

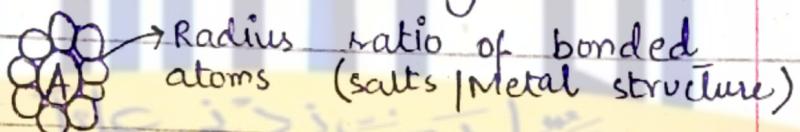
Ch: Stereochemistry and bonding in main group compounds

* Stereo → spacial arrangement → structure

* Structure → Close Packing (non-directed valency)
→ Open Packing (Directed valency)

1. Close Packing → Space around

central atom is filled with other atoms (like magnet)



But there remains some space due to the structure (circle)

2. Open Packing → Arrangement of atoms around central atom

depends on the orbital arrangement. Mostly in covalent compounds or coordinate covalent bonds.

i. → It is more stronger than close packing.

* Stereochemistry is present in open packing and absent in close

packing.

* Lattice Energy increases whose radius ratio matches and solubility decreases.

* Stereochemistry depends on the arrangement of orbitals.

Electronic Theory:

If an atom has incomplete valence shell, Then it wishes to complete its valence shell by coming with other atom and complete their octet or duplet.

It also moves towards valencies.

Electron Dot Formula:

electron dot formula explain us following features:

- Bonds

- central atom valency

- central atom information

- formal charge

The atom combine with other atom is known as valency.

1. Electrovalency (ionic bond),
non-directional

2. Covalency (covalent bond),
directional

3. Coordinate covalency, directional

1812 → Davy and Baziros →

valency → Electrical X

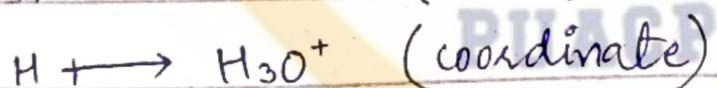
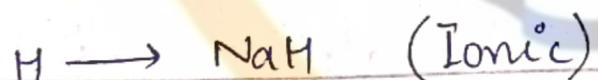
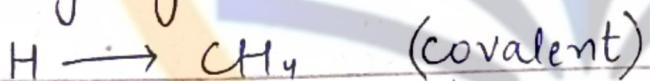
Organic compounds →

20th century → valency → Electronic distribution in an atom

- valence shell

- Electric current

Hydrogen can make:



$B\overset{3}{C}\overset{3}{l}_3 \rightarrow$ Lewis acid but boron's octet is not complete ('e⁻' deficient)



Theory of directed valency:

* Orbitals in combination are involved.

VSEPR Theory

lone pairs } valence electrons
Bond pairs }

- Electropositive atom will be the central metal atom.

- NH_3 , Nitrogen is electro +ve.

It must have more valency.

- valency shows زیاد سنترل اسٹرم ایں

جایی دوسرا اور اس س زیارہ electro +ve.

لہوں نے ہیو ہجس یا ٹراؤ جس

- Univalent atom cannot be central atom.

- e. POCl_3 has higher atomic number and can generate more valency.

- SOCl_2 has more atomic number and also more electropositive.

So, it is central atom. cf^{Li}'S₂cl

⇒ To complete the octet, we

must know the number of

valence e⁻'s which is determined

by group number.

$$BF_3 : \quad 1B = 3 \\ 3F = 7 \times 3 = \underline{21} \quad \xrightarrow{\text{group no.}}$$

24 total

As it has 3 e⁻'s and F also sharing 3 e⁻'s. So, it has total of 6 e⁻'s. So, it is e⁻ deficient.

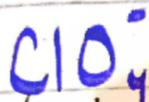


$$1 \text{ N} = 5$$

$$4 \text{ H} = 4$$

$$+ = -1$$

$$\text{Total e}^{-}\text{s} = 8$$



$$\downarrow \\ 7 + 4$$

$$1 \text{ Cl} = 7$$

$$= 11$$

$$4 \text{ O} = 24 \quad (6 \times 4)$$

e⁻ rich species

$$- = 1$$

$$\text{Total} = 32 \text{ e}^{-}\text{s}$$

Formal charge:

It is a hypothetical charge.

It is a good indication of charge carrying atom in a molecule.

e.g; NH₃

(i) n_v electrons

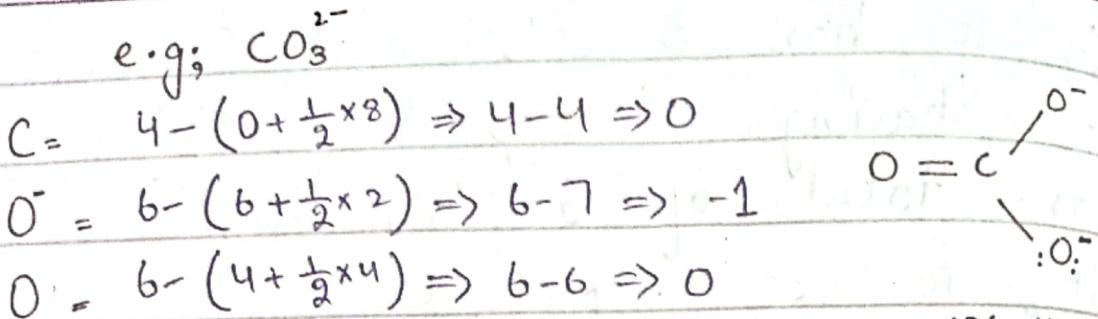
(ii) n_l lone pair

(iii) n_b bonds

$$\therefore n_v - (n_l + \frac{1}{2} n_b)$$

$$N = 5 - (2 + \frac{1}{2}(6)) \Rightarrow 5 - (2 + 3) \Rightarrow 5 - 5 \Rightarrow 0$$

$$H = 1 - (0 + \frac{1}{2} \times 2) \Rightarrow 1 - 1 \Rightarrow 0$$



Directional Theory of valency:

VSEPR Theory played a role in structural explanation. It explains how bonding take place between atoms of a molecule. When two orbitals overlap, e^- 's and orbital make bond in specific direction (p_x, p_y, p_z). Central atom plays important role in covalent bonding. e.g;

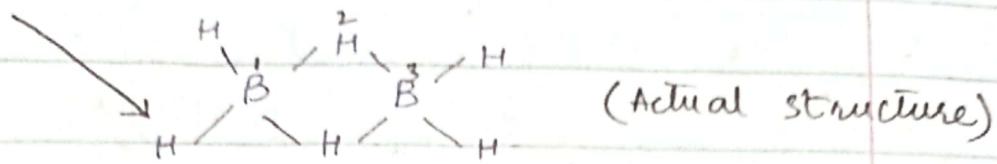
$\text{Cl}-\overset{\curvearrowleft}{\text{Be}}_{\substack{1s^2, 2s^2, 2p^2}}^{\curvearrowright 180^\circ}-\text{Cl}$. Its bond will form at maximum distance and generate sp hybridization.

- * In diamond, every carbon makes the sigma bond. It has no empty spaces and don't show any displacement. So, it is very hard. Its bonding is covalent.

- * Graphite is soft, as layers can show displacement over the layer. So, it is attached through soft bonds and in comparison to diamond, it is soft.

- * Square planar is distortion of octahedral.

B_2H_6 : Borans are always in dimeric form.



• Raman → emission is observed

• NMR → absorption is observed

• But 'B' has three bonds.

Because it is sp^2 hybridized.

Two types of bonds are possible

Type I $\rightarrow 2c-2e^-$ bond (terminal bonds)

Type II \rightarrow Bridge hydrogens



$3c-2e^-$ system.

Bridge bonds also known as bent bonds.

Empty bond of boron act as e^- acceptor.

The point 1,2 act as e^- donor.

And form bent bond &

connect with all of three atoms.

Bridge bond: Bond length is larger than

the remaining bonds.

Two peaks are shown in NMR.

So, we can predict that there is a bridge

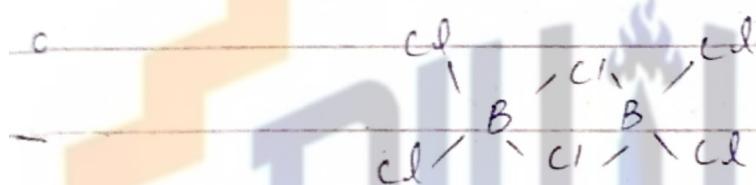
bond and we can observe that the second

structure is found in compound.

Shorter bond / Normal: If There is no 2 different peaks or peaks are of same line / structure. Then There is no bridging in The molecule. And struttur no. 1 is observed. (1.19 A°)

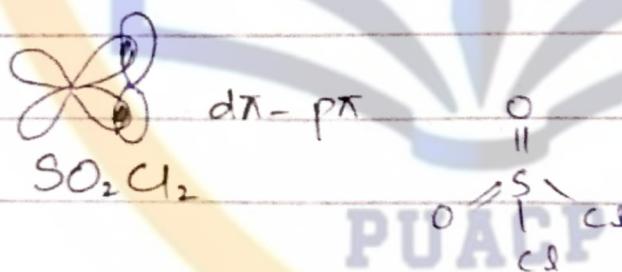
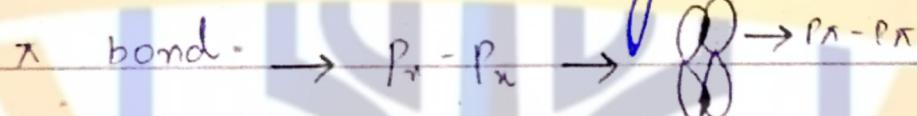
Stability To stable Themselves boranes show dimeric forms.

3c - 4e⁻ bond: B_2Cl_6



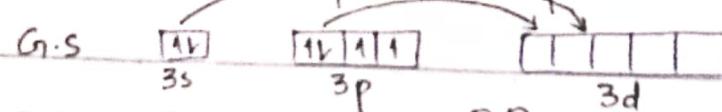
→ Coordinate covalent bond form.

$d\pi - p\pi$ bonding:

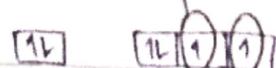


Bond with oxygen is $\text{d}\pi - \text{p}\pi$.

$$S = 1s^2, 2s^2, 2p^6, 3s^2, 3p^4, 3d^0$$



$$O = 1s^2, 2s^2, 2p^4$$



d -orbital of sulphur will combine with p -orbital of oxygen.
sideways overlapping occur

Overlapping occurs at same energy and oriented at same axis.

Ch: 02 Periodicity

In periodic table, H and He are simple atoms because they have only one orbital and behave simply, single orientation occurs and spherical in shape.

In periodic table, II period Li, Be, B, C, N, O, F, Ne has electro +ve and electro -ve nature. First half elements have electro +ve in nature and Second half elements are electro -ve in nature.

Period number tells us that how many shells are present in elements while column number tells us that how many valence e⁻'s are present in elements.

Anomaly exist in 2nd row.

Reason of Anomalous behaviour of head members or top members from rest of elements of its group:

- 1- 1st element of each group is very small in size than other elements of its group. Due to smaller radii, the electrostatic force of attraction b/w the protons and last shell e⁻'s is maximum.
- 2- These elements (head members) have high electronegativity than other members of their groups. Due to this reason, they can't be easily formed ionic compounds like other members of their group.
- 3- High charge to radius ratio
- 4- These elements also have only 4 valence orbitals ^(1s, 3p) available for bonding as compare to the other group elements. which have 9 valence orbitals (1s, 3p and 5d). So, top member can produce only 4 bonds while rest of the members may have higher valency than four. Due to this reason, boron can only form $[BF_4^-]$ while Aluminium can form $[AlF_6]^-$

Comparison of different theories:

→ VSEPR Theory:

- Tells us about direct valency.
- Covalent bond is directional in nature.
- Central atom and attached atoms are arranged at particular angles.
- Arrangement of orbitals around central atom.
- Provide information of molecular structure and their stability. Molecules acquire that structure in which angles are attained to keep the distance maximum.

→ It does not tell us about bond development.

⇒ VB Theory: Tells us about

- Development of bonds
- Bond strength
- Links b/w bonds and electronic configuration of atoms (No. of bonds link with valence shell e⁻s)

One extension of VBT is

Hybridization

• Excited state
electronic configuration

• Ground state
electronic configuration

⇒ It does not tell us more about structure of compounds.

⇒ CFT: Tells us about

- bonding in transition element complexes.

- colors → spectral lines information
- Magnetic properties

→ Spectral lines are produced due to the excitation and de-excitation of e^- s after splitting of d-orbitals when ligand approach to metal.



$t_{2g}^3 d_{3z^2}^{eg}$
 $d_{xy} d_{yz} d_{zx} t_{1g}$

d-orbital splittings

- ⇒ It does not tell more about relative energies of d-orbitals.
- Metal atom has uniform e⁻ density

around it (M) when ligand approach it they have their specific electric field and disturb metal's electron density.

→ Metal is electro+ve (electron giver) but on approaching ligands, it provides orbital that splits and form spectral lines by excitation and deexcitation.

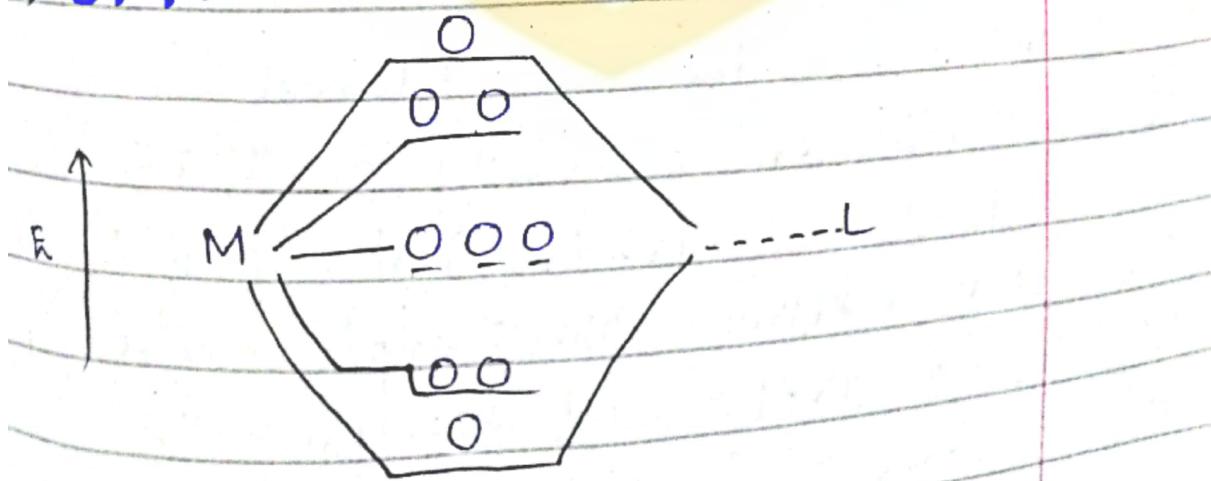
→ Orbitals involve are $d_{x^2-y^2}$ (on plane) and d_{z^2} (above and below the plane)

→ Provide limited info about energy (E. diff.)

→ It provides information about paramagnetism and diamagnetism also.

* It does not explain the way of overlapping.

→ LFT:



→ It provides detailed information about energy of orbitals.

→ It does not provide information about structure of complexes.

Chapter No: 02 Continue

2ND ROW ELEMENTS:

2nd row elements (Li, Be, B, C, N, O, F) show anomalous behaviour and differ from the rest of the elements of their respective groups. However, some elements like Boron, Nitrogen and Oxygen show anomaly to little extent, while Li, Be, C and F show anomalous (enough) difference in behavior both physical and chemical as compare to those of other group members.

⇒ Anomalous Behavior of Lithium:-

Lithium is the first element of group IA. It has an extremely small size and atomic radius. The last 's' orbital has one electron that experiences a high electrostatic attraction from the three protons present in the nucleus. Due

to this reason, polarization power of Li^+ is very high. These two reasons from the basis of anomalous behavior of Li.

1. Due to high polarization power of Li, it can form the covalent bond and this is its anomalous behavior because other alkali metals do not form covalent bond.

2. Lithium is quite hard as compare to other alkali metals like Na and K which are soft and can be cut down with a knife.

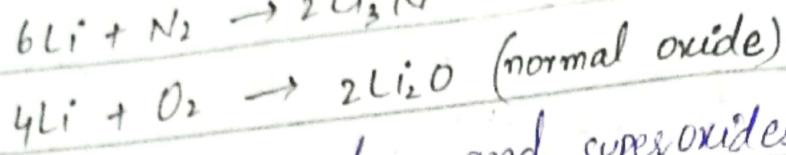
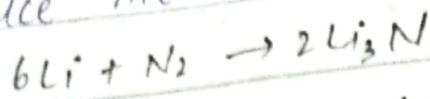
3. LiCl can form hydrates and can crystallize in the presence of moisture while other alkali metals can't form hydrates.

4. Li has high polarizing power due to higher charge/size ratio.

5. Li form complex compounds while rest of the alkali metals cannot do so.

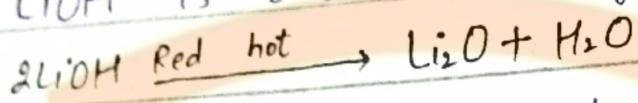
6. LiF is insoluble in water while rest of the alkali metal fluorides are soluble.

7- Li can react with N_2 and O_2 to produce nitrides and oxides.



Not form peroxides and superoxides.

8- LiOH is unstable at higher temp.



9- Li can react with carbon to produce Lithium carbide(Li_2C) while rest of the alkali metals cannot do so.

10- Lithium batteries are used in whole over the world. e.g= laptop, Mobile phones.

→ Anomalous Behavior of Beryllium:

Be is the top element of alkaline earth metals and due to its small size and ↑ charge/size ratio, it shows different properties than that of its group members which are as follows

1- Be produces covalent type hydrides while rest of the group II members form ionic or metallic hydrides.

2- Be also produce covalent halides while other elements produce ionic halides



3- Be metal donot react with acids

Like other alkaline earth metals do
it to produce Hydrogen.

4. BeSO_4 is fairly soluble in water

while other earth metal sulphates are
insoluble (because radius ratio does not
match) (lattice energy is required for solubility)

5. Be is resistant to complete oxidation
due to oxide layer formation at the
surface of bulk.

6. Its behaviour is amphoteric to little
extent and react with alkalis to
produce H_2 .



7. Be is fairly hard metal and
its hardness match with Fe almost.
Anomalous behavior of Carbon:

Carbon is the first member
of group 14 A and exhibits unique
properties that are distinctly different
from other members of its group. The
reason behind its different behaviour
is its extremely small size, highly
electronegative, increased ionization
enthalpy and absence of valence shell
and orbital. Main points of difference

* Every metal
does not
react with
acid.

who has
oxide
covering

are as follows:

1. Tetravalency: C is tetravalent and share its four electrons to produce four sigma bonds with monovalent atoms. C have the property to react with most elements of the periodic table especially with hydrogen, nitrogen, halogens, sulphur, oxygen, etc. To produce diverse variety of compounds. C can accommodate maximum four e⁻ pairs in valence shell as only s and p orbitals are available. Other members have a larger covalency due to the presence of d, orbital.

2. Catenation:- It is the property of an atom to link with similar atoms through covalent connections and long chains are produced. Among Group IV, only carbon has true property of catenation. Carbon can produce long chains which can span upto 70-80 carbon atoms. Only carbon can show this character due to high C-C bond energy.

3- Multiple bonding: Carbon can develop multiple bond with other (carbon or any hetero atom) to produce a variety of

unsaturated products:

4. High Ionization Energy: Carbon is purely non-metal and keeps \uparrow I.E which restrict it to develop ionic bonds. It is non-metal but inspite of it, one allotropic form of carbon shows conductivity. It is only non-metal which is conductor in graphite form.

5. Allotropy: Due to the catenation property carbon can exist in four allotropic forms:

(i) Diamond (ii) Graphite

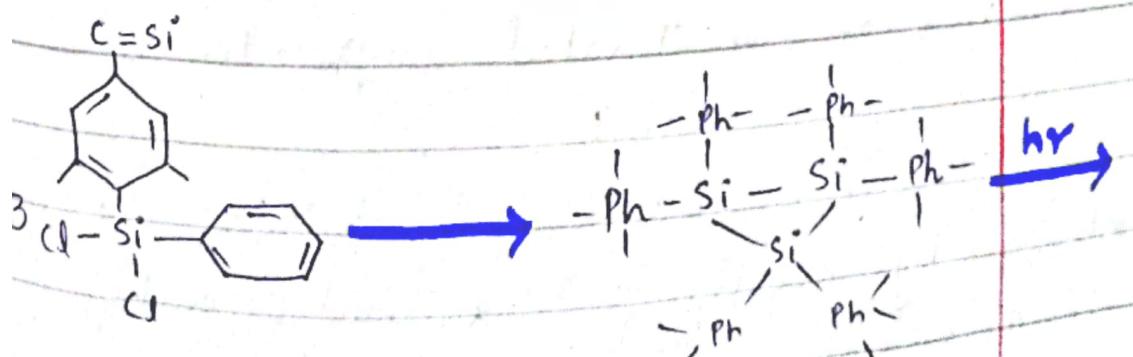
(iii) Lead (iv) Buckyballs (Fullerenes)

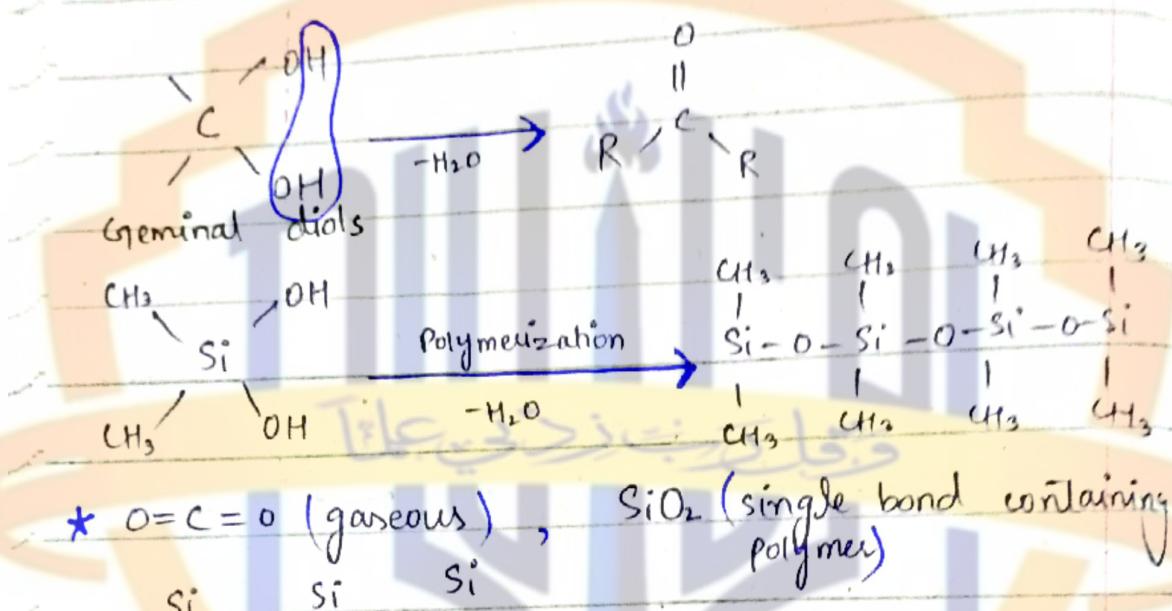
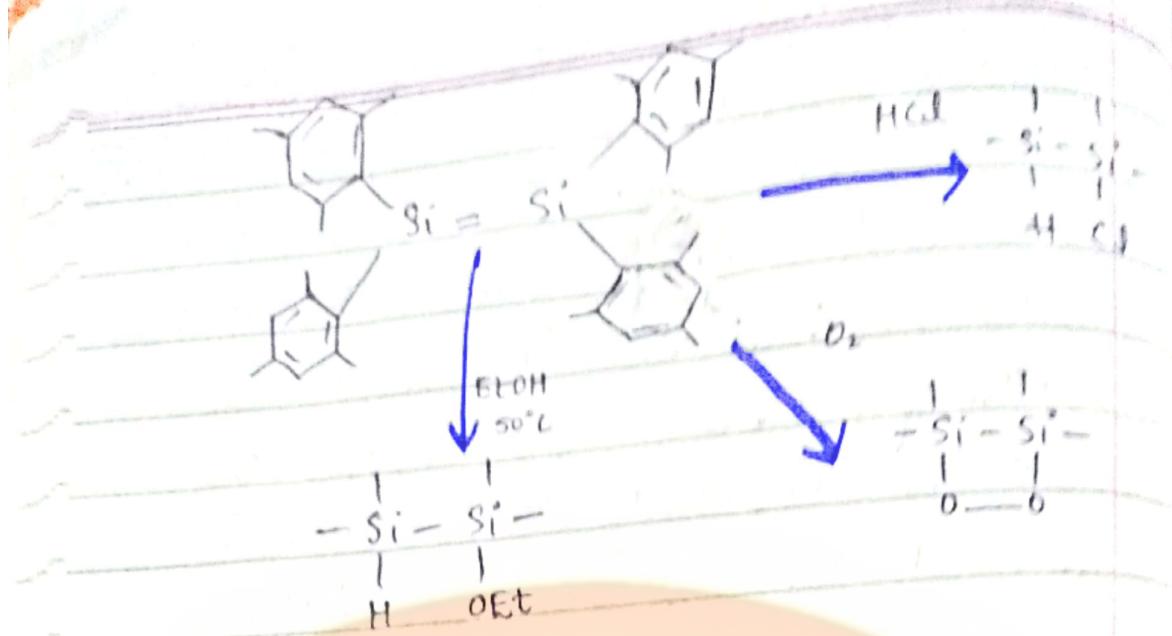
Anomalous behavior of oxygen and fluorine:

Use of p-orbital in π -bonding:

$\text{C}=\text{C}$ unsaturated compounds

π -bonds developed by sideways overlapping of p-orbitals. Carbon is essential element and cause production of unsaturated compound.





* Due to change in angle and bond length, the whole structure, color of silicon dioxide changes.

* These are slightly different from carbon compounds but also show some properties of unsaturated compounds.

Difference b/w :-

$C=C$

and

$Si=Si$

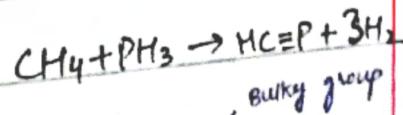
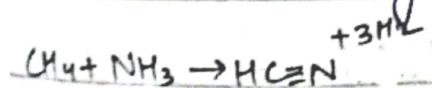
* Formed by overlap of $2p-2p$ orbital.	* Formed by overlap of $3p-3p$ orbital.
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<p>* 272 kJ/mol in size smaller, $\Psi_a \Psi_b$</p> <p>* overlap through more area and stronger bond.</p> <p>Nitrogen and Phosphorous</p> <p>P-orbital use in π-bonding</p> <p>* It exists in N_2 form in which it has two π-bonds and one sigma bonds.</p>	<p>* 105 kJ/mol</p> <p>* less area is used in overlapping and bond is softer comparatively.</p> <p>* It exists in P_4 form or in the form of red phosphorous while black phosphorous is most stable.</p>
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$$\text{N}_2 = 946 \text{ kJ/mol} \quad \text{P}_4 = 488 \text{ kJ/mol}^{-1}$$

Polymer = 800°C

- * Carbon can make bond with nitrogen in the form of cyanide ($\text{HC}\equiv\text{N}$) and shows more stability.
- * Carbon can make bond with phosphorous in the form of ($\text{HC}\equiv\text{P}$) and shows less stability.



P, As, Bi, Sb

