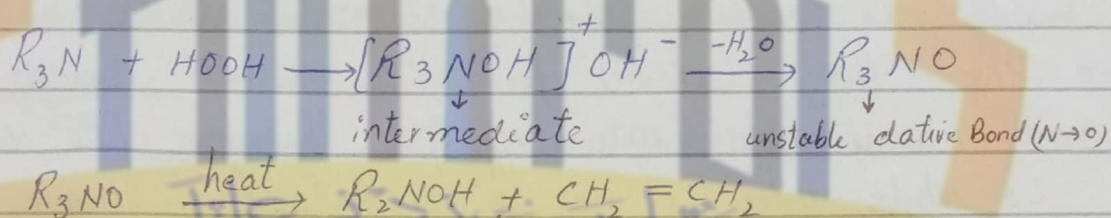


↳ Aromatic phosphine is more stable due to resonance.



Amine oxide:

↳ Amine oxide is unstable because N has no d-orbital, no $d\pi\text{-}p\pi$ bond and decomposes on heating below 700°C , produces ethene because of presence of $\beta\text{-H}$.

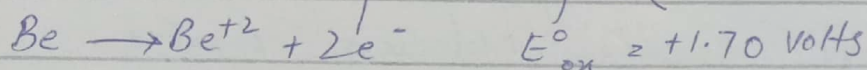


Q. Write two Similarities b/w Be and Al?

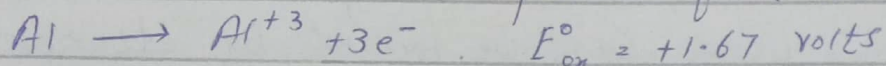
1. Polarizing powers, which are equal to charge/Radii ratio of Be^{+2} ($=6.45$) and Al^{+3} ($=6.00$) are of similar magnitude as;

Ion	Be^{+2}	Al^{+3}
Charge on ion	+2	+3
Ionic Radius (\AA)	0.31	0.50
Charge/Radii Ratio	$2/0.31 = 6.45$	$3/0.50 = 6.0$

2. The Standard oxidation potential of Be (+1.70 volts)

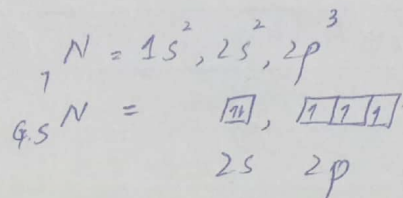
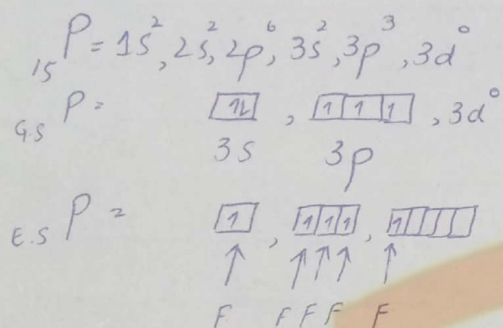


is very close to Standard oxidation potential of Al (+1.67 volts).



3. The electronegativity values of both the elements are the same ($\text{Be} = 1.5$ & $\text{Al} = 1.5$)

Q: Why PF_5 exists whereas NF_5 does not?



→ Excited State is not possible because there is not 'd' orbital

Reason:

→ Due to availability of 'd' orbital of Phosphorus in PF_5 , the electrons from '3s orbital' jumps to '3d' having hybridization of sp^3d therefore PF_5 exists.

→ While there is no 'd' orbital of Nitrogen in NF_5 , so no excitation of electron is possible. Therefore NF_5 never exists.

Q. Which type of Bonding is Stronger between $\pi\pi-p\pi$ and $d\pi-p\pi$ and Why?

A. The $d\pi-p\pi$ bond is Stronger than the $\pi\pi-p\pi$ Bond.

Reason:

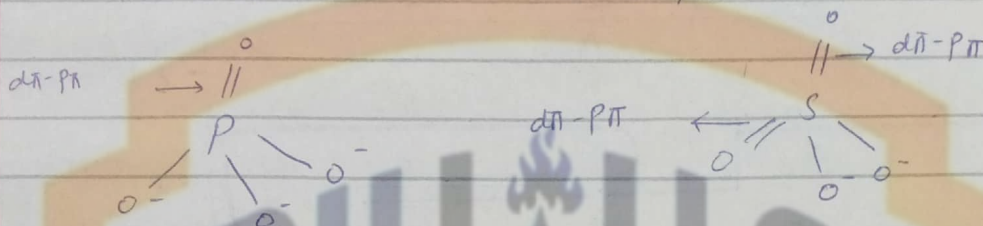
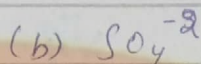
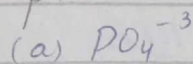
Due to a large level of overlap in the electron clouds in the $d\pi-p\pi$ bond, the extent of overlap is greater, resulting in a lower energy bonding molecular orbital.

Which elements can't form $d\pi-p\pi$ Bond?

This bond can't be formed by elements that do not have vacant d-orbitals. As a result period 2 elements do not have unoccupied d-orbitals and only

have vacant p-orbitals allowing them to form multiple π bonds. Period 3 and above elements have an empty d-orbital and can create $d\pi-p\pi$ multiple bonds.

Examples:



Q. Why PF_3 exists whereas NF_3 does not?

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LONG QUESTIONS

Q: Discuss periodic anomalies of the non-metals and post transition metals?

III A	IV A	V A	VI A	VII A	
B	C	N	O	F	→ Non-metals.
Al	Si	P	S	Cl	
Ga	Ge	As	Se	Br	→ post transition Non-metals
In	Sn	Sb	Te	I	
Tl	Pb	Bi	Po	At	
← transition metals.					

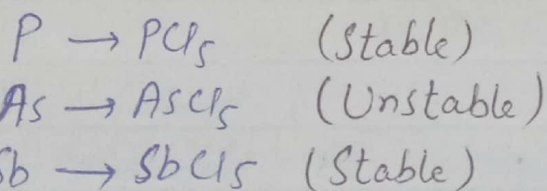
It is generally assumed that various properties of various families of periodic table change smoothly from less metallic (more electronegative) at the top of the family to more metallic (less electronegative) at the bottom of family.

Alkali metals on the left and noble gases on right.

Reluctance of Fourth-Row Non-metals to Exhibit Maximum valence:

There is a definite tendency of the non-metals of 4th row (As, Se, Br) to be unstable in their maximum oxidation state.

In Group VA:



AsCl₅ : → The synthesis of arsenic pentachloride eluded

chemists until comparatively recently.

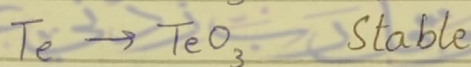
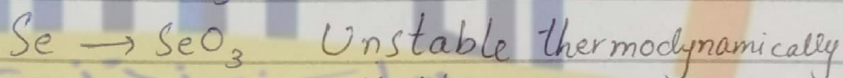
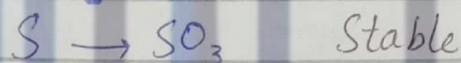
Reasons for Unstability:

- (i) Effective nuclear charge increase
- (ii) Poor Shielding Effect of 'd' orbital
- (iii) It decomposes at $\sim 50^\circ\text{C}$

-) AsBr_5
 -) AsI_5
 -) AsF_5 :
- } \rightarrow Both are still unknown

It is only stable arsenic due to more electro-negative atom 'F'. Arsenic shows anomalous behaviour.

(B) In Group VI A:



\Rightarrow The enthalpies of formation:

$$\text{SF}_6 = -1210 \text{ KJ/mol}$$

$$\text{SeF}_6 = -1117 \text{ KJ/mol}$$

$$\text{TeF}_6 = -1320 \text{ KJ/mol}$$

Note: [The more negative enthalpy of formation the greater the thermal stability.]

\rightarrow SeF_6 have less negative enthalpy of formation therefore it is unstable.

\Rightarrow Bond energies:

$$\text{S-F} = 317 \text{ KJ/mol}$$

$$\text{Se-F} = 285 \text{ KJ/mol}$$

$$\text{Te-F} = 330 \text{ KJ/mol}$$

Note: Bond energy \propto Stability of Bond

\rightarrow Se-F has less bond energy, therefore it is unstable.

c) In group VIIA Halogens:

Cl \rightarrow ClO_4^- Weak oxidizing agent

Br \rightarrow BrO_4^- Strong oxidizing agent

I \rightarrow IO_4^- Weak oxidizing agent

$\hookrightarrow \text{BrO}_4^-$ is Strong oxidizing agent than perchlorate and periodate.

$\text{HClO}_4 \rightarrow$ Strong acid $\rightarrow +7$ o.s (Stable)

$\text{HBrO}_4 \rightarrow$ Weak acid $\rightarrow +7$ o.s (Unstable)

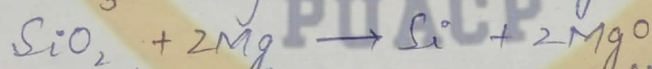
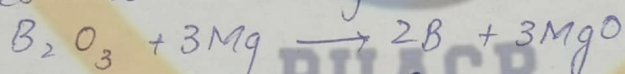
\hookrightarrow Bromine shows reluctance to exist in +7 o.s. in HBrO_4 and BrO_4^-

\downarrow \downarrow
 Perbromic acid Perbromate ion

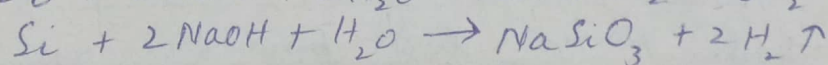
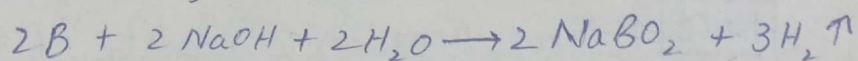
Q: Write diagonal Relationship between Boron and Silicon

Boron resembles Silicon in many of its properties with which it is diagonally related.

1) Both the elements can be prepared by Reducing their oxides with Mg.



2) Both the elements dissolve in alkalies (Boron only in fused while Silicon in fused as well as aqueous), forming meta-borate (BO_2^-) and meta-silicate (SiO_3^{2-}) and liberate H_2 .



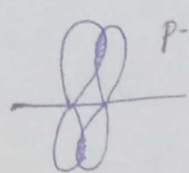
3) None of the elements is attacked by water

and non-oxidising acids.

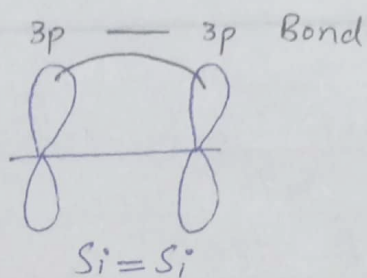
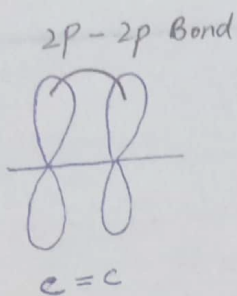
4. None of these elements occurs in the free state. Both are found as oxy-compounds, e.g.: borates and silicates.
5. Chemically both the elements are typical non-metals and are bad conductors of heat and electricity.
6. Both the elements exist in two allotropic forms viz. amorphous and crystalline. The crystalline form of both the elements is harder and elements are almost the same.
7. Both the elements have high melting points;
(B = 2300°C , Si = 1420°C)
8. Both the elements form mainly covalent compounds like hydrides.
9. Both the elements combine with metals like Mg and form borides and silicides respectively.
$$2\text{B} + 3\text{Mg} \rightarrow \text{Mg}_3\text{B}_2 \text{ (Boride)}$$
$$\text{Si} + 2\text{Mg} \rightarrow \text{Mg}_2\text{Si} \text{ (Silicide)}$$
10. Boron and Silicon combine with O_2 at elevated temperature to form stable oxides viz B_2O_3 & SiO_2
$$4\text{B} + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3$$
$$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$$

Q. Discuss $p\pi-p\pi$ bonding in the heavier congeners of group IV-A?

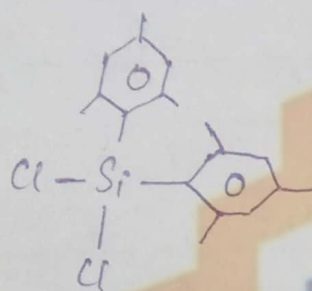
→ Alkenes have $\text{C}=\text{C}$, so that chemists started to look for $\text{Si}=\text{Si}$



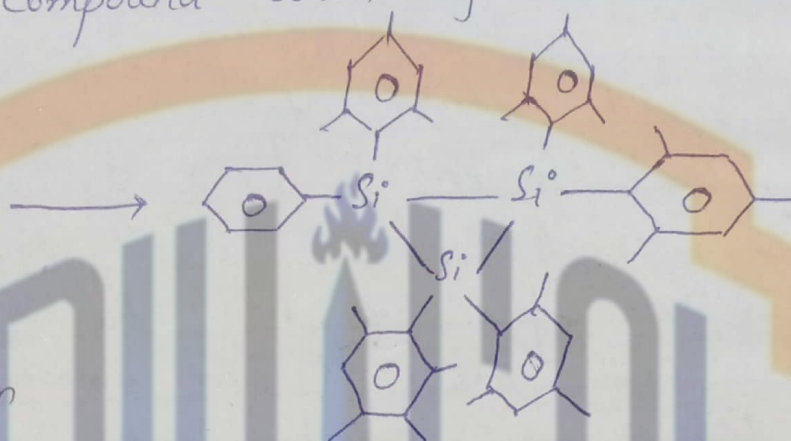
P-P Bond



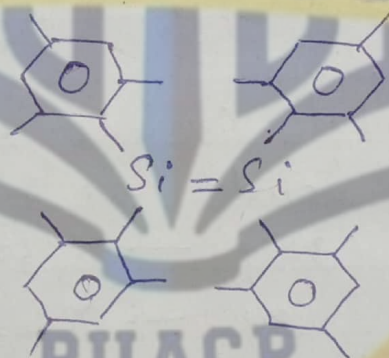
→ First stable compound was, cyclosilane



Diphenyl Silicon
dichloride

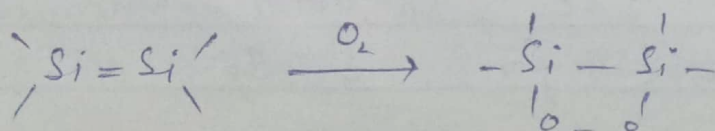
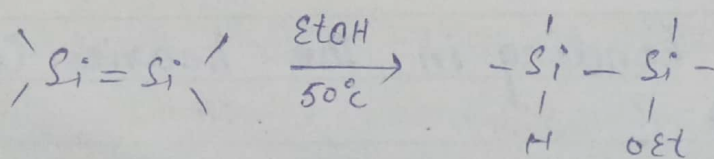
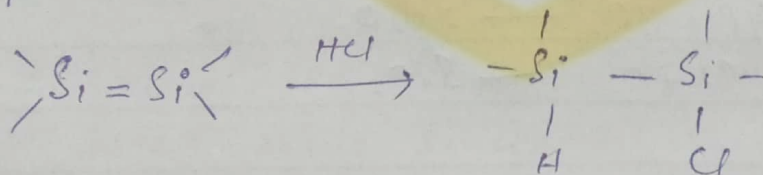


Cyclotrisilane

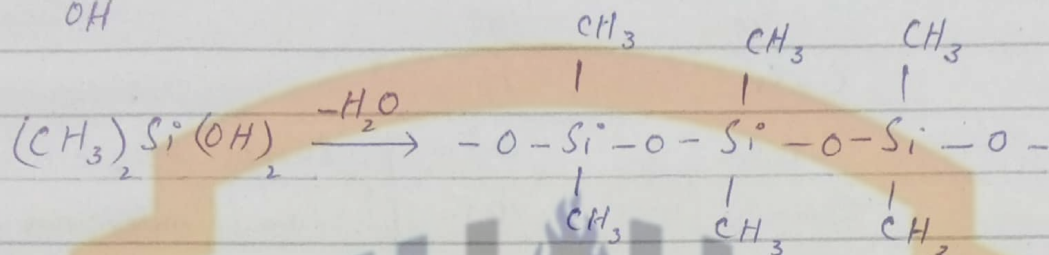
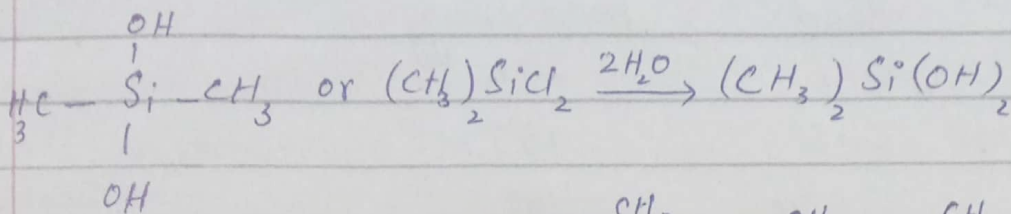


hν

→ It is possible to add atoms across Si=Si



→ The Gem-diols of Si is unstable.



very long chain stable polymer (Silicones)

⇒ Strength of $\text{Pn}-\text{Pn}$ Bond:

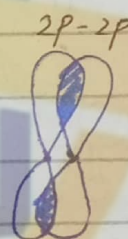
C → 2p-2p

Si → 3p-3p

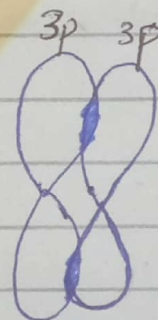
Ge → 4p-4p

and $2p-2p > 3p-3p > 4p-4p$

-) $2p-2p >$ → (i) More Strong
(ii) More effective overlap
(iii) High Bond energy
(iv) Small Size
(v) More hold on nucleus.



-) $3p-3p \rightarrow$ (i) Weaker Bond
(ii) Weak overlapping
(iii) Low Bond energy
(iv) Big Size
(v) More diffuse

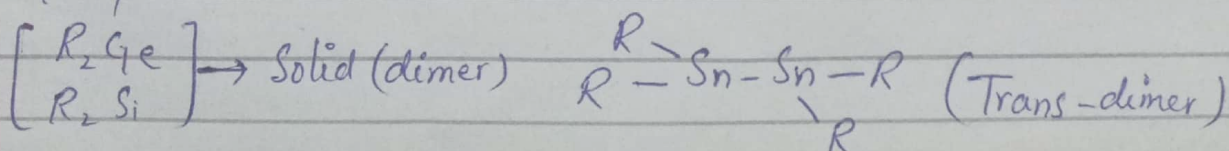


⇒ Magnitude of Wavefunction in overlap region:

$2p$ wave function $>$ $3p$ wave function

⇒ Divalent Structure of High Congeners:

Ge & Si both are divalent



Double
 \Rightarrow \uparrow Bond energies of group IV-A:

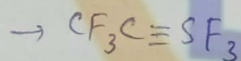
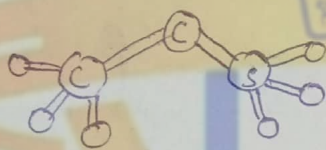
Bond	Bond energy
$C=C$	272
$C=Si$	159
$C=Ge$	130
$C=Sn$	79
$Si=Si$	105
$Ge=Ge$	105
$Si=Ge$	105

Except 2p, all have
 Same/Similar overlap

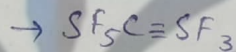
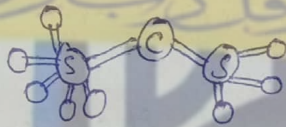
\rightarrow low bond energy \rightarrow less effective overlap.

\Rightarrow **Role of Bulky group:**

Introducing bulky groups (Substituents) gives stability



\rightarrow linear



\rightarrow non-linear

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