

1. CHEMICAL BOND
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2. LEWIS THEORY
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INTRODUCTION

LEWIS THEORY

VALENCE BOND THEORY

CRYSTAL FIELD THEORY

THREE CENTRED BOND MODEL

VALENCE BOND THEORY

Heitler and London developed this theory in 1927. Later, Pauling and Slater modified this theory (1931) to explain the directional nature of the covalent bond which predicts accurate geometry of the molecules. They further postulated that resonance structures should also be considered.

HEITLER – LONDON THEORY

This theory is based upon the pairing and the resultant neutralization of opposed electron spins.

POSTULATES

(1). In order for an atom to enter into chemical combination, it must have one or more unpaired electrons. The valency of a species is thus determined by the number of unpaired electrons which it has.

(2). Although participation in bond formation by paired electrons is formally ruled out, such electrons may be involved if they can be unpaired without the expenditure of the excessive energy.

(3). A chemical bond results in when two electrons are paired. For a stable bond formation, it is essential that the two electrons must have opposite spins.

PAULING – SLATER THEORY

POSTULATES

(1). The atoms which unite to form a molecule completely retain their identities in the resulting molecule.

(2). A covalent bond is formed by the overlap of atomic orbitals. If there are two atoms, each having unpaired electron, the atomic orbitals having unpaired electrons overlap to form covalent bond. The spins of the electrons are neutralized. If the atomic orbitals have parallel spins, repulsion will take place and no molecule will be formed.

(3). If the atomic orbitals are having more than one unpaired electron, multiple bond formation is possible. For example nitrogen molecule has triple covalent bond.

(4). The number of covalent bonds formed by an atom is equal to number of the unpaired electrons it has.

(5). The geometry of the molecules depends upon the directions of the overlapping orbitals.

(6). The strength of the covalent bond is proportional to the extent of the overlapping of the two atomic orbitals.

The extent of the overlap between a pair of atomic orbitals is given by the overlap integral:

$$S = \int \psi_A \psi_B dv$$

$\psi_A \psi_B$	The wave functions of the overlapping atomic orbitals.	
dv	An element of space over which the overlap occurs.	
S	Overlap integral	When "S" is positive, electronic charge is built up between the nuclei and stable bond results.
		When "S" is negative, electronic charge is reduced between the nuclei and repulsion between nuclei increases. Consequently the atoms move apart.
		When "S" is zero there is no net attraction or net repulsion.

(7). Overlapping takes place between orbitals of only those electrons, which take part in bond formation and not between orbitals of the other atoms.

(8). The overlapping axially will form a stronger bond between the two orbitals of the same energy contents.

(9). A spherically orbital, i.e., s - orbital does not show any directional preferences whereas non-spherical orbitals, viz. p, d, f etc. tend to form a bond in the direction of maximum electron density within the orbital, i.e., along their axes.

SOME QUALITATIVE FAILURES OF THE SIMPLE THEORIES CRITICISM AND COMPARISON OF SIMPLE MODELS

FAILURES OF VALENCE BOND THEORY

(1). It does not explain the formation of molecules such as PCl_5 , SF_6 and IF_7 in which the central atom is having 10, 12 and 14 electrons respectively instead of an octet of electrons.

(2). It did not explain the bonding in the electron deficient molecules like B_2H_6 ; in these molecules the central atoms have less electrons than the required octet of electrons.

(3). It did not explain the existence of paramagnetic molecules like NO , NO_2 and ClO_2 .

(4). It failed to explain the nature of attractive forces that would become operative when a covalent bond is formed.

(6). It failed to explain the geometry of molecules like H_2O , NH_3 etc.

(7). Theory only explains the formation of covalent bond in which the shared pair of electrons comes from two different atoms. However it offers no explanation for the formation of a co-ordinate covalent bond in which bond pair is donated by one of the bonded atoms.

(8). According to VBT, oxygen molecule should be diamagnetic, i.e., all the electrons present on it should be paired. Experimentally, the oxygen molecule has been found to be paramagnetic, indicating the presence of unpaired electrons on oxygen molecule.

(9). It fails to explain the odd electrons molecules or ions like H_2^+ ion in which no pairing of electrons occurs.

(10). For a particular molecule or ion, one has to write several canonical structures and even then one is not sure that the true structure which is only a resonance hybrid of these structures. Thus it is not possible to write one structure, which offers explanation for the structural features of the molecule or ion.

(11). It fails to explain the bonding in metals and intermetallic compounds.

(12). It fails to explain the presence of partial ionic character of a covalent bond.

(13). In the AB_5 type molecule which of d – orbitals (d_z^2 or $d_{x^2-y^2}$) is used and why. This theory has no explanation.

(14). This theory does not decide about the cis or trans shape of AB_4E_2 . It is VSEPR theory that explains trans shape with two lone pairs of electrons at axial positions.

FAILURES OF VSEPR THEORY

(1). The theory is as simple as Lewis theory. It does not explain how electrons avoid each other repulsion as they are in the same domain (i.e., electrons in a bond). It does not explain the relative strengths of the different covalent bonds.

(2). It is largely restricted to main group species. It can be used for transition element compounds where the "nd" orbital is either empty or filled but partially filled "nd" orbital affects stereochemistry. This effect can be explained better by using CFT.

EXAMPLE:

Complexes of transition elements having d^8 are square planar but according to Gillespie – Nyholm theory it should be tetrahedral.

(3). It fails for most of the 14 – electrons systems. It does not provide a correct structure for XeF_6 or $[SbF_6]^{3-}$ species (distorted octahedral).

(4). It does not explain the shapes of molecules, which have very polar bonds. Li_2O should have the same structure like water but in fact, Li_2O is linear.

(5). It is unable to explain the shapes of molecules having extensive delocalized π – electrons systems e.g., $[CH_3]^-$ should be trigonal pyramidal structure but it is planar.

(6). It fails to make distinction among the electrons present in the different type of orbitals i.e., s, p, d and f of valence shell.

(7). It does not explain the shape of certain compounds having inert pair of electrons.

EXAMPLE:

AX_6E has six bond pair and one lone pair so it should be distorted octahedral but it has regular geometry.

(8). It fails to predict exact bond angles in molecules such as H_2O and NH_3 having distorted geometries.

(9). It fails to explain the difference in bond angles of series of compounds (NH_3 , PH_3 , AsH_3 , SbH_3) in which central atoms are different but surrounding atoms are same and electron pairs are also same.

SIMILARITIES BETWEEN VBT AND MOT

- (1). Valence bond theory and molecular orbital theory use VARIATION PRINCIPLE.
VARIATION PRINCIPLE
The wavefunction which gives the lowest energy of the system is close to accurate wavefunction of the system.
- (2). The electron distribution for a given molecule is similar.
- (3). The both theories deal with the normal covalent bond. There is sharing of electron density and concentration of electron density between the nuclei.
- (4). The sigma and pi bond can be distinguished in both the quantum mechanical treatments.
- (5). In both the theories, atomic orbitals of the atoms must overlap and should have appropriate symmetry about the molecular axis to form a bond.
- (6). Both the theories postulate that covalent bond has directional character.

DIFFERENCES BETWEEN VBT AND MOT

- (1). Valence bond theory does not provide a clear picture of the energy changes involved during bond formation. The MOT gives minor changes during bond formation, which gives information about the contribution of covalent and ionic character.
 - (2). VBT is useful in predicting the symmetry of the molecules using the idea of hybridization.
- EXAMPLE:** sp^3 hybridized structure belong to tetrahedral symmetry (point group T_d).
 d^2sp^3 hybridized structure belong to octahedral symmetry (point group O_h).
- (3). In quantum mechanical treatment of the hydrogen molecule, different mathematical calculations are used.
 - (4). VBT uses concept of resonance, the MOT uses the idea of delocalization. The term resonance energy is used in VBT and term delocalization energy is used MOT.
 - (5). In quantum mechanics, the valence bond theory deals with the partial ionic character as:

$$\Phi_{\text{molecule}} = \Phi_{\text{covalent}} + \lambda' \Phi_{\text{ionic}}$$

Where λ' refers to the degree to which the partial ionic character is possible.

In quantum mechanics, the molecular orbital theory deals with the partial ionic character as:

$$\sigma = N (\psi_A + \psi_B)$$

Where ψ_A and ψ_B are the wavefunctions for the atomic orbitals of two atoms say H – atoms. The N is the normalizing constant.

(6). MOT explains the electronic transitions that occur in the molecules in the visible and ultraviolet regions. The excited states are not easily explained by the valence bond theory.

(7). The paramagnetic character of O_2 molecule can be easily explained by the MOT but VBT is not able to explain such properties of the molecules.

(8). VBT does not explain the donor and acceptor relationship in the co – ordinate covalent bond properly but MOT explains bonds in terms of bond order.

(9). VBT does not consider the formation of odd electron molecules or ions such as H_2^+ , NO etc. but MOT explains them properly by giving concept of fractional bond orders.

(10). The M.Os are formed by LCAO – approximation method. In VBT the A.Os give an interatomic orbital by the combination of the wavefunctions of the unpaired electrons of the two separate orbitals.

(11). In MOT the A.Os lose their individual identity. In VBT the A.O's retain their individual character to large extent.

(12). The M.Os are polycentric in MOT , but A.Os are monocentric in VBT.

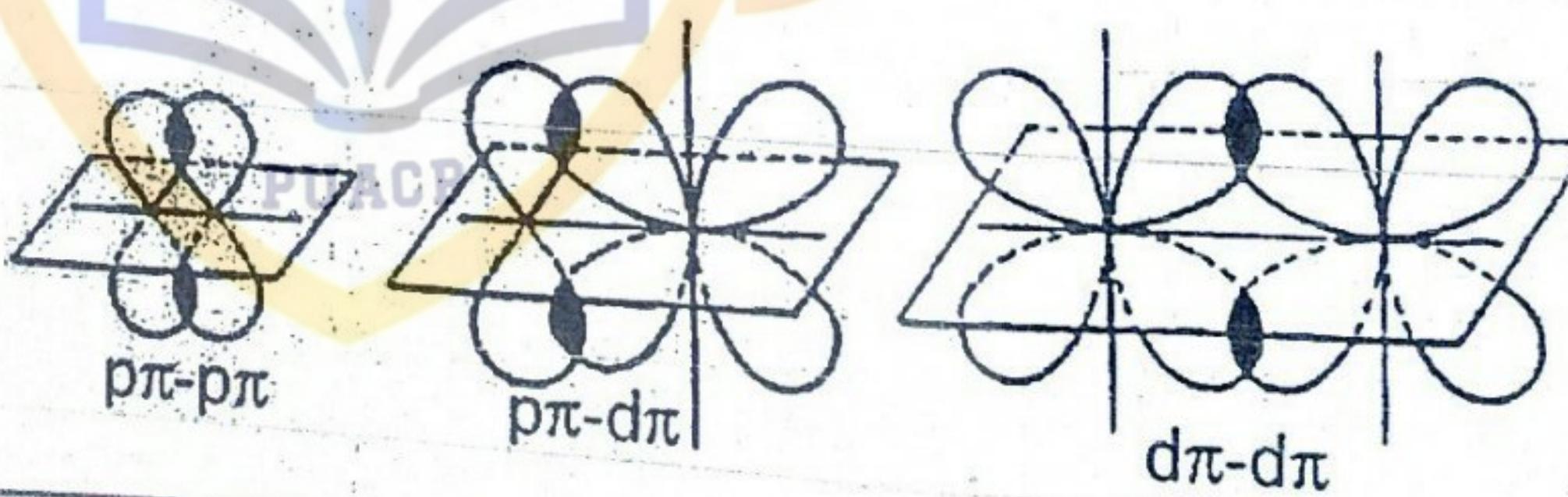
$d\pi - p\pi$ BONDS

DEFINITION

A π - bond is formed by the sideways overlap of two half filled co-planar p - orbitals or a p and a d - orbitals or two d - orbitals, in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei.

PERMITTED COMBINATIONS OF ATOMIC ORBITALS FROM SYMMETRY POINT OF VIEW

FIRST ORBITAL	SECOND ORBITAL	TYPE OF MOLECULAR ORBITAL FORMED
s	s p_x $d_{x^2-y^2}$ d_{z^2}	σ
p_x	s p_x $d_{x^2-y^2}$ d_{z^2}	σ
p_y	p_y d_{xy}	π
d_z	p_z d_{xz}	π
$d_{x^2-y^2}$	s p_x $d_{x^2-y^2}$ d_{z^2}	σ
d_{z^2}	s p_x $d_{x^2-y^2}$ d_{z^2}	σ
d_{xy}	p_y d_{xy}	π
d_{xz}	p_z d_{xz}	π
d_{yz}	d_{yz}	δ (delta molecular orbital)



PROPERTIES

- (1). It should be made clear that a π - bond is formed between two atoms only when they are already bonded with a sigma bond except C_2 .
- (2). It has a nodal plane.
- (3). Electrons in pi bond are less tightly than electrons of sigma bond. Pi bonds are usually weaker than sigma bonds.
- (4). From the perspective of quantum mechanics, this bond's weakness is explained by significantly less overlap between the component p-orbitals or d - orbitals due to their parallel orientation.

$d\pi - p\pi$ BONDING

The 'd' orbitals are also involved in pi bonding in the case of hypervalence. The $d\pi - p\pi$ is common for the third period elements (specially Si - Cl) and is not important for the elements of the fourth and higher periods. The $d\pi - p\pi$ is more favourable than the $p\pi - p\pi$ bond for the atoms of third and higher periods.

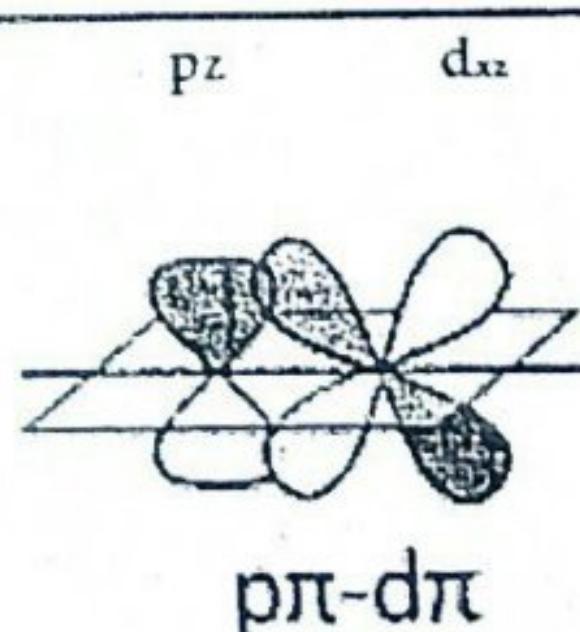
~~It is effective if the size of d - orbital is similar to the size of p - orbital. On moving across a period the size of the atom and the size of the d - orbitals decreases from Si to Cl. The decrease in the size of 3d orbitals in this series leads to the stronger $d\pi - p\pi$ bond.~~

EFFECTS OF $d\pi - p\pi$

- (1). The $d\pi - p\pi$ bonding shortens the bond length and increases the bond angle.
- (2). It changes the energy of t_{2g} orbitals of the metal. The each of the t_{2g} orbitals forms two π - M.O.s. This results in the splitting of t_{2g} orbitals into two sets triply - degenerate M.O.s.
- (3). The π - bonding in complexes throws more light on the order of the ligands in spectrochemical series.

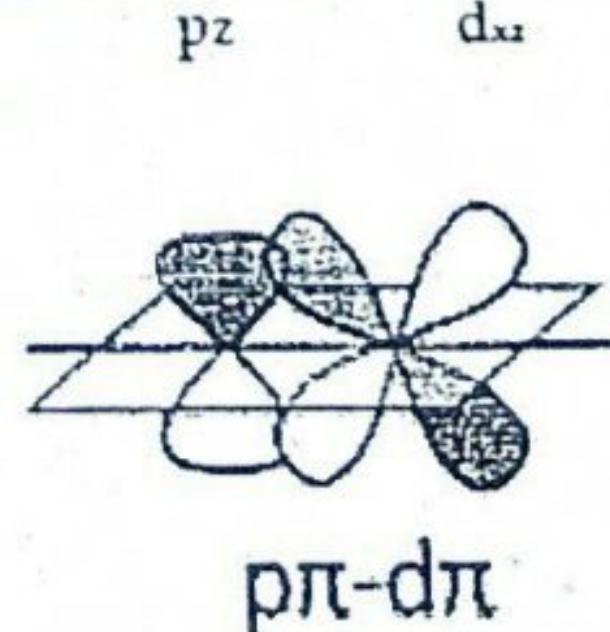
EXAMPLE

There is combination of metal d_{xz} and p_z orbital of carbon monoxide in metal carbonyls



EXAMPLE

There is combination of metal d_{xz} and p_z orbital of ethene in the $K[PtCl_3(CH_2=CH_2)]$.



THE EXPERIMENTAL EVIDENCE FOR $d\pi - p\pi$ BONDING

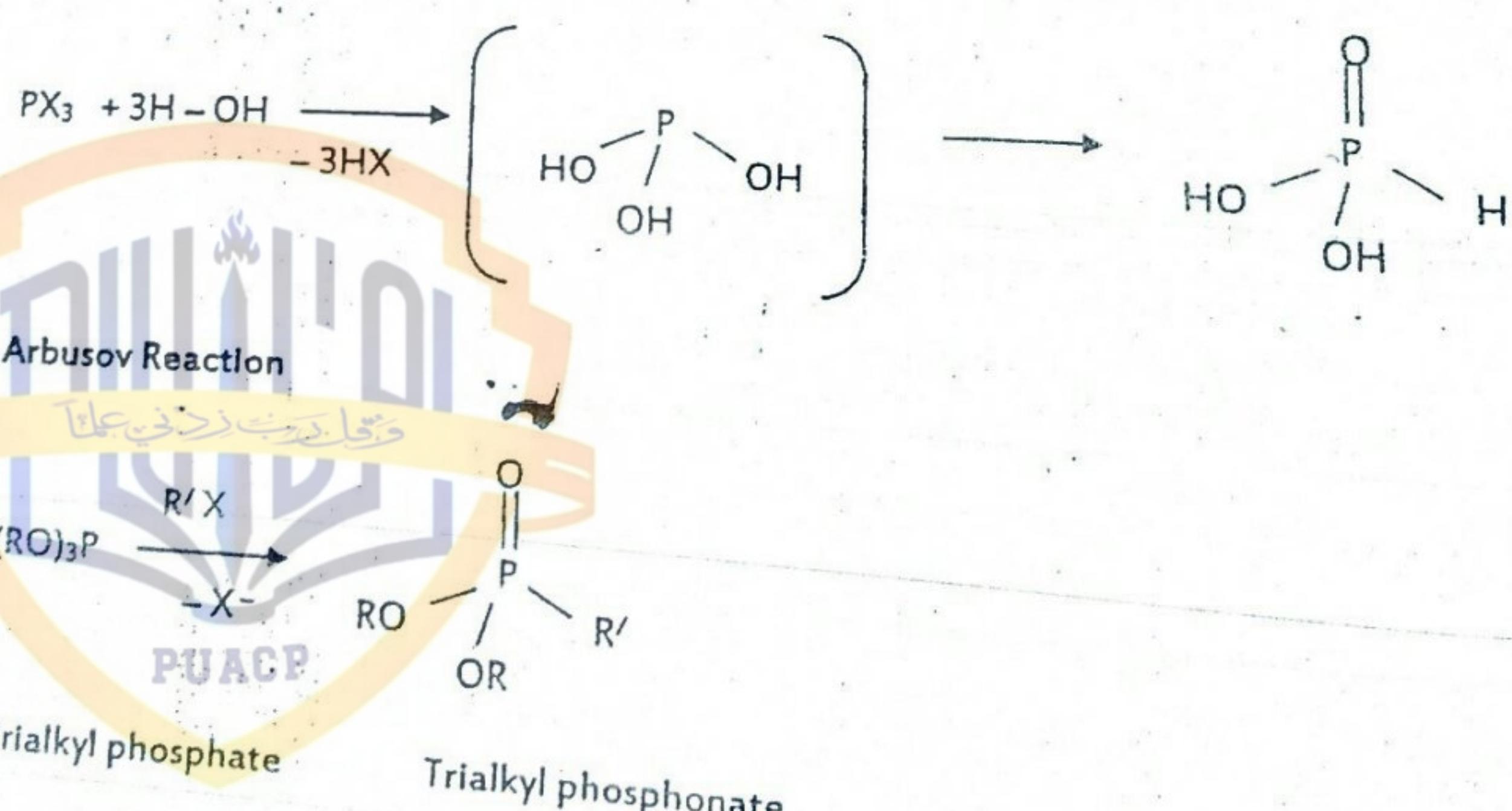
(1). THE PHOSPHORUS – OXYGEN ($P = O$) BOND IN PHOSPHORYL COMPOUNDS

A sigma bond is detected when two atoms at a distance considerably shorter than the sum of their van der Waal's radii. A pi bond is detected by bond shortening or strengthening, stabilization of a charge distribution etc.

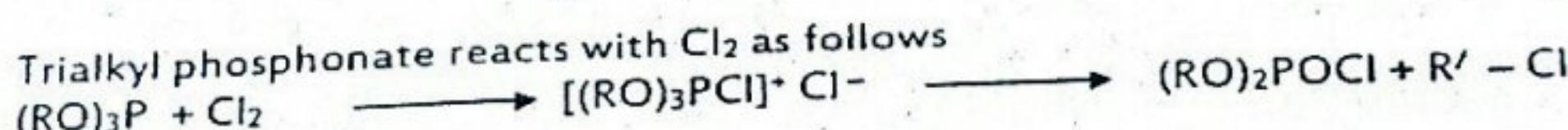
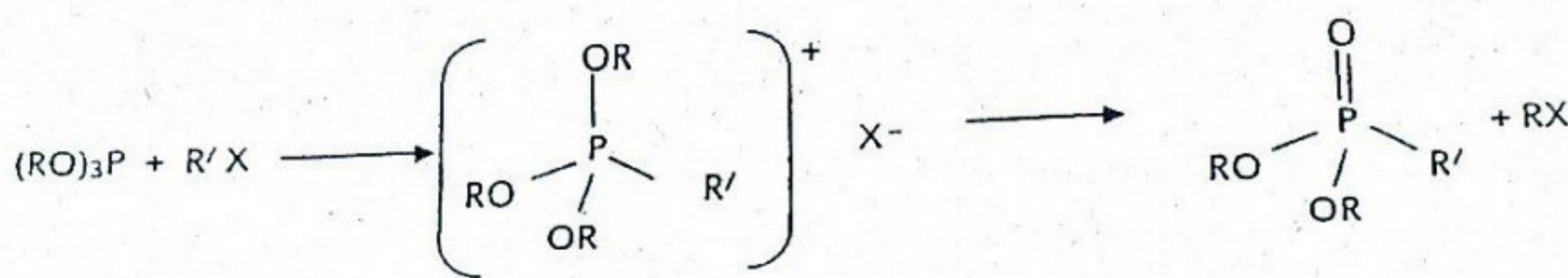
Oxidation of aliphatic phosphines	Oxidation of aromatic phosphines	Oxidation of aliphatic amines
<p>Most tertiary phosphines undergo oxidation to phosphine oxide.</p> $2R_3P + O_2 \longrightarrow 2R_3PO$ <p>Aliphatic triphosphine must be protected from air. Phosphine oxides are thermally stable e.g., $(CH_3)_3P = O$ is stable below $700^\circ C$. It is not reduced with Na metal</p> <p>Reasons</p> <ol style="list-style-type: none"> 1) No $\beta - H$ 2) $d\pi - p\pi$ bonding 	<p>Triaryl amine phosphines are stable but also undergo oxidation.</p> $2Ph_3P + [O] \xrightarrow[\text{or } KMnO_4]{HNO_3} 2Ph_3PO$ <p>It is also stable below $700^\circ C$ and not reduced by sodium metal.</p>	<p>There is no need to protect aliphatic amines from the atmosphere. Trialkyl amines are oxidized to trialkyl amine oxide with formic acid as follows:</p> $R_3N + HCOOH + [O] \xrightarrow{-CO} [R_3NOH]^+ OH^-$ $[R_3NOH]^+ OH^- \longrightarrow R_3NO + H_2O$ <p>Trialkyl amine oxide decomposes on heating as follows:</p> $(CH_3 - CH_2)_3 - NO \xrightarrow{\Delta} (CH_3 - CH_2)_2NOH + H_2C = CH_2$ <p>Reasons</p> <ol style="list-style-type: none"> 1) $\beta - H$ is available 2) No $d\pi - p\pi$ bonding

(2). PREPARATION OF PHOSPHOROUS ACID.

Lower phosphorous acids are prepared from trihalides due to the tendency of "P" to form $P \rightarrow O$ or $P = P$ bond.



In the presence of equimolar amount of R/X



(3)

Comparison of phosphine oxides with Amine oxides

Triethyl phosphine oxide $(CH_3 - CH_2)_3PO$	Triethyl amine oxide $(CH_3)_3NO$
Dipole moment = 4.37 D	Dipole moment = 5.02D
They does not form hydrates	They form hydrates e.g., $(CH_3)_3NO \cdot H_2O$
They are less basic	They are more basic
They have $d\pi - p\pi$ bonding $(C_2H_5)_3P^+ \rightarrow O^- \longleftrightarrow (C_2H_5)_3P = O$ (I) (II)	They have dative bond and single structure $(CH_3)_3N \rightarrow O$
This the cause of decrease in the dipole moment.	They do not have $d\pi - p\pi$ bonding. There is no "d" orbital in nitrogen atom.
P to O bond is stronger in $R_3P = O$ and stable	N to O bond has no extra stability
Bond dissociation energy is 500 – 600 kJ/mol. It is greater than the P to O single bond.	Bond dissociation energy is 200 – 300 kJ/mol. It is similar to N to O single bond.

(4). IR SPECTRA

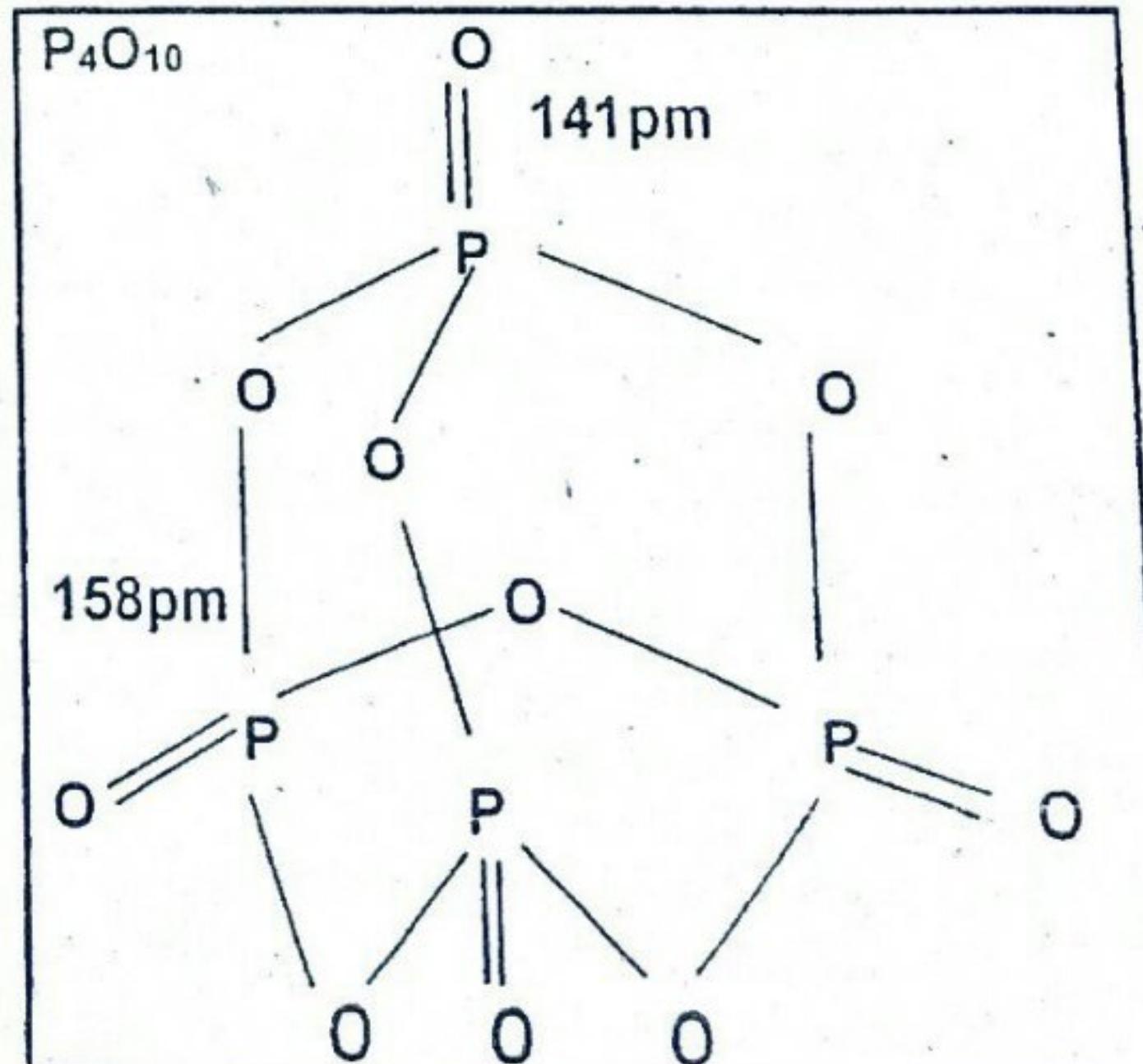
The highest stretching frequency (\bar{v}) of $P=O$ is in F_3PO and lowest is in Cl_3PO . There is sigma bond between O and P but O forms $d\pi - p\pi$ with P using its p – orbital in the overlap of d – orbital of P. This results in the strengthening of $P = O$ bond and increase in stretching frequency of $P = O$ bond.

(5). BOND LENGTH

The bond length of P to O bond in phosphorus compounds corresponds to $P = O$.

$$\begin{aligned} \text{No. of P – O single bonds} &= 12 \\ \text{Bond length of P – O bond} &= 158 \text{ pm} \\ \text{No. of P = O double bonds} &= 4 \\ \text{Bond length of P = O bond} &= 141 \text{ pm} \\ \\ \text{Ratio} &= \frac{\text{P = O bond length}}{\text{P – O Single bond length}} \\ &= \frac{141 \text{ pm}}{158 \text{ pm}} = 0.89 \end{aligned}$$

This ratio is almost same as $C=C$ to $C-C$ or $C=O$ to $C-O$.



(6). Comparison of phosphorus ylids and ammonium ylids

COMPARISON OF PHOSPHORUS YLIDS AND AMMONIUM YLIDS	
$R_3P^+ - CH_2^- \longleftrightarrow R_3P = CH_2$	$R_3N^+ - CH_2^-$
They are isoelectronic with phosphine oxide. They are stable. They are not quite basic to attract proton from water. They are not dissolved in water unless strong acid is present.	They are not stable. They are quite basic to attract proton from water. They are dissolved in water.

 $d\pi - p\pi$ BONDING or π -BONDING In Heavier Congeners

The $d\pi - p\pi$ bonding is accepted with uncertainty in phosphorus and sulphur compounds. The problems faced in phosphorus and sulphur systems during the formation of $d\pi - p\pi$ bonding are :

- 1). Large promotion energy for promotion of electron from np to $(n-1)d$ in the excited state of electronic configuration.
 - 2). Diffuse character of π -bonds.
- These problems are larger in the heavier congeners like As, Sb, Se, Te etc. The small phosphorus atom can form π -bonds with metals. The softness in ligand can be equated with its ability to accept electron from soft metal ions in $d\pi - d\pi$ bonding (back bonds).

WALSH DIAGRAMS

Walsh diagram is a graph between orbital binding energy and metrical parameter like bond angle or bond length. It was introduced by A.D Walsh in 1953. It is an achievement of Molecular Orbital Theory. It explains

Geometry of small molecule [Particular bond angle of the molecule]

Spectra of small molecule [Transition of localized electrons]

SALIENT FEATURES

- 1). Orbital undergoes a change in energy with the change in the bond angle. One can predict the equilibrium bond angle for a molecule.
- 2). Walsh diagram can be plotted for a molecule using the Hartree – Fock orbital energies.
- 3). Usually core orbital ("1s" for B, C, N, O, F, Ne) are not included in the Walsh Diagram. They are low in energy and do not change much with change in the bond angle. Only valence orbitals are included in the Walsh Diagram.
- 4). The amount of stabilization or destabilization of the M.Os is based on the amount of increase or decrease in the in-phase overlap of the A.Os used to make each molecular orbital.
- 5). It is necessary to calculate the electrons that will populate the orbitals in the Walsh Diagram. Then one can find the electronic configuration which will provide the lowest overall energy (the most stable geometry).
- 6). AH_2 molecules with 4 valence electrons should be linear in their ground state. AH_2 molecule containing 5 – 8 valence electrons should be bent in their ground state. Energy trend for B.MOs is opposite to ABMOs.

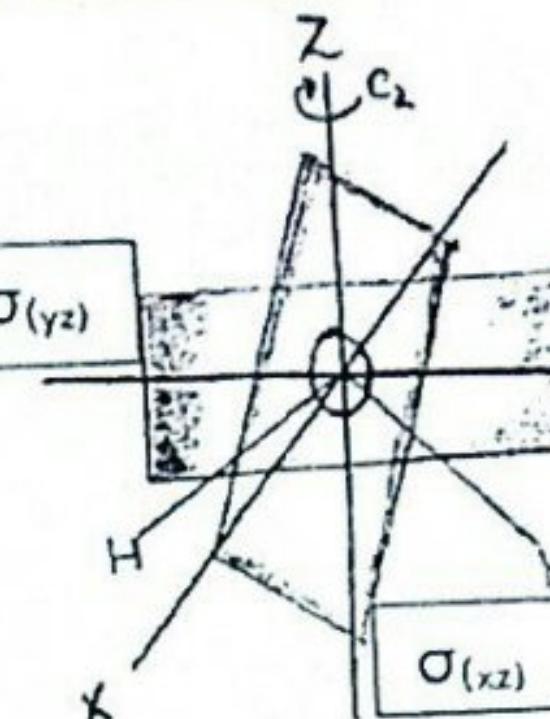
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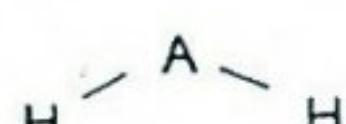
WALSH DIAGRAMS FOR TRIATOMIC MOLECULES
CORRELATION OF THE ATOMIC ORBITALS FOR BENT AND LINEAR MOLECULES

Consider AH_2 type molecules
 Symmetries of A.Os and LGOs in Point Group C_{2v} (Bent)

SYMMETRY OPERATIONS					A.Os AND LGOs
Mulliken Labels	E	C_2	σ_v or $\sigma_{(xz)}$	σ_v or $\sigma_{(yz)}$	
a_1	1	1	1	1	$2\text{p}_z \quad 2\text{s}$ $1\text{s}+1\text{s}$
a_2	1	1	-1	-1	
b_1	1	-1	1	-1	2p_x
b_2	1	-1	-1	1	2p_y $1\text{s}-1\text{s}$



Bent or Angular

 $\text{H}_2\text{O}, \text{NH}_2^-$ 

Explanation

${}^8\text{O} = 1\text{s}^2, 2\text{s}^2, 2\text{p}^2_x, 2\text{p}^1_y, 2\text{p}^1_z$	Atomic orbitals of central atom "A"
Atomic orbitals of central atom "A"	
${}^1\text{H} = 1\text{s}^1$ 1) Ligand Group Orbitals of two "H" atoms	
$\text{H} + \text{H} [1\text{s}+1\text{s}]$	

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Symmetries of A.Os and LGOs In Point Group D_{oh} (Linear)

<ul style="list-style-type: none"> If A.O or M.O has centre of inversion (centre of symmetry) then it is gerade = g (Symmetric w.r.t center of inversion) If A.O or M.O has no centre of inversion (centre of symmetry) then it is ungerade = u (Antiyymmetric w.r.t center of inversion) [Gerade = even Ungerade = Unven] σ_{BMO} has no node and σ_{ABMO} has a node. π_{BMO} has one nodal plane and π_{ABMO} has a nodal plane and a node. 	<p>C_∞</p> <p>σ_h</p> <p>σ_g</p> <p>π</p> <p>A</p> <p>H</p> <p>H</p> <p>X</p> <p>Z</p>
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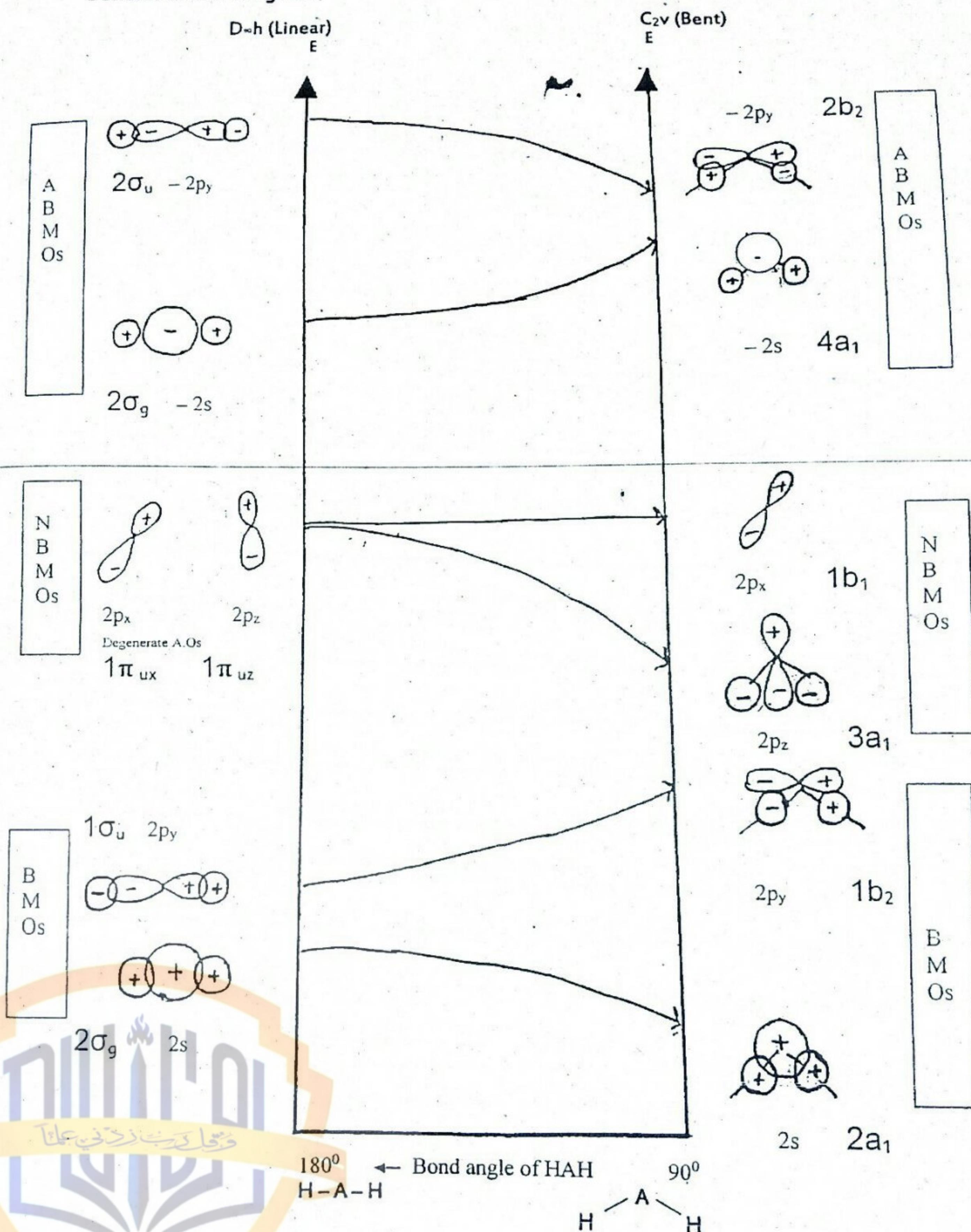
Linear BeH₂

H-A-H

Explanation

${}^4\text{Be} = 1s^2, 2s^2, 2p_x^0, 2p_y^0, 2p_z^0$ <p>Atomic orbitals of central atom "A"</p> <p>σ_g</p> <p>$2s$</p> <p>$2p_x$</p> <p>$2p_y$</p> <p>$2p_z$</p> <p>X</p> <p>Z</p>	<p>Atomic orbitals of central atom "A"</p> <p>σ_u</p> <p>$2p_z$</p> <p>X</p> <p>Z</p>
${}_1\text{H} = 1s^1$ <p>1) Ligand Group Orbitals of two "H" atoms</p> <p>$\text{H} + \text{H} [1s + 1s]$</p> <p>$\sigma_g$</p> <p>$\sigma_g$</p> <p>$1s$</p> <p>$\text{H} + \text{H} [1s + 1s]$</p> <p>$\sigma_g$</p> <p>$X$</p> <p>$Z$</p>	<p>2) Ligand Group Orbitals of two "H" atoms</p> <p>$\text{H} - \text{H} [1s - 1s]$</p> <p>$\sigma_u$</p> <p>$\sigma_u$</p> <p>$1s$</p> <p>$\text{H} - \text{H} [1s - 1s]$</p> <p>$\sigma_u$</p> <p>$X$</p> <p>$Z$</p>

General Walsh Diagram



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Energy Discussion

$2a_1$ has lesser energy than $2\sigma_g$ due to greater overlap (more tightly bound) between "2s" A.O of central atom and LGOs.

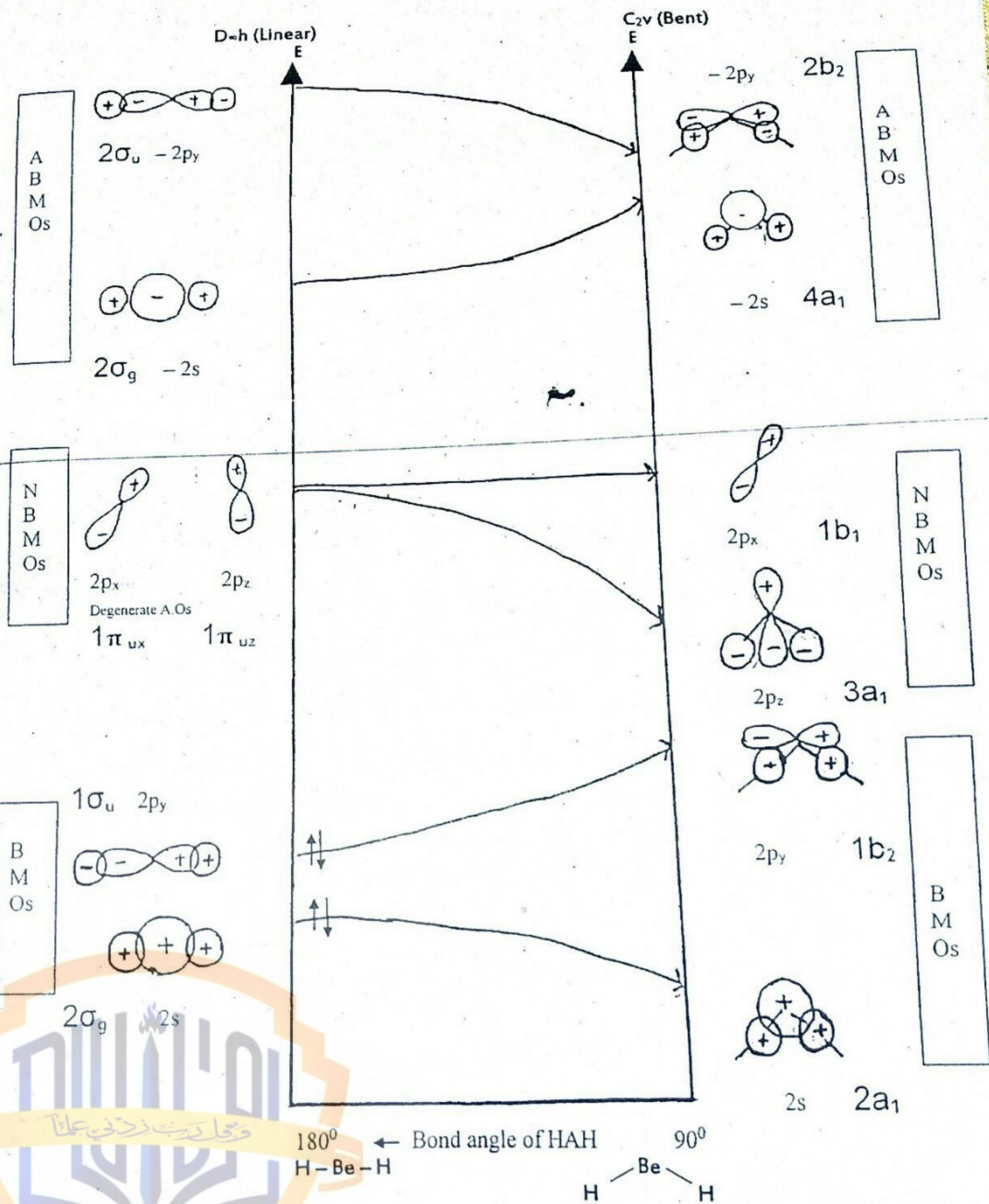
$1b_1$ has higher energy than $1\sigma_u$ due to poor overlap (less tightly bound) between "2p_y" A.O of central atom and LGOs.

There is less decrease in the energy of $2a_1$ and there is more increase in the energy of $1b_1$.

$3a_1$ is more stabilized. $1b_1$ is neither stabilized nor destabilized.

Explanation of Symmetry Symbols

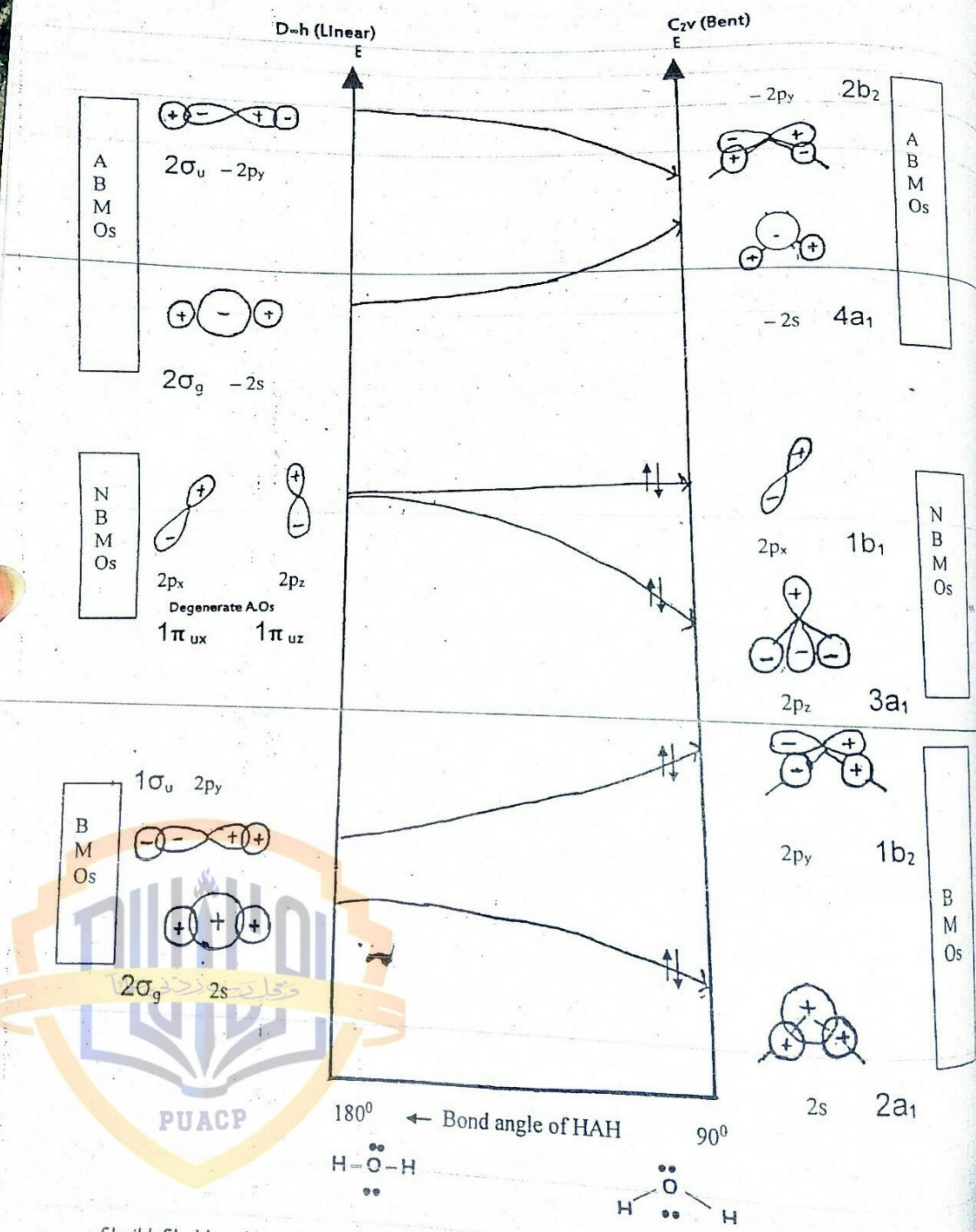
Symbol	Meaning
+1	Symmetric behaviour
-1	Antisymmetric behaviour
a ₁ , e, b ₂	Mulliken Labels
a	Symmetric w.r.t principal axis of rotation
b	Symmetric w.r.t second axis of rotation or σ_v
g	Symmetric w.r.t centre of inversion (i)
u	Antisymmetric w.r.t centre of inversion (i)
e	Two dimensional or doubly degenerate
t	Three dimensional or triply degenerate
Prime (')	Symmetric w.r.t σ_h
Double Prime (")	Antisymmetric w.r.t σ_h
$2C_3 = C_3^1 \text{ and } C_3^2$	$C_3^1 =$ Symmetric w.r.t clockwise rotation by an angle of $360^\circ/3$ $C_3^2 =$ Symmetric w.r.t anticlockwise rotation by an angle of $360^\circ/3$
S_3	Symmetric w.r.t rotation by C_3 then $\sigma_h \perp C_3$
D_n	Molecule has $nC_2 \perp C_n$

Walsh Diagram For BeH_2 

Stable Ground State Electronic Configuration for the geometry of high symmetry(Actual VSEPR Shape) = $\text{BeH}_2 [2\sigma_g^2 \ 1\sigma_u^2]$

Unstable Ground State Electronic Configuration for the geometry of low symmetry(Distorted shape) = $\text{BeH}_2 [2a_1^2 \ 1b_2^2]$

Walsh Diagram For H_2O



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Stable Ground State Electronic Configuration for the geometry of high symmetry(Actual VSEPR Shape) = H_2O [$2a_1^2$ $1b_2^2$ $3a_1^2$ $1b_1^2$]

Unstable Ground State Electronic Configuration for the geometry of low symmetry(Distorted shape) = H_2O [$2\sigma_g^2$ $1\sigma_u^2$ $1\pi^2_{u_x}$ $1\pi^2_{u_z}$]

WALSH DIAGRAMS FOR TETRATOMIC MOLECULES

CORRELATION OF THE ATOMIC ORBITALS FOR Trigonal Planar AND Triangular Pyramidal MOLECULES

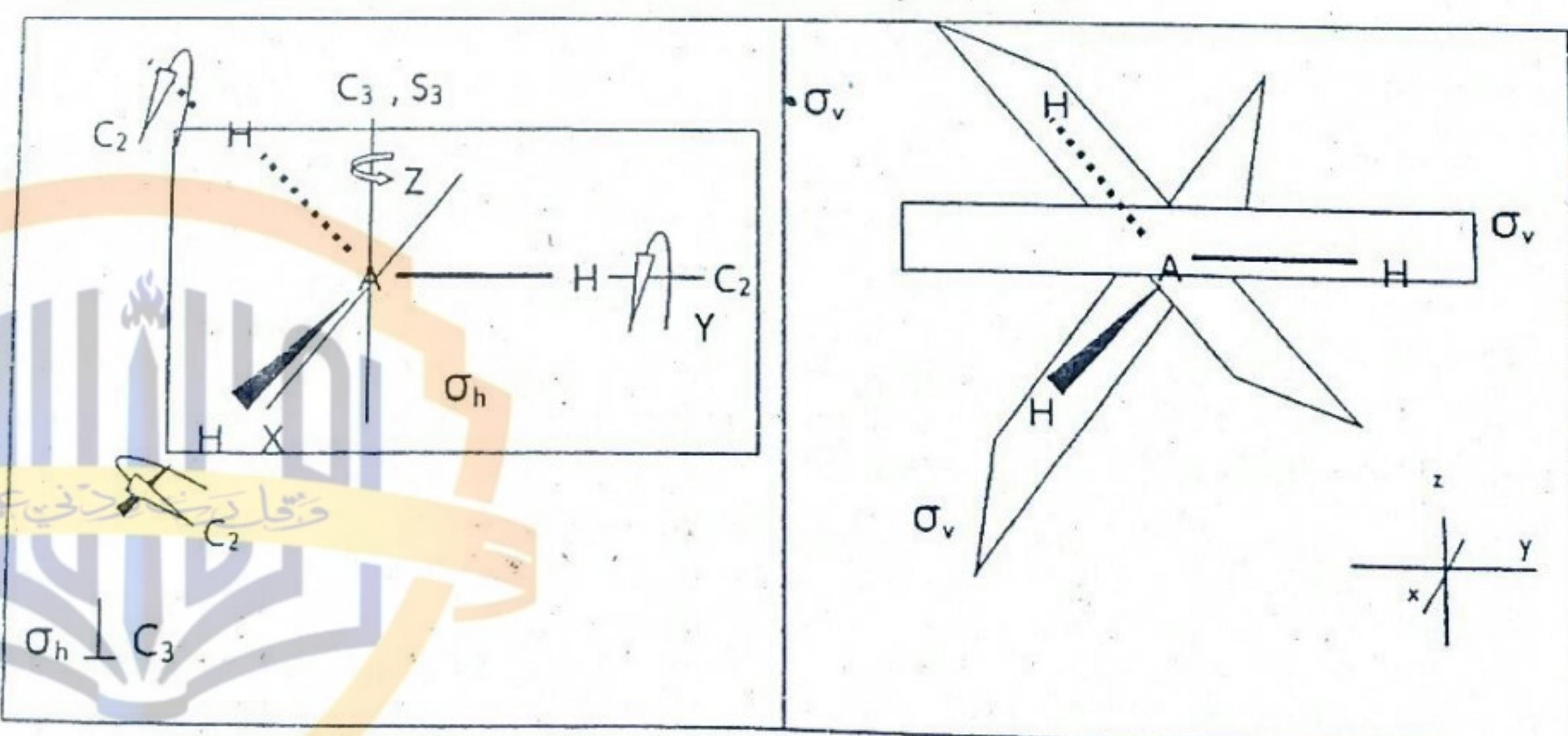
Symmetries of A.Os and LGOs In Point Group D_3h (Trigonal Planar)

SYMMETRY OPERATIONS Trigonal Planar Molecule of Point Group D_3h							A.Os AND LGOs
Mulliken Labels	E	$2C_3$	$3C_2$	σ_h	$3\sigma_v$	$2S_3$	
a'_1	1	1	1	1	1	1	$2s$ $1s+1s+1s$
a'_2	1	1	-1	1	-1	1	
e'	2	-1	0	2	-1	0	$2p_x$ $2p_y$ $1s-1s+1s$ $1s+1s-1s$
a''_1	1	1	1	-1	-1	-1	
a''_2	1	1	-1	-1	-1	1	$2p_z$
e''	2	-1	0	-2	1	0	

Trigonal planar Molecule [BH_3 or BF_3]

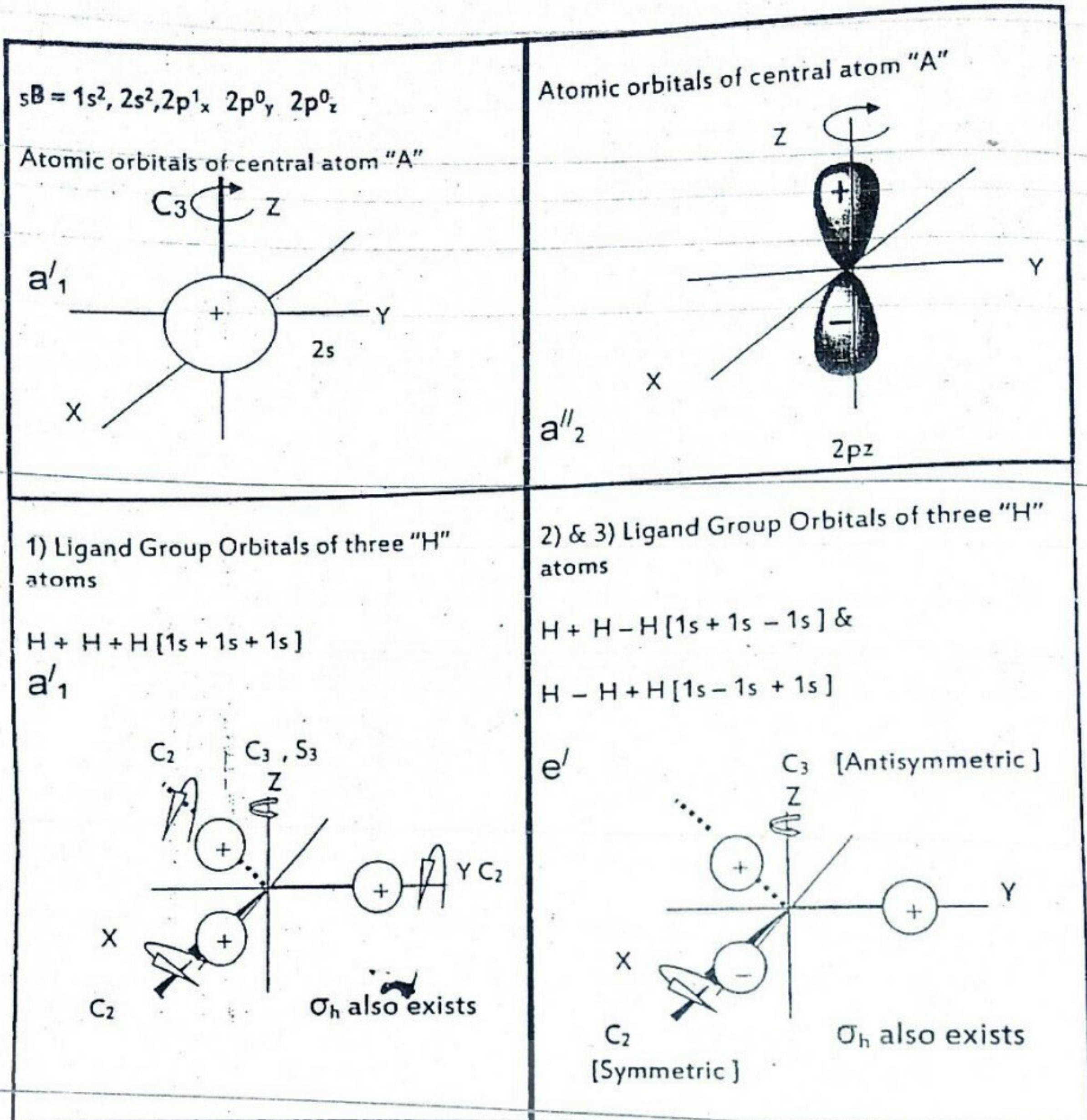
Symmetry Operations

Explanation



Sheikh Shahbaz Ali

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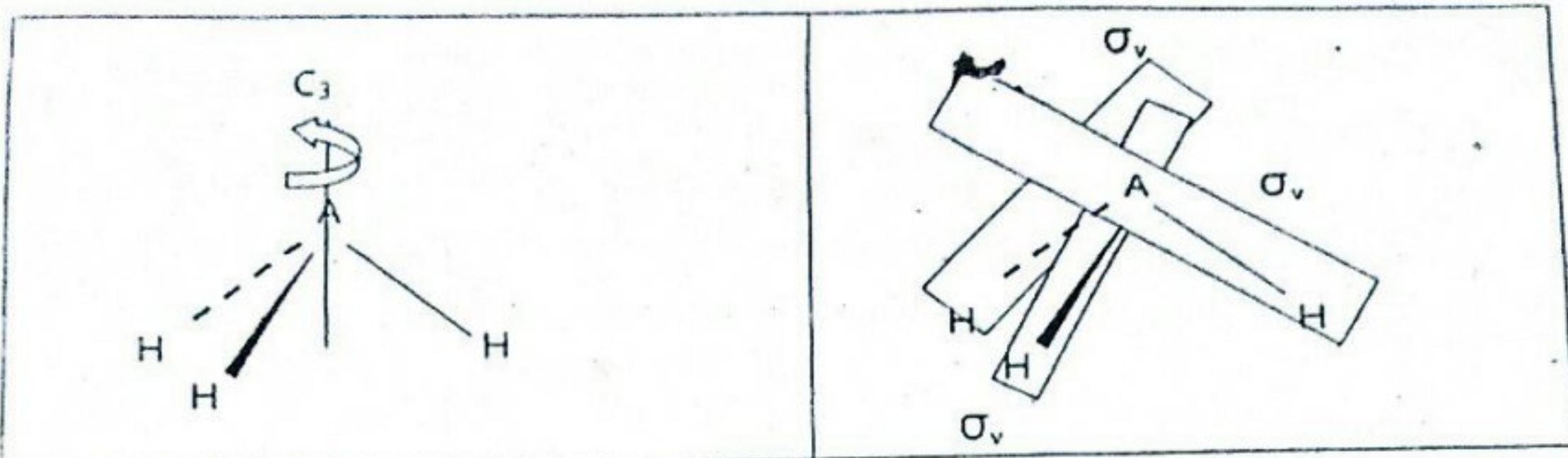
Consider AH_3 type molecules Triangular pyramidal Molecule [NH_3 or NF_3]
 Symmetries of AOs and LGOs In Point Group C_3v (Triangular pyramidal)

SYMMETRY OPERATIONS				AOs AND LGOs		
Mulliken Labels	E	$2C_3$	$3\sigma_v$			
a_1	1	1	1	$2p_z$	$2s$	$1s+1s+1s$
a_2	1	1	-1			
e	2	-1	0	$2p_x$	$2p_y$	$1s-1s+1s$
						$1s+1s-1s$

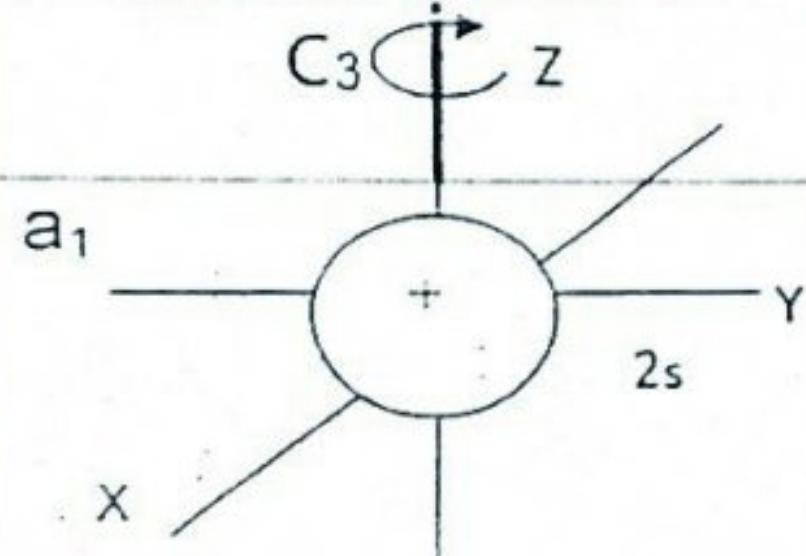
Triangular pyramidal Molecule [NH₃ or NF₃]

Symmetry Operations

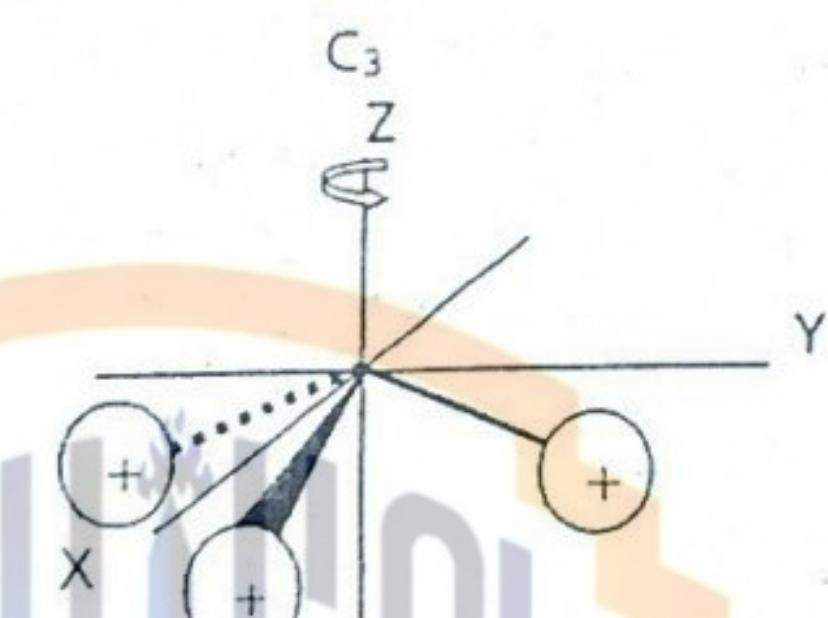
Explanation

 ${}^7\text{N} = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^1_z$

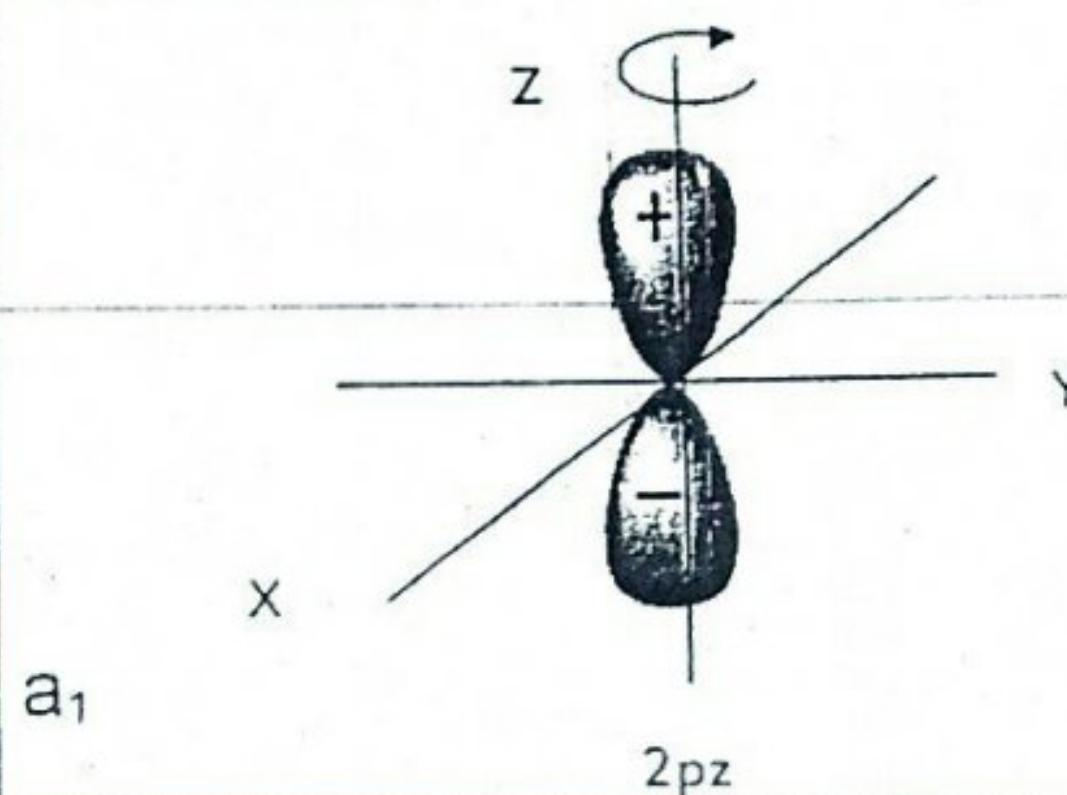
Atomic orbitals of central atom "A"



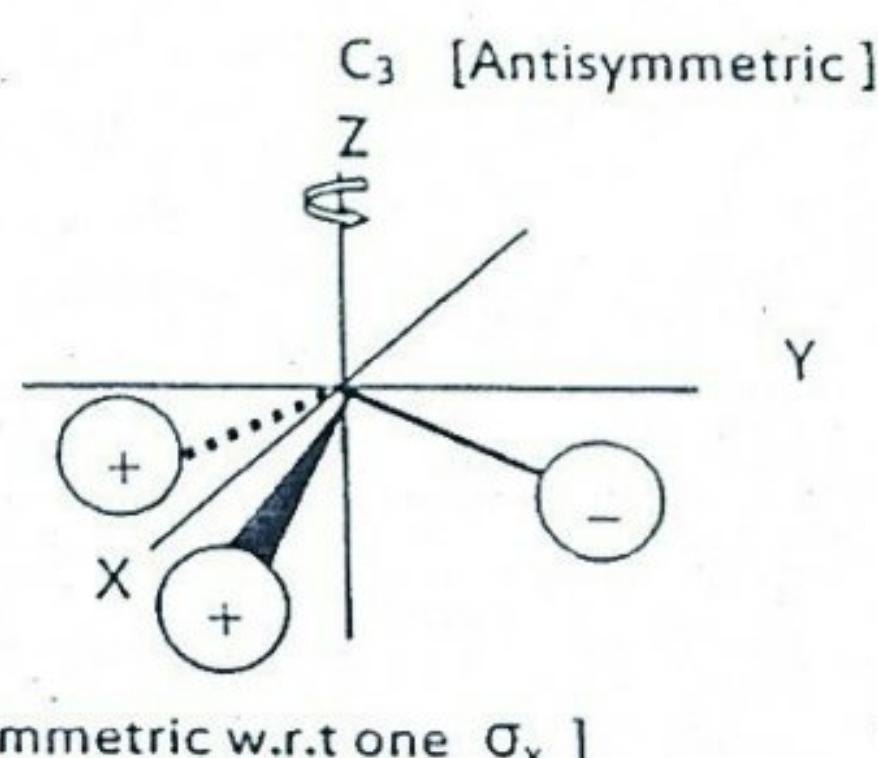
1) Ligand Group Orbitals of three "H" atoms

 $\text{H} + \text{H} + \text{H} [1s + 1s + 1s]$ a_1 

Atomic orbitals of central atom "A"

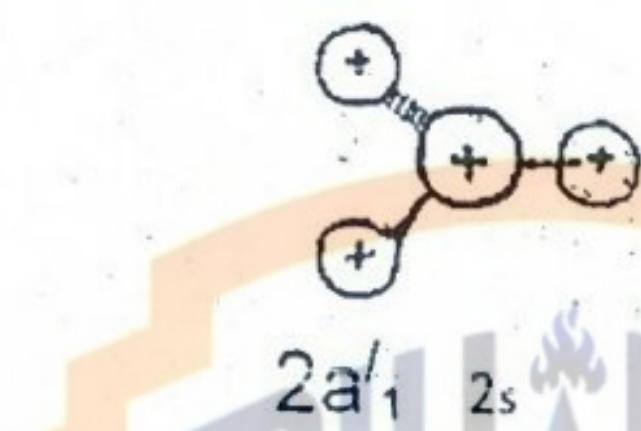
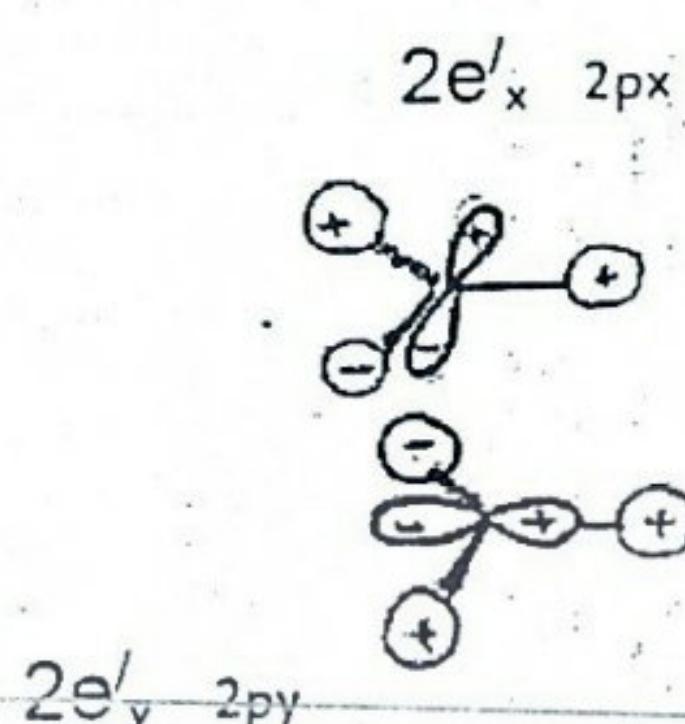
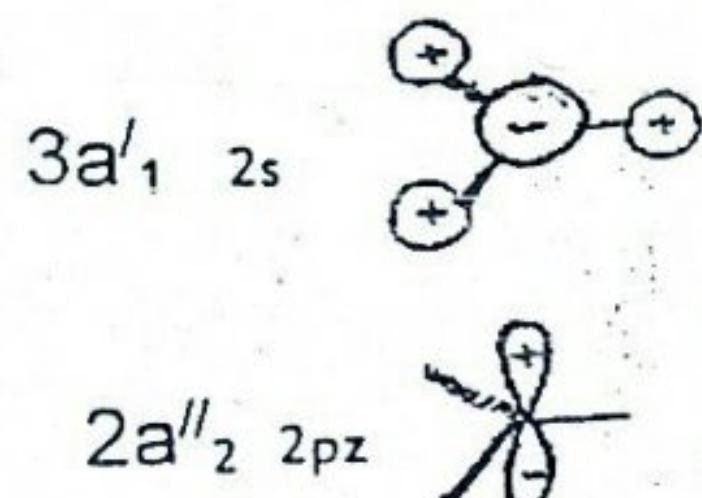
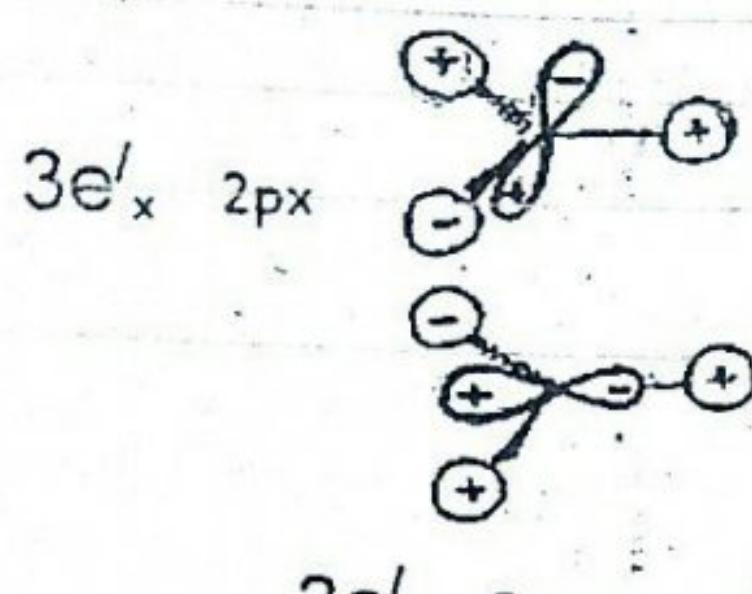


2) & 3) Ligand Group Orbitals of three "H" atoms

 $\text{H} + \text{H} - \text{H} [1s + 1s - 1s] &$ $\text{H} - \text{H} + \text{H} [1s - 1s + 1s]$ e 

General Walsh Diagram For AH_3 Molecule

D_{3h} (Trigonal planar)
E

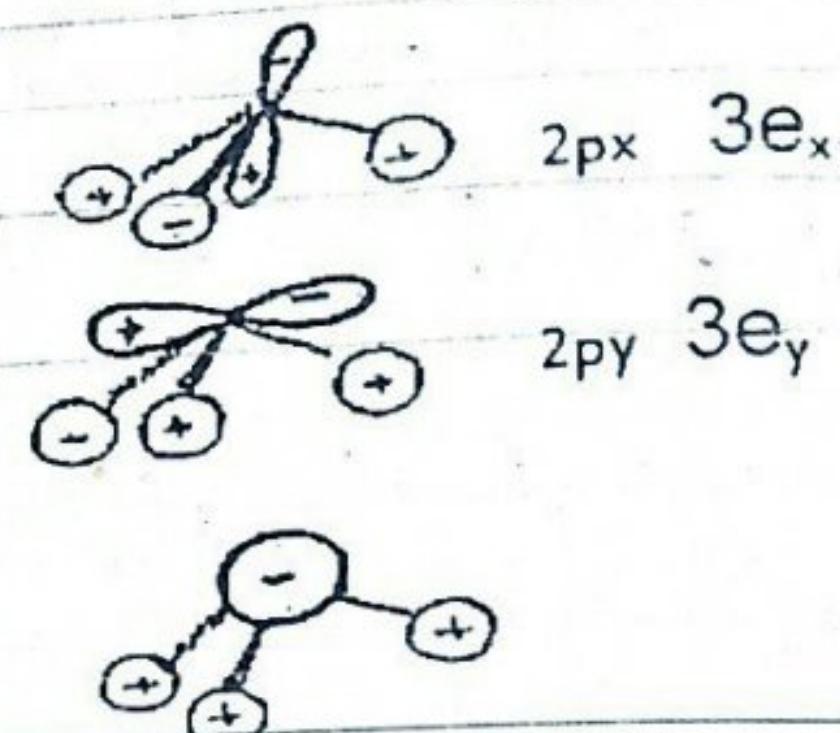


120° ← Bond angle of HAH

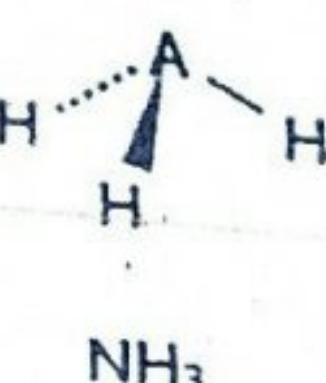
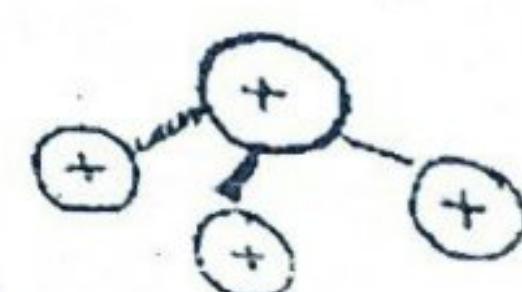
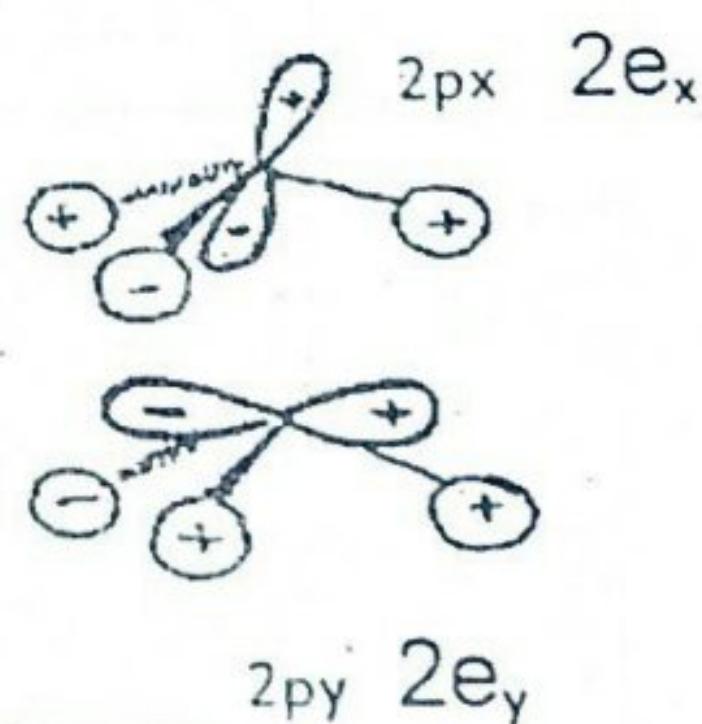
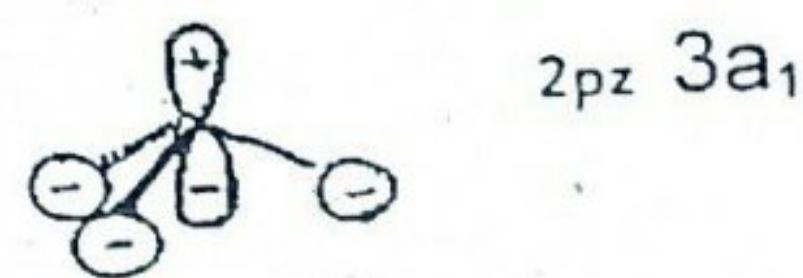
H—A—H

BH_3

C_{3v} (Triangular pyramidal)
E



4a₁ 2s



A
B
M
Os

N
B
M
Os

B
M
Os

Energy Discussion

$2a'_1$ has greater energy than $2a_1$ due to smaller overlap.

$2e'_y$ and $2e'_x$ have equal energy(doubly degenerate).

$2e_y$ and $2e_x$ have equal energy(doubly degenerate).

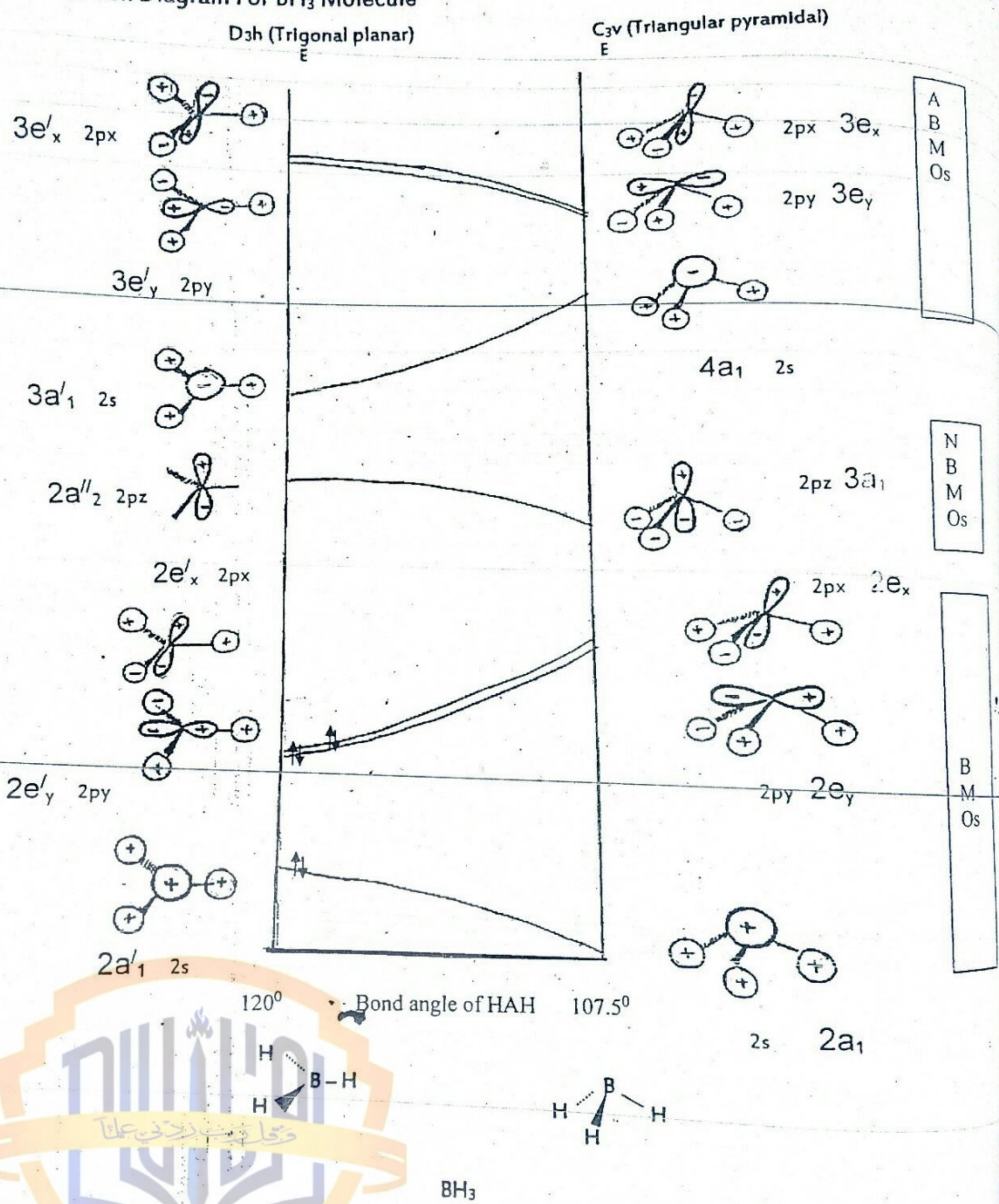
$2e'_y$ and $2e'_x$ have lesser energy than $2e_y$ and $2e_x$ due to greater overlap.

$2a''_2$ is nonbonding M.O for the Trigonal planar molecule.

$3a_1$ nonbonding M.O for the Trigonal pyramidal molecule but $2p_z$ of central atom has same symmetry as LGO that is a_1 . There is interaction and lead to decrease in energy.
Energy trend for B.MOs is opposite to ABMOs.



Walsh Diagram For BH_3 Molecule

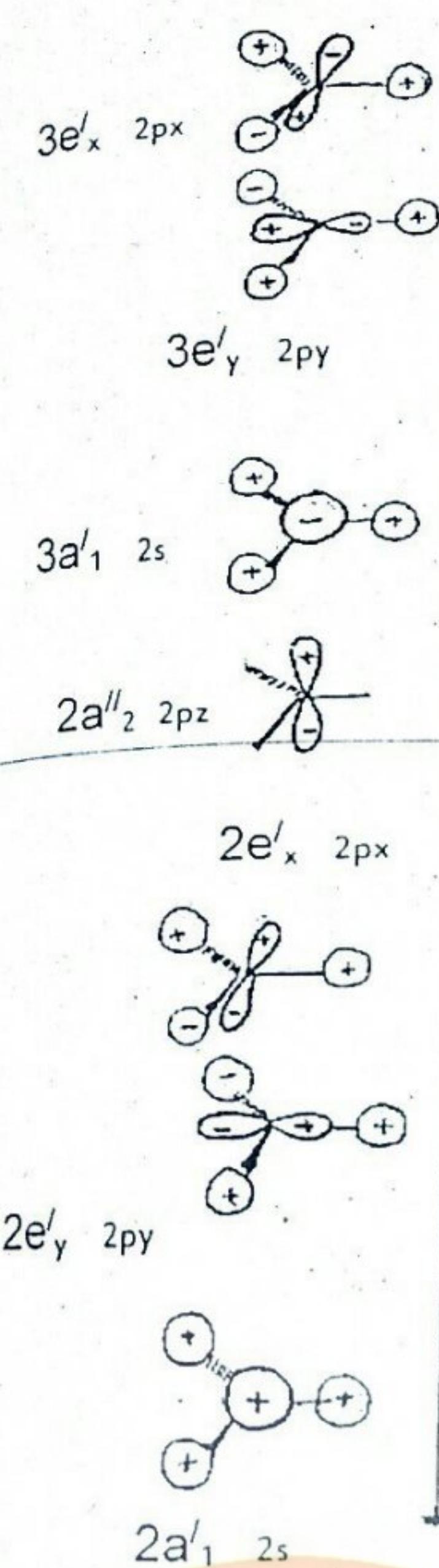


Stable Ground State Electronic Configuration for the geometry of high symmetry (Actual VSEPR Shape) = BH_3 [$2a'_1{}^2$ $2e'_y{}^2$ = $2e'_x{}^2$]

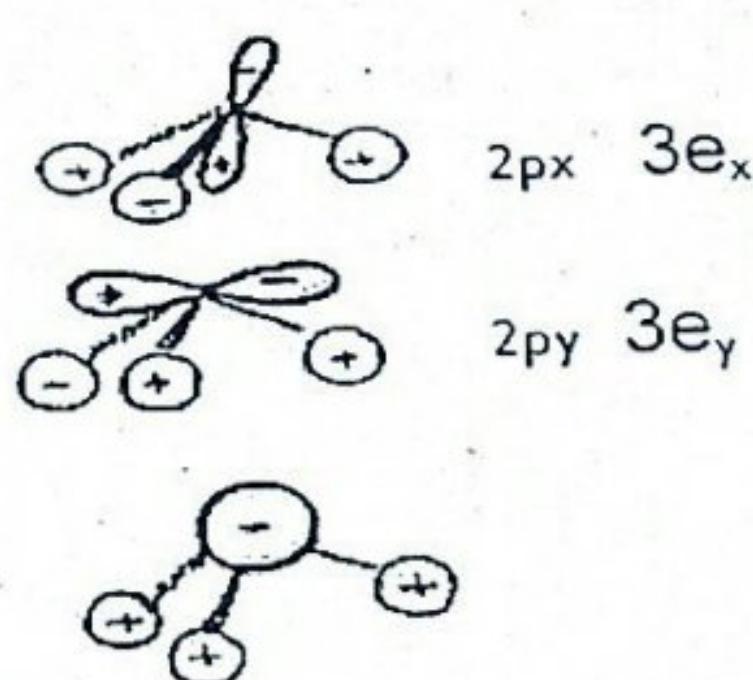
Unstable Ground State Electronic Configuration for the geometry of low symmetry (Distorted shape) = BH_3 [$2a_1{}^2$ $2e_y{}^2$ = $2e_x{}^2$ $3a_1{}^2$]

Walsh Diagram For NH₃ Molecule

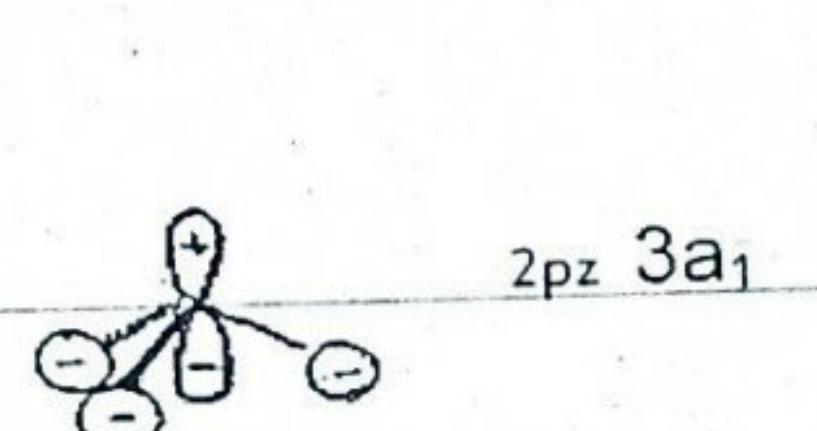
D_{3h} (Trigonal planar)
E



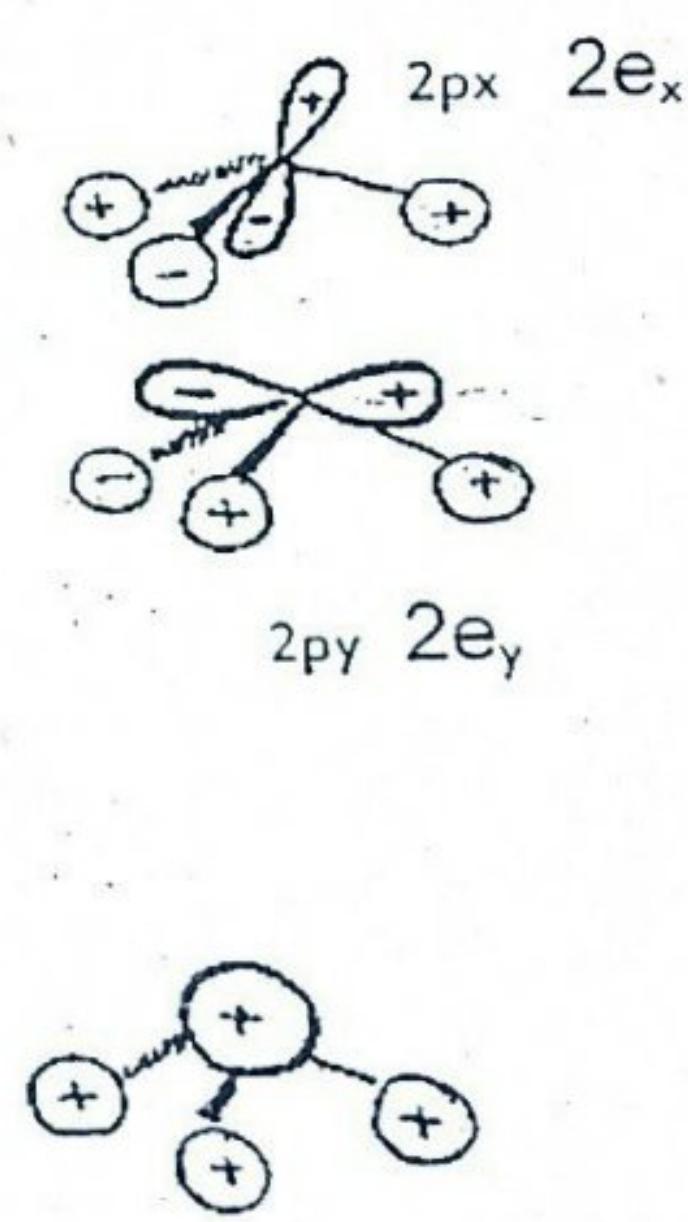
C_{3v} (Triangular pyramidal)
E



A
B
M
Os



N
B
M
Os



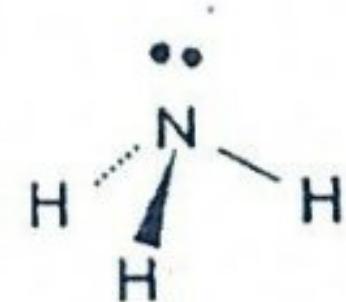
B
M
Os

120°

Bond angle of HAH

107.5°

BH₃



Stable Ground State Electronic Configuration for the geometry of high symmetry (Actual VSEPR Shape) = NH₃ [2a₁² 2e_y² = 2e_x² 3a₁²]

Unstable Ground State Electronic Configuration for the geometry of low symmetry (Distorted shape) = NH₃ [2a'₁² 2e'_y² = 2e'_x² 2a''₂²]

Chem - 406

INORGANIC CHEMISTRY

Special theory - I

B.S(Hons) - Semester VII

CHAPTER #2

PERIODICITY

SYLLABUS

- First and second row anomalies
- The use of d - orbitals by non - metals
- Reactivity and d - orbitals participation
- The use of p - orbitals in the pi - bonding
- Periodic anomalies of non - metals
- Periodic anomalies of post - transition metals



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کالج فوٹو سٹیپٹ
نرگس بلاک 511-B ٹلکت ناں کراچی

ITALICS - GASES, BOLD = LIQUIDS, NORMAL = SOLIDS.

MODERN PERIODIC TABLE

	VIIIA or O	2He	10Ne	18Ar	36Kr	54Xe	86Rn	118Uuo
17	VIIA		<i>19F</i>	<i>17Cl</i>	35Br	<i>53I</i>	85At	<i>117Uus</i>
16	VIA	8O	16S	34Se	52Te	84Po	<i>116Uuh</i>	
15	VA		<i>7N</i>	<i>15P</i>	<i>33As</i>	<i>51Sb</i>	83Bi	
14	IVA	<i>6C</i>	<i>14Si</i>	32Ge	<i>50Sn</i>	<i>82Pb</i>	<i>114Uuq</i>	
13	IIIA	<i>5B</i>	<i>13Al</i>	<i>31Ga</i>	<i>49In</i>	<i>81Tl</i>	<i>113Uul</i>	
12	IIB		<i>30Zn</i>	<i>48Cd</i>	<i>80Hg</i>	<i>112Uub</i>		
11	IB		<i>29Cu</i>	<i>47Ag</i>	<i>79Au</i>	<i>111Uuu</i>		
10	VIIIB		<i>28Ni</i>	<i>46Pd</i>	<i>78Pt</i>	<i>110Uun</i>		
9	VIIIB		<i>27Co</i>	<i>45Rh</i>	<i>77Ir</i>	<i>109Uue</i>		
8	VIIIB		<i>26Fe</i>	<i>44Ru</i>	<i>76Os</i>	<i>108Uuo</i>		
7	VIIIB		<i>25Mn</i>	<i>43Tc</i>	<i>75Re</i>	<i>107Uus</i>		
6	VIB		<i>24Cr</i>	<i>42Mo</i>	<i>74W</i>	<i>106Uuh</i>		
5	VB		<i>23V</i>	<i>41Nb</i>	<i>73Ta</i>	<i>105Unp</i>		
4	IVB		<i>22Ti</i>	<i>40Zr</i>	<i>72Hf</i>	<i>104Ung</i>		
3	IIIB		<i>21Sc</i>	<i>39Y</i>	<i>57La</i>	<i>89Ac</i>		
2	IIA	<i>4Be</i>	<i>12Mg</i>	<i>20Ca</i>	<i>38Sr</i>	<i>56Ba</i>	<i>88Ra</i>	
1	IA	<i>1H</i>	<i>3Li</i>	<i>11Na</i>	<i>19K</i>	<i>37Rb</i>	<i>55Cs</i>	<i>87Fr</i>

LANTHANOIDS

58Ce	59Pr	60Nd	61Pm	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb	71Lu
------	------	------	------	------	------	------	------	------	------	------	------	------	------

ACTINOIDES

90Th	91Pa	92U	93Np	94Pu	95Am	96Cm	97Bk	98Cf	99Es	100Fm	101Md	102No	103Lr
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FACTS AND FIGURES:

Number of groups = VIII or 18
 Total elements = 118
 Number of metalloids = 7
 Man made elements = 118 - 93

Number of periods = 7
 Number of metals = 93
 Number of non-metals = 18
 Gases = 11, liquids = 2, Solids = 105

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PERIOD NAME	S-BLOCK ELEMENTS	P-BLOCK ELEMENTS	d-BLOCK ELEMENTS	f-BLOCK ELEMENTS	TOTAL ELEMENTS
FIRST PERIOD (VERY SHORT PERIOD)	2	-	-	-	2
SECOND AND THIRD PERIODS (SHORT PERIODS)	2	6	-	-	8 (each)
FOURTH AND FIFTH PERIODS (LONG PERIODS)	2	6	10	-	18(each)
SIXTH AND SEVENTH PERIODS (VERY LONG PERIODS)	2	6	10	14	32(each)

FAMILY NAME	DESCRIPTION	FAMILY NAME	DESCRIPTION
Alkali metal	Group IA elements.	Pnicogens	Group VA elements.
Alkaline earth metals	Group IIA elements.	Chalcogens	Group VIA elements.
Halogen	Group VIIA elements	Noble or inert gases	Group VIIIA elements.
Transition elements	d and f block elements.	Outer transition elements	d block elements.
Inner transition elements	f block elements.	Lanthanoids	$_{58}\text{Ce} - {}_{71}\text{Lu}$
Actinoids	$_{90}\text{Th} - {}_{103}\text{Lr}$	Transuranium elements	Elements with Z > 92.
Normal or representative elements	s and p - block elements.		
Coinage metals	Group IB elements.		

► FIRST AND SECOND ROW ANOMALIES

(A). SIMILARITIES AND DIFFERENCES IN THE FIRST ROW ELEMENTS

INTRODUCTION:

First ten elements (H – Ne) show considerable anomalous behaviour than the remaining elements. These elements are present in the first period and second period. The first row of most anomalous elements of the periodic table contains elements of second period.

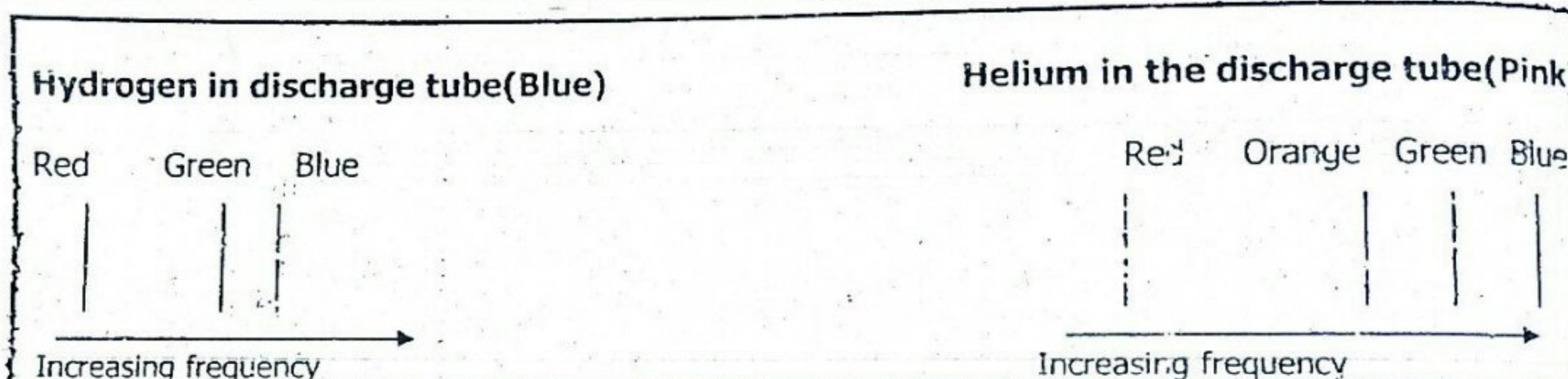
SIMILARITIES AND DIFFERENCES BETWEEN HYDROGEN AND HELIUM

SIMILARITIES (RESEMBLANCES)

- (1). Both hydrogen and helium are colourless, odourless and tasteless gases.
- (2). Both hydrogen and helium have their electrons in the s – subshell.
- (3). Position of both elements in the periodic table is controversial.
- (4). Both hydrogen and helium have two stable isotopes.
Stable isotopes hydrogen (Greek – water former) = ${}^1_1\text{H}$ and ${}^2_1\text{H}$.
Stable isotopes helium (Greek – helios, sun) = ${}^3_2\text{He}$ and ${}^4_2\text{He}$.
- (5). Both are the lightest of all the gases.
- (6). Both are the most abundant elements in the universe.
- (7). Both exist in free state.
- (8). Both hydrogen and helium are non-polar gases having only London dispersion forces as the only dominant intermolecular forces.

DISSIMILARITIES (DIFFERENCES)

- (1). Hydrogen has incomplete duplet but helium has a complete duplet.
- (2). Hydrogen exists as diatomic molecules but helium exists as monatomic molecules.
- (3). Hydrogen can be placed at the top of group IA, IVA or VIIA but helium is s-block element but it is placed with p-block elements.
- (4). Ionization energy of helium is greater than that of hydrogen.
- (5). Hydrogen is the most abundant element in the universe (90% atom of H) but helium is the second most abundant element in the universe (9% atoms of He).
- (6). Hydrogen forms halides and oxides but helium does not.
- (7). Hydrogen occurs in free as well as combined form but helium occurs only in free state.
- (8). Hydrogen is a remarkable reducing agent but helium is an inert gas.
- (9). Hydrogen is combustible but helium is not.
- (10). The line spectra of both the elements are different.



(B). SIMILARITIES AND DIFFERENCES IN THE FIRST ROW ELEMENTS

SIMILARITIES (RESEMBLANCES)

- (1). There are two shells i.e., K, L in the atoms of all the elements of first row.

${}^3\text{Li}$	${}^4\text{Be}$	${}^5\text{B}$	${}^6\text{C}$	${}^7\text{N}$	${}^8\text{O}$	${}^9\text{F}$	${}^{10}\text{Ne}$
K=2, L=1	K=2, L=2	K=2, L=3	K=2, L=4	K=2, L=5	K=2, L=6	K=2, L=7	K=2, L=8

- (2). All the elements of the first row (Li – Ne) are representative or normal elements.
- (3). All the elements of the first row (Li – Ne) exhibit peculiar or anomalous behaviour in their respective groups.
- (4). All the members of the first row (Li – F) form oxides.

Li_2O	BeO	B_2O_3	CO_2	NO_2	O_3	O_2	F_2O
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- (5). All the members of the first row (Li – F) form chlorides.

LiCl	BeCl_2	BCl_3	CCl_4	NCl_3	Cl_2O_7	ClF
---------------	-----------------	----------------	----------------	----------------	-------------------------	--------------

- (6). All the elements of first row do not involve d-orbital in the bonding. So there is no π - π bonding in the compounds of these elements.
- (7). All the elements of this row do not have expanded octet in their compounds.
- (8). All the elements of first row do not exhibit "s-inert pair effect" in their compounds.

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DISSIMILARITIES (DIFFERENCES)

- (1). The atomic numbers are consecutive in the elements of first row.

₃ Li	₄ Be	₅ B	₆ C	₇ N	₈ O	₉ F	₁₀ Ne
-----------------	-----------------	----------------	----------------	----------------	----------------	----------------	------------------

- (2). The number of valence electrons in the elements increases incrementally from left to right.

ELEMENT	₃ Li	₄ Be	₅ B	₆ C	₇ N	₈ O	₉ F	₁₀ Ne
VALENCE ELECTRONS	1	2	3	4	5	6	7	8

- (3). The elements of this period have different valencies.

- (4). The atomic radii decrease while going from left to right in this row of elements.

- (5). Metallic character reduces while going from left to right in this row of elements.

₃ Li	₄ Be	₅ B	₆ C	₇ N	₈ O	₉ F	₁₀ Ne
METAL	METAL	METALLOID	NON-METAL	NON-METAL	NON-METAL	NON-METAL	NON-METAL

- (6). Chemical reactivity is the highest at the two extremes ("Li" and "F") and is the lowest in the centre. The reactivity on the left extreme is most electropositive whereas on the extreme right it is the most electronegative.

- (7). Oxides of the elements on the left are basic and of the elements on the right are acidic in nature and oxides of the elements in the centre are amphoteric (Greek - amphi - of both kinds).

_{Li} ₂ O	BeO	_B ₂ O ₃	CO ₂	NO ₂	O ₂	F ₂ O
Ionic	Covalent/ ionic	Covalent	Covalent	Covalent	Covalent	Covalent
Basic	Amphoteric	Acidic	Acidic	Acidic	Neutral	Acidic
Hydrolysis reaction	Insoluble	Slightly soluble	Hydrolysis reaction	Hydrolysis reaction	Slightly soluble	Hydrolysis reaction

- (7). Hydroxides of Li - F also differ in their nature.

LiOH	Be(OH) ₂	B(OH) ₃	H ₂ CO ₃	HNO ₃	H ₂ O	HO _F
Strong alkali	Amphoteric	Weak acidic	Weak Acidic	Strong Acidic	Amphoteric	Weak Acidic

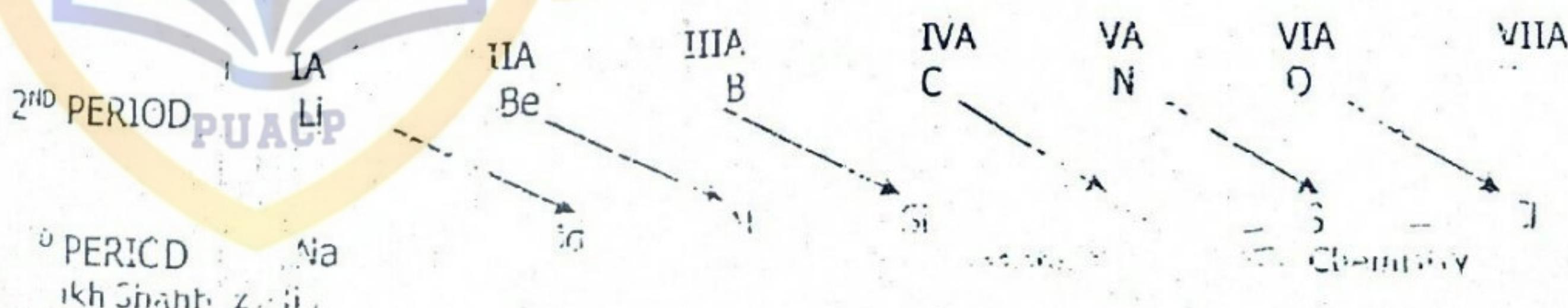
- (8). The chlorides of these elements differ as follows:

LiCl	BeCl ₂	BCl ₃	CCl ₄	NCl ₃	Cl ₂ O ₇	ClF
Ionic	Covalent	Covalent	Covalent	Covalent	Covalent	Covalent
Basic	Amphoteric	Acidic	Acidic	Acidic	Neutral	Acidic
Dissolves	Dissolves	Hydrolysis	No reaction	Hydrolysis	Hydrolysis	Hydrolysis

DIAGONAL RELATIONSHIP OF FIRST ROW OF MOST ANOMALOUS ELEMENTS

DEFINITION:

The first few members of the second period show similar behaviour to the elements of the next group belonging to the third period. This is called diagonal relationship or similarity.



(A). DIAGONAL

RELATIONSHIPS BETWEEN
LIHTIUM AND MAGMESIUM

Lithium resembles magnesium with which it is diagonally related. The resemblances are usually due to a similarity in ionic size and high polarizing power of Li^+ and Mg^{2+} ions.

SIMILARITIES (RESEMBLANCES)

- (1). Both lithium and magnesium are more electropositive than beryllium but less electropositive than sodium.
- (2). Lithium and magnesium reacts slowly with water.
- (3). Both lithium and magnesium combine directly with nitrogen and carbon to form nitrides and carbides.



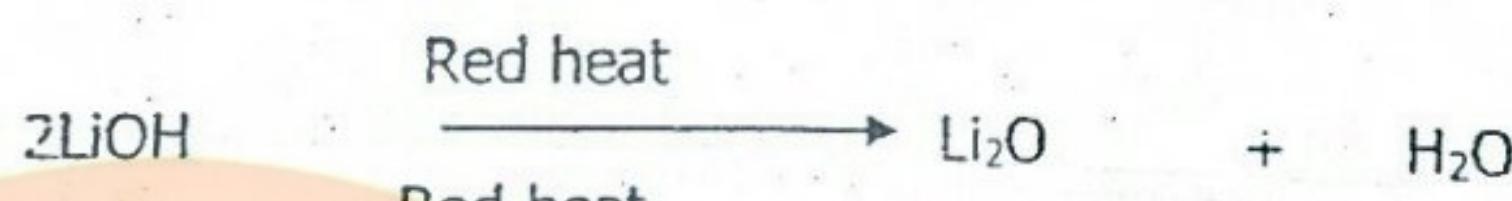
These are decomposed by water giving ammonia.



- (4). Lithium when treated in air or oxygen, gives the normal oxide, Li_2O . Magnesium under similar conditions, forms a normal oxide, MgO only.

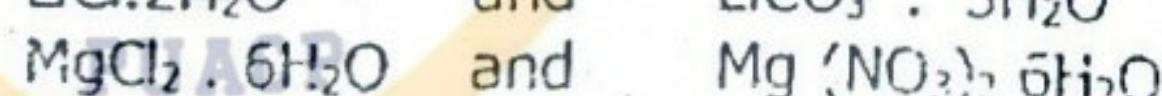
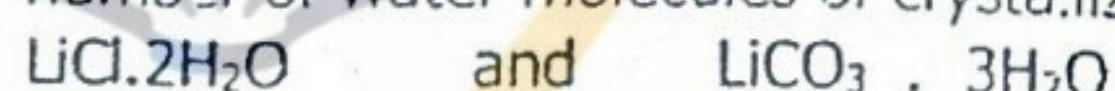


- (5). Lithium hydroxide, like magnesium hydroxide is sparingly soluble in water and decomposes at red heat to form the oxide.



- (6). The solubilities of lithium salts resemble those of the corresponding magnesium salts and differ markedly from those of the other alkali metals. Thus the fluorides, carbonates are phosphates of lithium and magnesium are sparingly soluble in water.

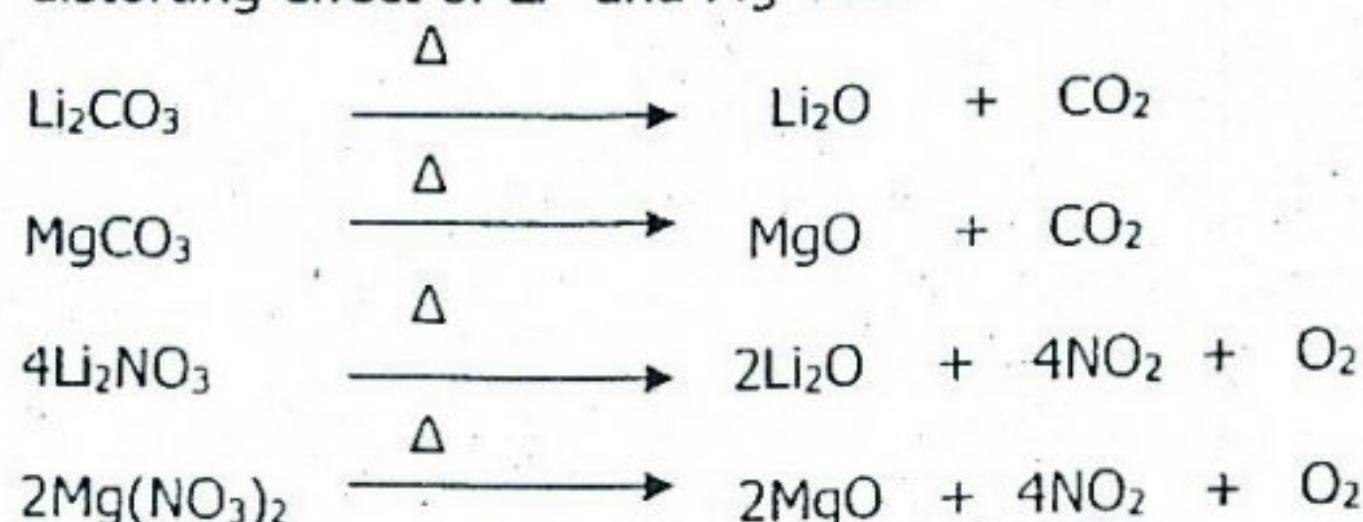
- (7). Li^+ and Mg^{2+} have great tendency to form hydrates because of strong their strong polarizing power. Thus a number of lithium and magnesium salts crystallized from water with definite number of water molecules of crystallization. For example,



The salts of other alkali metals are not hydrated.

Rehman hahbaz Ali

- (8). The oxy-compounds of lithium and magnesium such as carbonates and nitrates possess low thermal stability and decompose to form the respective oxides. This is because of the strong distorting effect of Li^+ and Mg^{2+} ions on the charge cloud of the anions,



- (9). Lithium forms alkyls and aryls similar to magnesium, which form Grignard reagents.

(B). DIAGONAL RELATIONSHIPS BETWEEN BERYLLIUM AND ALUMINIUM

REASONS FOR SIMILARITIES

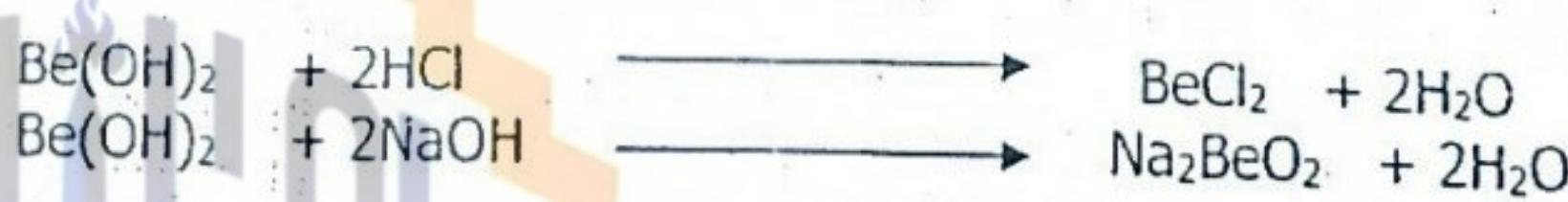
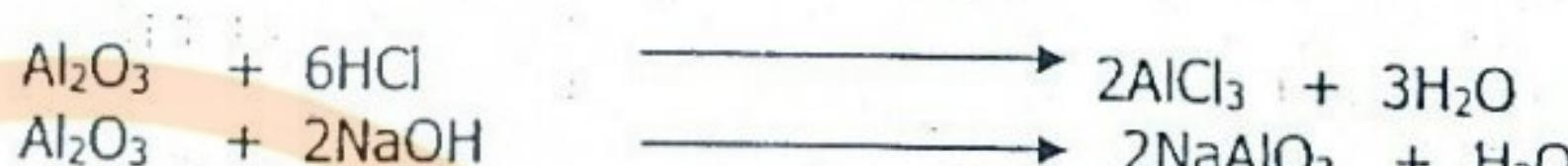
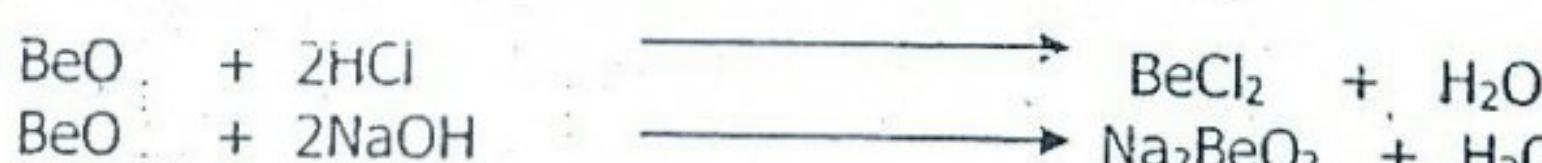
- (1). There is similarity in the ionic potentials (i.e., $\text{Be}^{2+} = 48$, $\text{Al}^{3+} = 56$). The result is that polarizing powers of Be^{2+} and Al^{3+} are of similar magnitude. Acidity of cation is also same.
- (2). The standard oxidation potentials of beryllium and aluminium are quite close to each other.

SIMILARITIES (RESEMBLANCES)

- (1). Both Be and Al metals dissolve readily in $3\text{MH}_2\text{SO}_4$ but very slowly in nitric acid in which the metal are rendered passive due to the formation of inert film on the surface of metals.
- (2). Be and Al both react with strong alkalies liberating hydrogen gas and forming beryllate and aluminate ions.



- (3). Oxides and hydroxides of both the metals are amphoteric in nature. They dissolve in acids as well as in alkalies giving their corresponding salts and beryllate and aluminate ions respectively.



The anhydrous halides (except fluorides) of both Be and Al are covalent in nature and as such dissolve in organic solvents and fume in moist air.

(5). The carbides of Be and Al yield methane on hydrolysis.

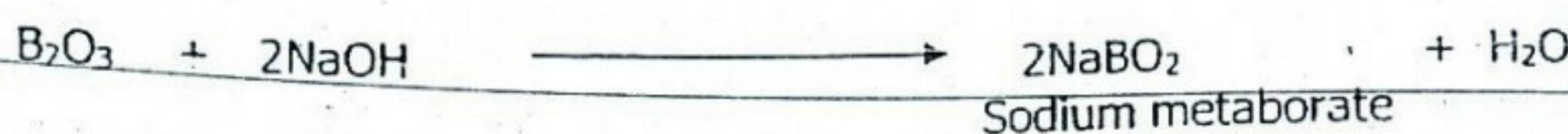


SIMILARITIES (RESEMBLANCES)

(C). DIAGONAL RELATIONSHIPS BETWEEN BORON AND SILICON

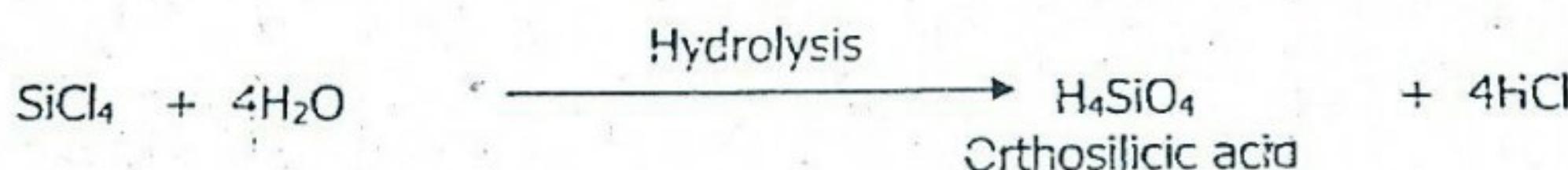
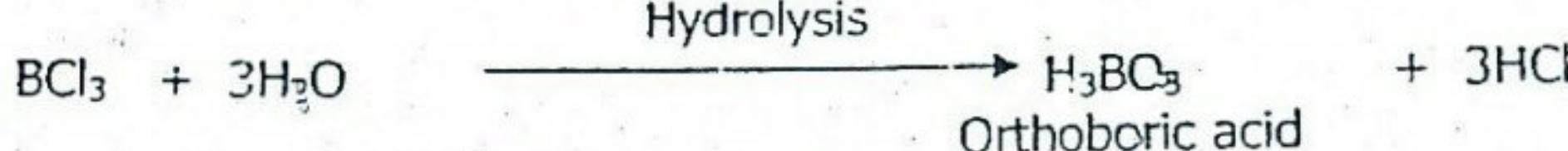
- (1). Both B and Si are semiconductors of electricity in their crystalline form and possess high melting points.

(2). Both boron and silicon form oxides such as Be_2O_3 and SiO_2 respectively which are acidic in nature. They dissolve in alkalies to form borates and silicates.



- (3). Boron and silicon form hydroxides which are weak acids with no basic properties.

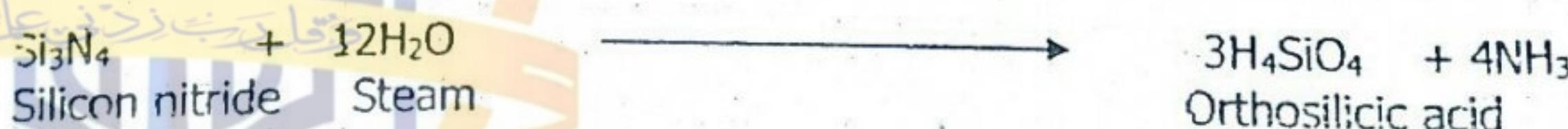
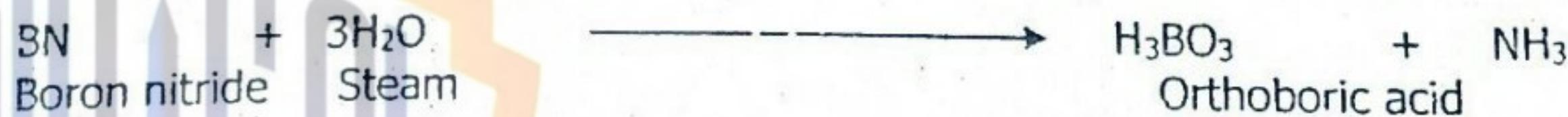
(4). Boron and silicon halides (except BF_3) readily hydrolyse to give their corresponding acids.



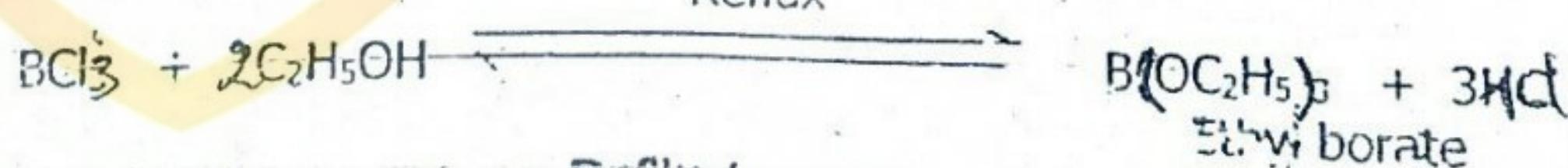
- (5). Hydrides of boron and silicon known as boranes and silanes respectively, are covalent in nature and have similar method of preparation.



- (6). The nitrides of both boron and silicon decompose steam and liberate ammonia.



- (7). The alkoxides $B(OR)_3$ and $Si(OR)_4$ may be prepared similarly by refluxing benzene solution of the anhydrous boron trichloride and silicon tetrachloride with ethanol.



Sidney + Gifford

Reflux

Siccegphay + Hrgl
-chelirat

(D). DIAGONAL RELATIONSHIPS OF CARBON – PHOSPHORUS, NITROGEN – SULPHUR AND OXYGEN – CHLORINE

All the metallic properties have been lost in these elements and so charge – to – size ratios have little meaning. However, the same effects appear in the electronegativities of these elements, which show a strong diagonal effect.

The electronegativities are based on the Pauling thermochemical electronegativities not on the ionization – electron affinity.

$C = 2.55$	$N = 3.04$	$O = 3.44$	$F = 3.98$
$Si = 1.90$	$P = 2.19$	$S = 2.58$	$Cl = 3.16$

CONCLUSIONS OR DISCUSSION

- (1). The similarity in electronegativities of diagonally related pair of elements is lesser than the similarity in their ionic potential.
- (2). The heavier element in the diagonal pair always has a lower electronegativity.
- (3). While searching for an element similar to carbon, phosphorus is a better choice than silicon.
- (4). From diagonal resemblances we can find the differences between say lithium and sodium.

VERTICAL RELATIONSHIPS OF THE FIRST ROW OF MOST ANOMALOUS ELEMENTS WITH THE OTHER ELEMENTS

- Peculiar behaviour of lithium.
- Peculiar behaviour of beryllium.
- Peculiar behaviour of boron.
- Peculiar behaviour of carbon.
- Peculiar behaviour of nitrogen.
- Peculiar behaviour of oxygen.
- Peculiar behaviour of fluorine.
- Similarities and differences between boron and aluminium.
- Similarities and differences between carbon and silicon.
- Similarities and differences between oxygen and sulphur.

REASONS FOR PECULIAR/ANOMALOUS BEHAVIOUR

- (1). First member of every group is the smallest in size.
- (2). It has the highest charge density of ion.
- (3). It has the low value of electropositivity or high value of electronegativity.
- (4). It has extraordinary large values of ionization energy.
- (5). It has a small value of electron affinity.
- (6). There is non – availability of d – orbitals in the first members of each family.

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PECULIAR BEHAVIOUR OF LITHIUM

- (1). Some differences of lithium from other alkali metals, are given below:
-
- (2). **MELTING AND BOILING POINTS:**
Lithium possesses higher melting point and boiling point.
- (3). **HARDNESS AND DENSITY:**
Lithium is much harder and lighter than the other alkali metals.
- (4). **SOLUBILITY OF SALTS:**
The lithium salts of anions with high charge density are generally less soluble in water than those of the other alkali metals, e.g., LiOH , LiF , Li_3PO_4 , Li_2CO_3 .
- (5). **COMPLEX FORMATION:**
Lithium forms stable complex compounds, although complex formation generally is not a property of alkali metals. One of the complexes formed by lithium is $[\text{Li}(\text{NH}_3)_4]^+$.
- (6). **STABILITY OF SALTS:**
Lithium salts of large polarizable anions are less stable than those of other alkali metals. Unlike other alkali metals, lithium does not form bicarbonates, tri-iodide or hydrogen sulphide at room temperature.
- (7). **STABILITY OF HYDRIDE**
Lithium hydride is more stable than the hydrides of the other alkali metals.
- (8). **NATURE OF COMPOUNDS**
Lithium compounds are more covalent, that is why, its halides are more soluble in organic solvents and the alkyls (e.g., methyl lithium) and aryls (e.g., phenyl lithium) of lithium are more stable than those of other alkali metals.
- (9). **REACTIVITY:**
Lithium is the least reactive metal of the alkali metals.
- (10). **NATURE OF CHLORIDES:**
Lithium chloride has an exothermic heat of solution, whereas chlorides of sodium and potassium have endothermic heats of solution.
- (11). **REACTION WITH AIR:**
When burnt in air lithium forms only normal oxide, whereas the other alkali metals form peroxide and superoxides.

$$4\text{Li} + \text{O}_2 \longrightarrow 2\text{Li}_2\text{O}$$
- (12). **REACTION WITH ACETYLENE**
When acetylene is passed over strongly heated lithium, it does not produce lithium acetylidyde, but other alkali metals form the corresponding metallic acetylides.

$$2\text{Na} + \text{C}_2\text{H}_2 \longrightarrow \text{Na}^+\text{C}\equiv\text{C}^-\text{Na}^+ + \text{H}_2$$

(Sodium acetylidyde)
- (13). **REACTION WITH NITROGEN:**
Lithium reacts with nitrogen to form nitride, while the other members of the group do not give this reaction.

$$6\text{Li} + \text{N}_2 \longrightarrow 2\text{Li}_3\text{N}$$

(Lithium nitride)
- (14). **REACTION WITH CARBON:**
Lithium carbide is the only alkali metal carbide formed readily by the direct reaction.

$$4\text{Li} + \text{C} \longrightarrow \text{Li}_4\text{C}$$

(Lithium carbide)

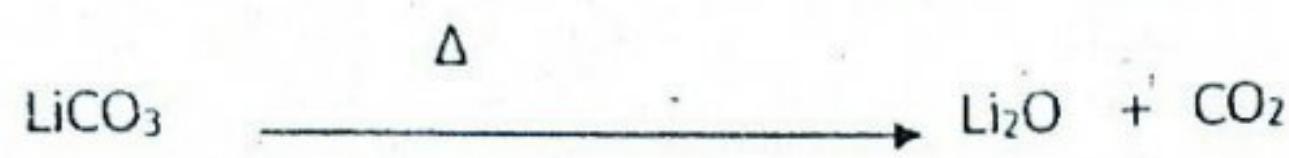
REACTION WITH WATER:

Lithium reacts very slowly with water, while other alkali metals react violently.

Assistant Prof. S. S. Joshi

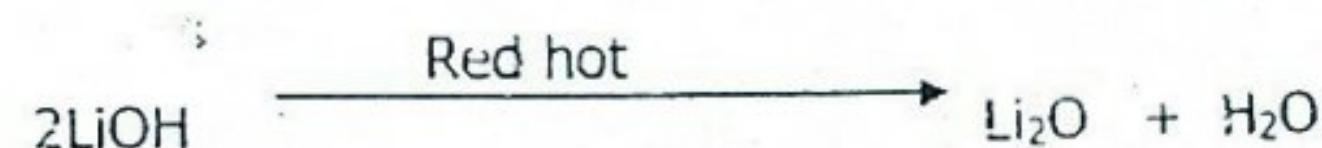
(15). THERMAL DECOMPOSITION OF CARBONATES AND NITRATES

Lithium has low electropositive character, thus its carbonates and nitrate are not so stable and therefore decompose giving lithium oxide. Carbonates of other alkali metals do not decompose. Decomposition of lithium nitrate gives different products than the nitrates of other alkali metals.



(16). THERMAL DECOMPOSITION OF HYDROXIDE:

Lithium hydroxide when strongly heated, form lithium oxide but the other alkali metal hydroxides do not show this behaviour.



PECULIAR BEHAVIOUR OF BERYLLIUM

The main points of difference are:

(1). DENSITY:

Beryllium is the lightest member of its family.

(2). HARDNESS:

Beryllium metal is almost as hard as iron and hard enough to scratch the glass. The other alkaline earth metals are much softer than beryllium but still harder than the alkali metals.

(3). MELTING POINT AND BOILING POINTS:

The melting and boiling points of beryllium are higher than other alkaline earth metals.

(4). REACTION WITH WATER:

As reducing agents, the group IIA metals are all powerful enough to reduce water, at least in principle. However, with water, beryllium forms insoluble oxide coating that protects it from further attack.

(5). OXIDATION:

Beryllium in particular is quite resistant towards complete oxidation, even by acids, because of its BeO coating.

(6). REACTION WITH ALKALIES:

Beryllium is the only member of its group, which reacts with alkalies to give hydrogen. The other members do not react with alkalies.

(7). LIBERATION OF H₂ FROM ACIDS:

Beryllium does not liberate hydrogen from acids readily but while other members of its family do so.

(8). NATURE OF OXIDE AND HYDROXIDE:

Oxides and hydroxides of beryllium are amphoteric while that of other members of its family are basic.

(9). **SOLUBILITY OF SULPHATE:**

Beryllium sulphate is soluble in water while sulphates of other metals are either sparingly soluble in water or insoluble in water.

(10). **NATURE OF COMPOUNDS:**

In general the compounds of beryllium are covalent while compounds of other alkaline - earth metals are ionic.

PECULIAR BEHAVIOUR OF BORON

The main points of difference are:

(1). **NON - METALLIC NATURE:**

Boron is the only element in group IIIA which is non-metallic in behaviour. It is a bad conductor of electricity.

(2). **NUMBER OF VALENCE ELECTRONS:**

It is the only element with less than four electrons in the outermost shell which is not a metal.

(3). **OXIDATION STATE:**

Boron always uses all the three of its valence electrons for bonding purposes and its common oxidation states +3 and -3.

(4). **FORMATION OF MOLECULAR ADDITION COMPOUNDS:**

One of the outstanding features of the chemistry of boron is its ability to form molecular addition compounds.

(5). **UNSTABILITY OF CATION :**

Boron does not form ionic compounds with sulphate, nitrate or other anions because boron does not form a stable cation.

PECULIAR BEHAVIOUR OF CARBON

The main points of differences are:

(1). **METALLIC CHARACTER:**

Carbon and silicon are non-metals while the other members of the family are metalloids or metals.

(2). **CATENATION OR SELF - LINKAGE:**

Carbon has a tendency to form long chains of identical atoms. The type of linkage of identical atoms with each other is called catenation or self-linkage. The property of catenation decreases on moving down the group from carbon to lead. This is due to the decrease in the element - element bond energy.

(3). **ESSENTIAL ELEMENT IN ORGANIC COMPOUNDS**

The maximum tendency of catenation associated with carbon forms the basis of the carbon compounds, which constitute organic chemistry. Carbon is the essential element in the organic compounds.

(4). **MULTIPLE BOND FORMATION**

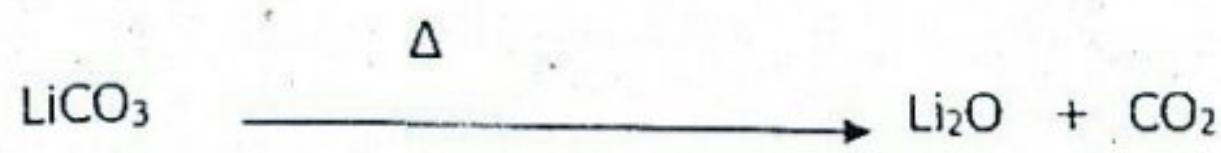
Carbon has tendency to form multiple bonds formation e.g., $C=C$ (in alkenes), $C\equiv C$ (in alkynes)

$C=O$ (in CO_2 , in organic compounds with carbonyl and carboxylic groups), $C\equiv S$ (in CS_2 , in thiourea) and $C\equiv N$ (in $H_2N-C\equiv N$, in alkannitriles).

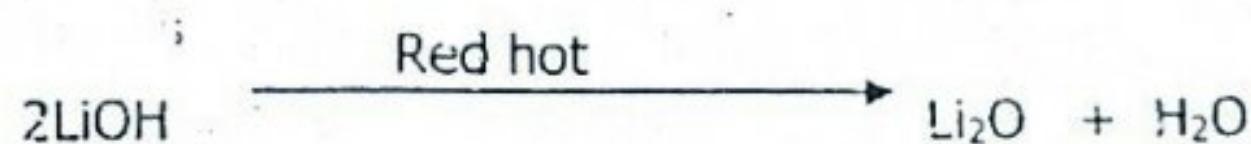
Chem - 406

INORGANIC CHEMISTRY**Special theory - I****(15). THERMAL DECOMPOSITION OF CARBONATES AND NITRATES**

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(5). **COMPLEX FORMATION**

Carbon does not form complexes due to unavailability of d - orbitals whereas the other members can form complexes. They can accommodate more than 8 electrons in the valence shell.

EXAMPLE: $[\text{SiF}_6]^{2-}$ is a complex of silicon formed by reaction SiF_4 with 2F^- ions.

(6). **OXIDE FORMATION**

Carbon forms variety of oxides like CO , CO_2 , C_3O_2 ($\text{O} = \text{C} = \text{C} = \text{C} = \text{O}$), CsO_2 and C_{12}O_9 .

PECULIAR BEHAVIOUR OF NITROGEN

The main points of differences are:

(1). **PHYSICAL STATE:**

Nitrogen is gas while other elements of this group are solid.

(2). **ATOMICITY:**

Nitrogen forms diatomic molecule (N_2) while other elements form tetra - atomic molecules e.g., P_4 , As_4 and Sb_4 .

(3). **ALLOTROPY:**

Nitrogen does not show allotropy while other elements (except Bi) show allotropy.

(4). **OCCURRENCE:**

Nitrogen occurs in free state while other elements do not occur in free state.

(5). **OXIDATION STATES:**

Nitrogen shows a variety of oxidation states while other elements do not.

+1 in N_2O (Nitrous oxide)	+2 in NO (Nitric oxide)	+3 in N_2O_3 (Nitrous anhydride)	
+4 in N_2O_4 (Dinitrogen tetroxide)	+5 in N_2O_5 (Nitric anhydride)	-1 in NH_2OH (Hydroxyl amine)	-3 in NH_3 (Ammonia)

(6). **COMPLEX FORMATION:**

Nitrogen cannot form complexes due to non - availability of d - orbitals but other elements of its group form complexes.

(7). **NATURE OF HYDRIDE:**

Hydride of nitrogen i.e., NH_3 is stable and non - poisonous while hydrides of other members of its family are progressively less stable but they are poisonous. Also, the hydride of nitrogen exists in the associated form due to the presence of hydrogen bonding.

(8). **STABILITY OF CHLORIDES:**

NCl_3 is highly reactive and unstable while the trichlorides of the remaining elements are progressively more stable and less reactive. Nitrogen does not form pentachloride while "P" and "Sb" form such pentachlorides.

(9). **FORMATION OF SULPHIDE:**

Nitrogen does not form a sulphide while all other elements do form.

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PECULIAR BEHAVIOUR OF FLUORINE

The halogens form a homologous series but fluorine differs from the other halogens in many respects which is due to following reasons:

- (i). Small size of F atom and of F^- ion.
- (ii). High first ionization energy and electronegativity.
- (iii). Low dissociation energy of F_2 molecule as compared to Cl_2 and Br_2 .
- (iv). Restriction of the valence shell to an octet.

The main points of differences are:

- (1). **REACTIVITY:**
Its molecule has low dissociation energy and high reactivity while other halogens react slowly under similar conditions.
- (2). **OXIDATION STATE:**
Owing to restriction of its valence to an octet and the highest electronegativity, it is restricted to -1 oxidation state. While other halogens can show higher oxidation state.
- (3). **NATURE OF FLUORIDES:**
Fluorides are ionic and have ionic lattice while other halides have frequently molecular lattices.
- (4). **LATTICE ENERGY OF FLUORIDES:**
Ionic fluorides have higher lattice energy than the other halides.
- (5). **SOLUBILITY OF FLUORIDES:**
Fluorides of Ca, Mg, Ba and Sr are insoluble in water. This insolubility is due to the higher lattice energy of fluorides than other halides.
- (6). **STABILITY OF FLUORIDES:**
The fluorides are more stable with respect to the dissociation into elements.
Owing to small size of the 'F' atom or ' F^- ' ion there will be a better overlap of orbitals and consequently leads to shorter and stronger bonds with elements other than O, N and itself.
- (7). **INERTNESS OF COMPOUNDS:**
Many fluoro compounds e.g., CF_4 and SF_6 show inertness due to the restriction of valence shell of fluorine to an octet.
- (8). **COMBINATION WITH NOBLE GASES:**
Fluorine is the only element that combines directly with noble gases like Kr, Xe and Rn forming their fluorides.
- (9). **NATURE OF HALOGEN ACIDS:**
HF is a weak acid due to hydrogen bonding while other halogen acids are strong due to complete ionization in water.
- (10). **FORMATION OF HEXAHALIDES:**
Fluorine is the most electronegative element and gives SF_6 while other members do not form hexahalides with sulphur.

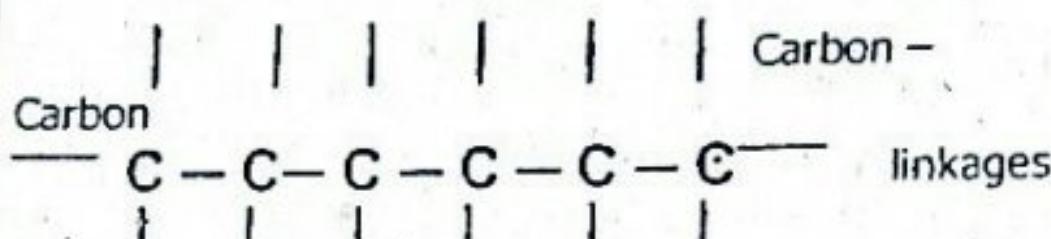
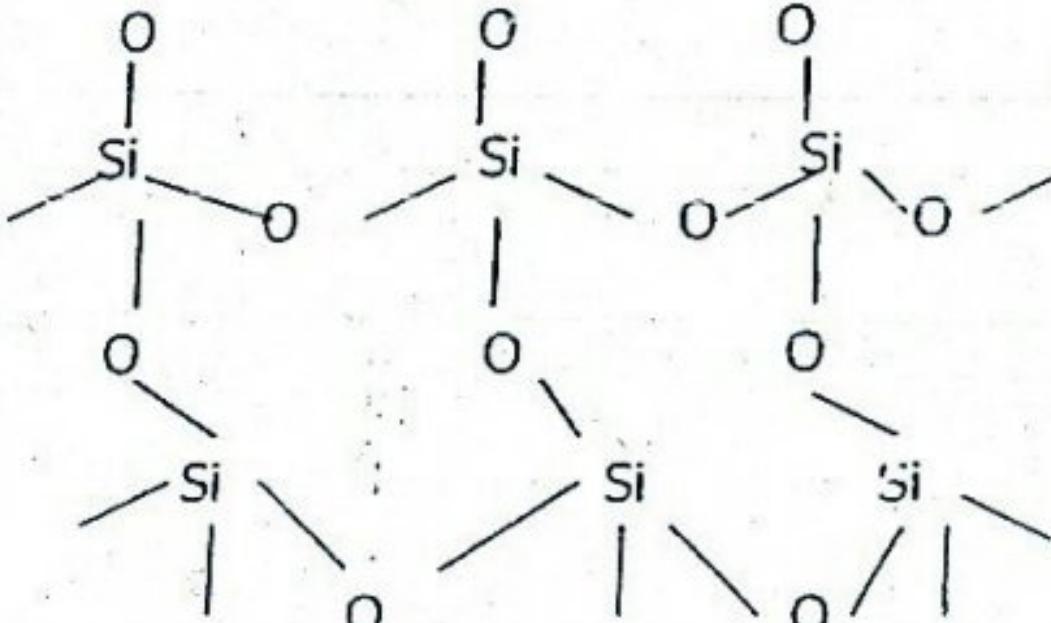
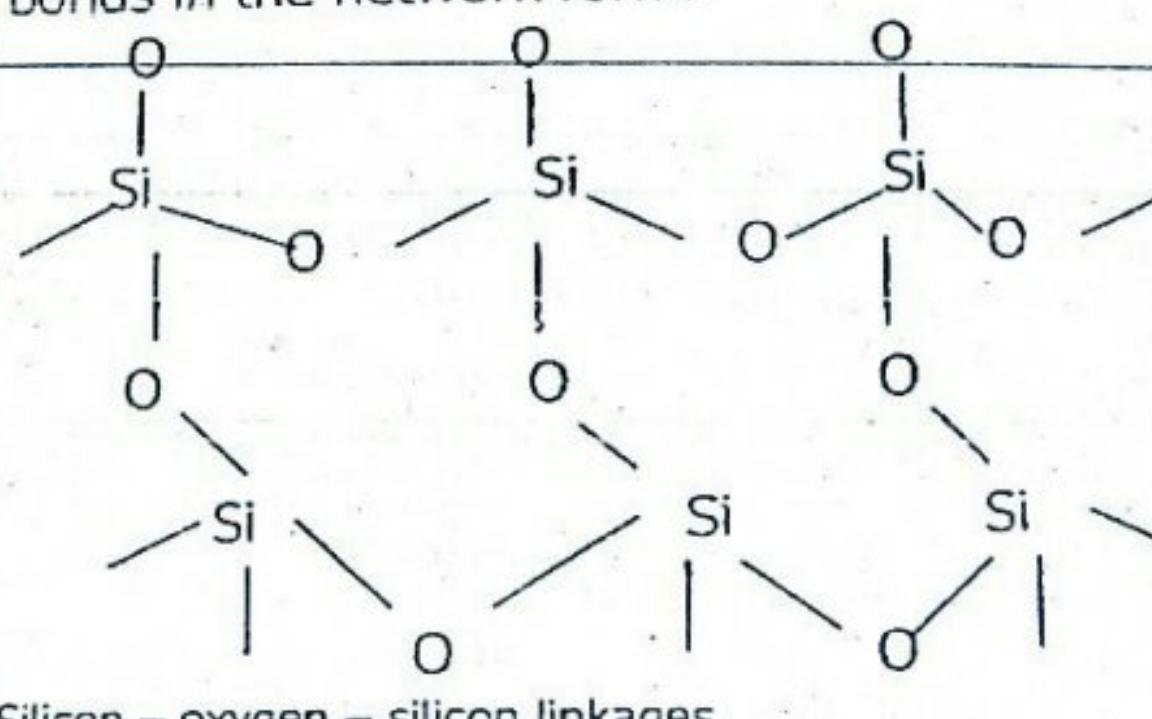
SIMILARITIES AND DIFFERENCES BETWEEN BORON AND ALUMINIUM

SIMILARITIES	DIFFERENCES
<ul style="list-style-type: none"> Both B and Al form covalent compounds, e.g., BCl_3 and AlCl_3. 	<ul style="list-style-type: none"> (1) Boron is quite hard with high m.p. while other members of the group are soft with low m.p.
<ul style="list-style-type: none"> The chlorides are volatile and hygroscopic. They are hydrolysed by water. 	<ul style="list-style-type: none"> (2) Boron is a bad conductor while other members are good conductors of electricity.
$\text{B}_2 + 3\text{H}_2 \longrightarrow 2\text{BH}_3$	$\text{B}(\text{OH})_3 + 3\text{H}_2O$
$\text{Al}_2 + 3\text{H}_2 \longrightarrow 2\text{AlH}_3$	$\text{Al}(\text{OH})_3 + 3\text{H}_2O$
<ul style="list-style-type: none"> Both B and Al form chlorides which react with water to give ammonia. 	<ul style="list-style-type: none"> (3) Due to smaller size and higher Z, boron is non-metal while other members of the group are metals.
$\text{B}_2 + 3\text{H}_2O \longrightarrow \text{H}_2\text{BO}_3 + 3\text{H}_2$	
$\text{Al}_2 + 3\text{H}_2O \longrightarrow \text{Al}(\text{OH})_3 + 3\text{H}_2$	
<ul style="list-style-type: none"> Both B and Al form oxides when they are heated in air. 	<ul style="list-style-type: none"> (4) Boron does not displace hydrogen from acids. But other members do. For example,
$\text{B}_2 + \text{O}_2 \longrightarrow 2\text{B}_2\text{O}_3$	$2\text{Al} + \text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3 + 3\text{H}_2$
$\text{Al}_2 + \text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3$	In this, since boron is oxidized to basic oxide while Al becomes neutral.
<ul style="list-style-type: none"> Both B and Al react with alkalis to evolve hydrogen. 	<ul style="list-style-type: none"> (5) Oxides and hydroxides of boron are acidic in nature.
$\text{B}_2 + 6\text{NaOH} \longrightarrow 2\text{Na}_2\text{B}_2\text{O}_3 + 3\text{H}_2$ Sodium borate	$2\text{B}_2\text{O}_3 + 3\text{H}_2O \longrightarrow 2\text{H}_2\text{BO}_3$ (boric acid)
(or) $2\text{H}_2O + 2\text{NaOH} \longrightarrow 2\text{NaBO}_2 + 2\text{H}_2$ Sodium borate	Hydroxides and oxides of Al are amphoteric in nature.
	$2\text{Al}_2\text{O}_3 + 3\text{H}_2O \longrightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2$
	$2\text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + \text{Al}_2\text{O}_3$ Sodium metaborate = aluminum oxide
	<p>On the other hand other members form basic oxides and hydroxides.</p>
	<ul style="list-style-type: none"> (6) Water or steam has no action on boron but other members decompose steam to give out hydrogen.
	$2\text{Al} + 3\text{H}_2O \longrightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2$

Similarities of other elements such as BCl_3 and AlCl_3 behave as Lewis acids, because their B^{3+} and Al^{3+} ions are electron deficient.

SIMILARITIES AND DIFFERENCES BETWEEN CARBON AND SILICON

Carbon and silicon are the only non-metals in the group IVA.

SIMILARITIES	DIFFERENCES
<p>(1). Carbon has the peculiar property of forming long carbon chains; silicon forms long chains of alternating silicon and oxygen atoms:</p> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div>	<p>(1). There is similarity in the formulae of the compounds of the carbon and silicon but the properties of the compounds of these two elements are different. Carbon dioxide differs from SiO_2 as follows: Carbon dioxide is a gas while silica is hard solid. This is because of the formation of multiple bonds between carbon and oxygen in CO_2. It exists as discrete linear molecules. But in SiO_2, there are single bonds in the network form.</p> <div style="text-align: center;">  </div>
<p>(2). Carbon and silicon both form acidic oxides, whereas the oxides of germanium, tin and lead are amphoteric in nature. (CO_2 and SiO_2)</p>	<p>(2). Carbon form variety of oxides like CO, CO_2, C_3O_2 ($\text{O} = \text{C} = \text{C} = \text{C} = \text{O}$), C_5O_2 and C_{12}O_9. SiO_2 is feebly acidic and insoluble in water but CO_2 is acidic in nature and soluble in water.</p>
<p>(3). Both carbon and silicon form covalent bonds. (CHCl_3, chloroform, CHBr_3 and CHI_3 and SiHCl_3, silicon chloroform, SiHBr_3, SiHI_3).</p>	<p>(3). SiCl_4 is highly hydrolysable liquid with pungent smell but CCl_4 is a stable liquid. The properties of chloroform and silicon chloroform also differs.</p>
<p>(4). Both form hydrides and chlorides. (CH_4, C_2H_6, CCl_4 and SiH_4, Si_2H_6, SiCl_4).</p>	<p>(4). SiH_4 is easily decomposed by the alkalies, silver nitrate and copper salts while CH_4 is a stable compound. CX_4 is fully saturated but SiX_4 gives addition products with substances like ammonia.</p>
<p>(5). Both form acid of the formula H_2MO_3. (Carbonic acid, H_2CO_3 and metasilicic acid, H_2SiO_3) and [Oxalic acid($\text{COOH})_2$ and silico - oxalic acid($\text{SiOOH})_2$]</p>	<p>(5). Metasilicic acid is more stable than the carbonic acid. Silico - oxalic acid ($\text{SiOOH})_2$ is not stable than oxalic acid($\text{COOH})_2$ and it is easily hydrolysed also.</p>
<p>(6). Hydroxides of both are acidic in nature.</p>	<p>(6). Maximum covalency of carbon is four but that of silicon is 6.</p>
<p>(7). Carbon is the essential and most abundant elements in the organic compounds. Whereas silicon is second most abundant compound in the earth's crust after oxygen.</p>	<p>(7). Silicon is widely used as semiconductor but carbon is not.</p>

SIMILARITIES AND DIFFERENCES BETWEEN OXYGEN AND SULPHUR

SIMILARITIES	DIFFERENCES
(1). Both oxygen and sulphur have same outer electronic configuration of ns^2, np^2 .	(1). Oxygen has two allotropic forms i.e., O_2 and O_3 but sulphur three allotropic forms i.e. α - sulphur(rhombic), β - sulphur(monoclinic) and γ - sulphur(plastic).
(2). Both oxygen and sulphur are usually divalent.	(2). Oxygen is colourless and odourless gas at ordinary temperature but sulphur is pale-yellow solid at ordinary temperature with faint smell.
(3). Both oxygen and sulphur exhibit allotropic forms.	(3). Oxygen is sparingly soluble in water but sulphur is not soluble in water.
(4). Both oxygen and sulphur have polyatomic molecules. Oxygen has diatomic O_2 while sulphur has S_2 and S_8 molecules.	(4). Oxygen helps in combustion but sulphur is itself combustible.
(5). Both combine with metals to form oxide (O^{-2}) and sulphide(S^{-2}) with oxidation state of -2.	(5). Oxygen is paramagnetic in nature but sulphur is diamagnetic in nature. Oxygen is more widely distributed in nature than sulphur.
(6). Both combine with non-metals and form covalent compounds (a). H_2O and H_2S . (b). CO_2 and CS_2 etc.	(6). Oxygen does not react with water but when steam is passed through boiling sulphur a little hydrogen sulphide and sulphur dioxide are formed. $S + 2H_2O \longrightarrow 2H_2O + SO_2$
(7). Both are typical non-metals.	(7). Oxygen shows -2 oxidation state but sulphur shows oxidation state of -2, +2, +4 and +6.
(8). Both are found in free and combined states on earth.	(8). Oxygen does not react with acids. Sulphur is readily oxidized by conc. sulphuric acid and nitric acid. $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$ $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
(9). Both show analogy in their compounds. (a). C_2H_5OH , ethyl alcohol and C_2H_5SH , ethyl mercaptan. (b). $(C_2H_5)_2O$, ether and $(C_2H_5)_2S$, thioether.	(9). Oxygen does not react with alkalis but sulphur is boiled with alkali solution to form sulphide and thiosulphate. $4S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

NOTE: Oxygen does not form co-ordination compounds due to the non-availability of d-orbitals but sulphur forms co-ordination compounds. Oxygen is more electronegative than sulphur. Heat of formation of water is greater than that of H_2S .

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THE USE OF P - ORBITALS IN THE PI - BONDING

The occurrence of double and triple bonds for Si and P was rare as compared to C = C, C = O, C ≡ C, C ≡ N etc. It was thought that only, C, O, N etc. could form stable π - bond. The double bond are found in heavier non - metals. They get stabilized by protecting them with bulky group. The number of triple bond is a smaller in heavier non - metals(perhaps a dozen).It means multiple bonds are more common in the elements of 2nd period.

Order of strength of π - bonds are:

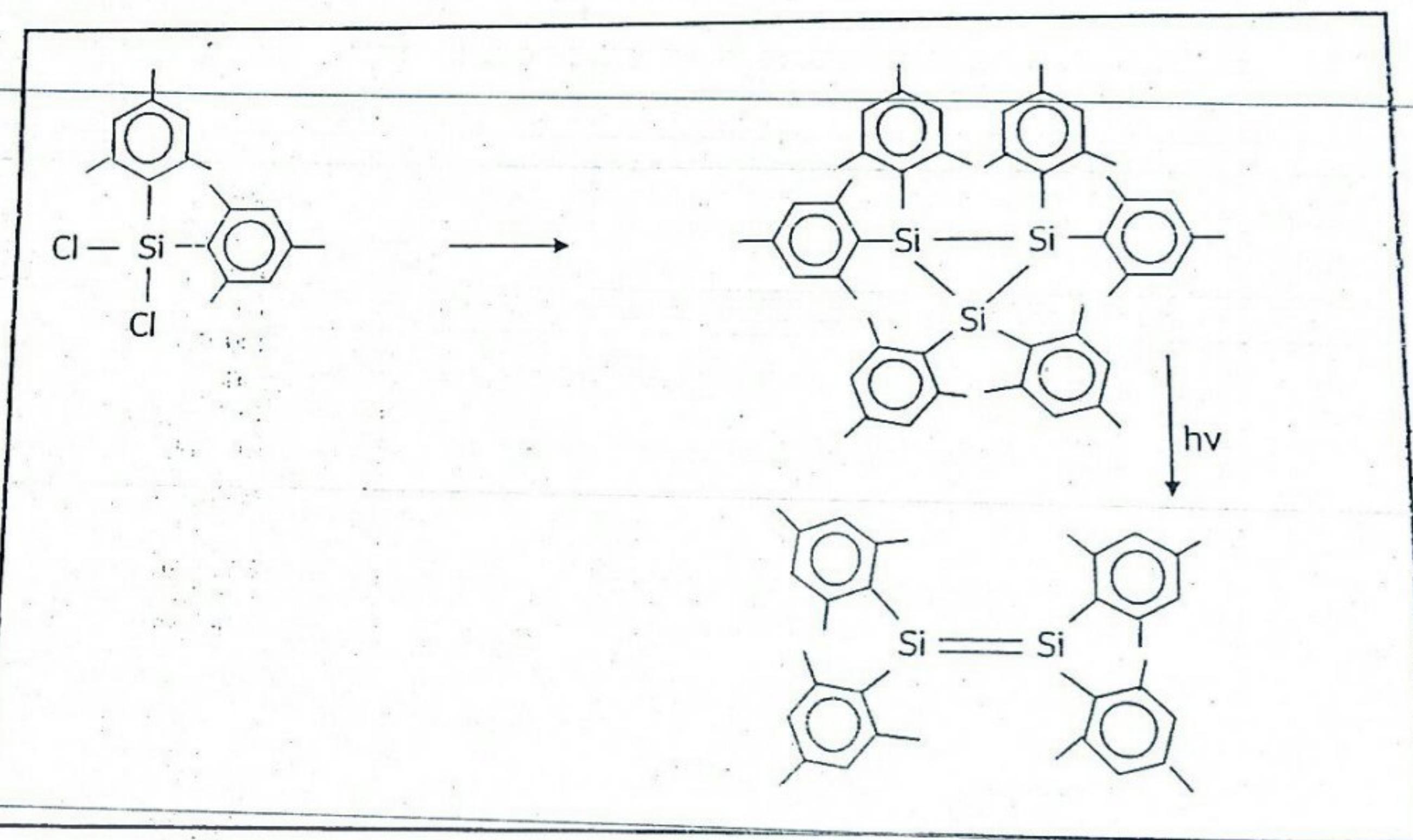
C = C > C = Si > C = Ge > C = Sn

and C = C > Si = Si ~ Ge = Ge

Group IV Elements

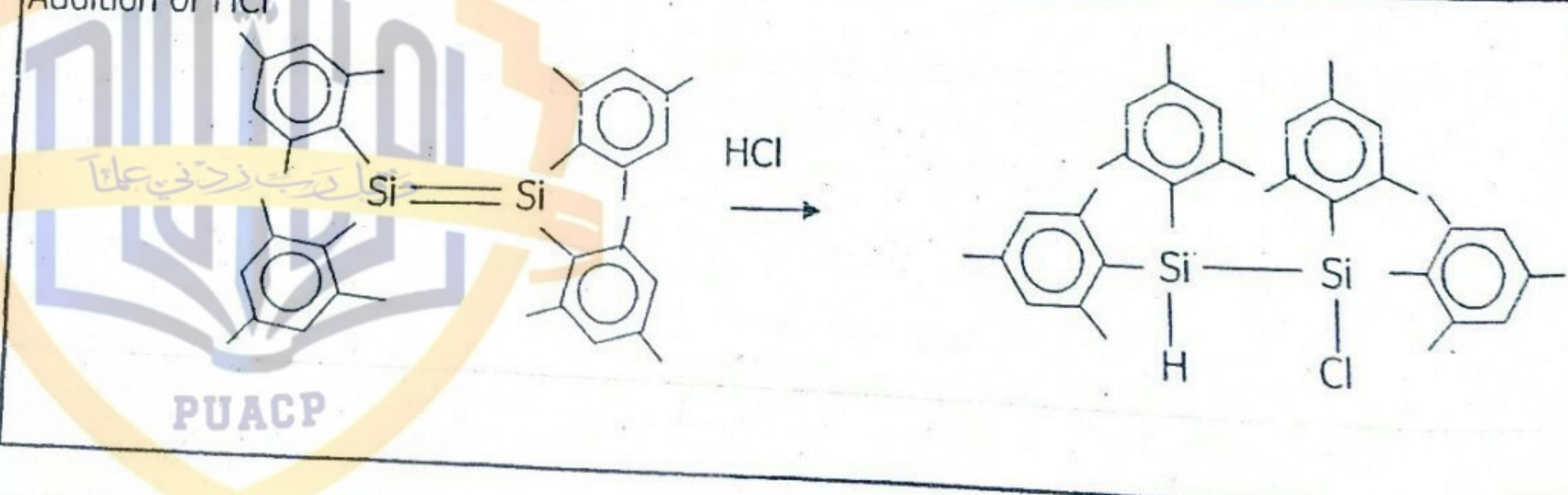
C = Si and Si = Si Bond

Rearrangement of cyclotrisilane



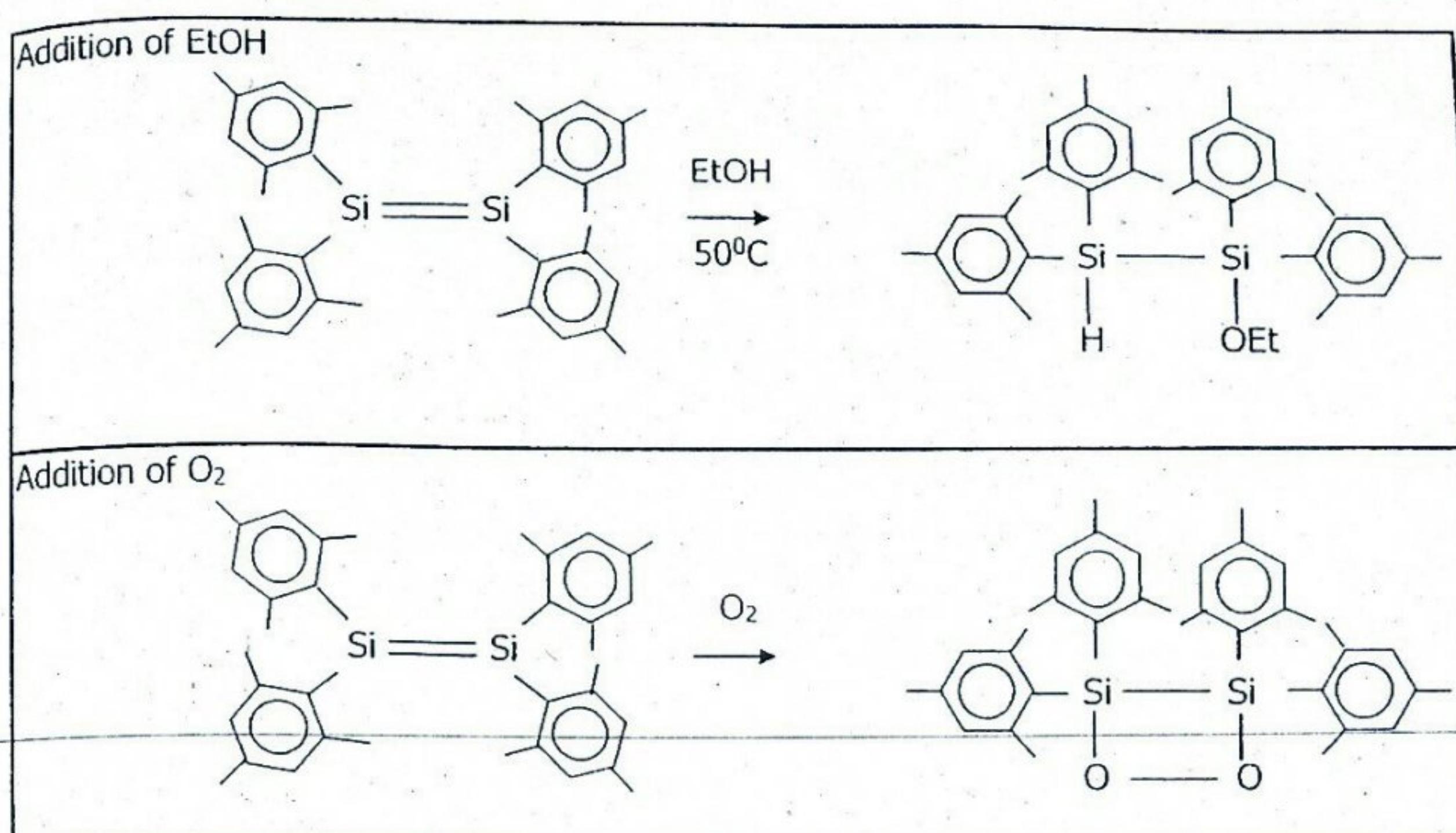
Similarities between C= C and Si = Si
There is possibility of electrophilic addition

Addition of HCl



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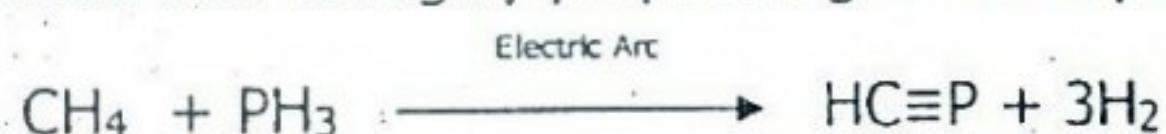


Germanium and Tin

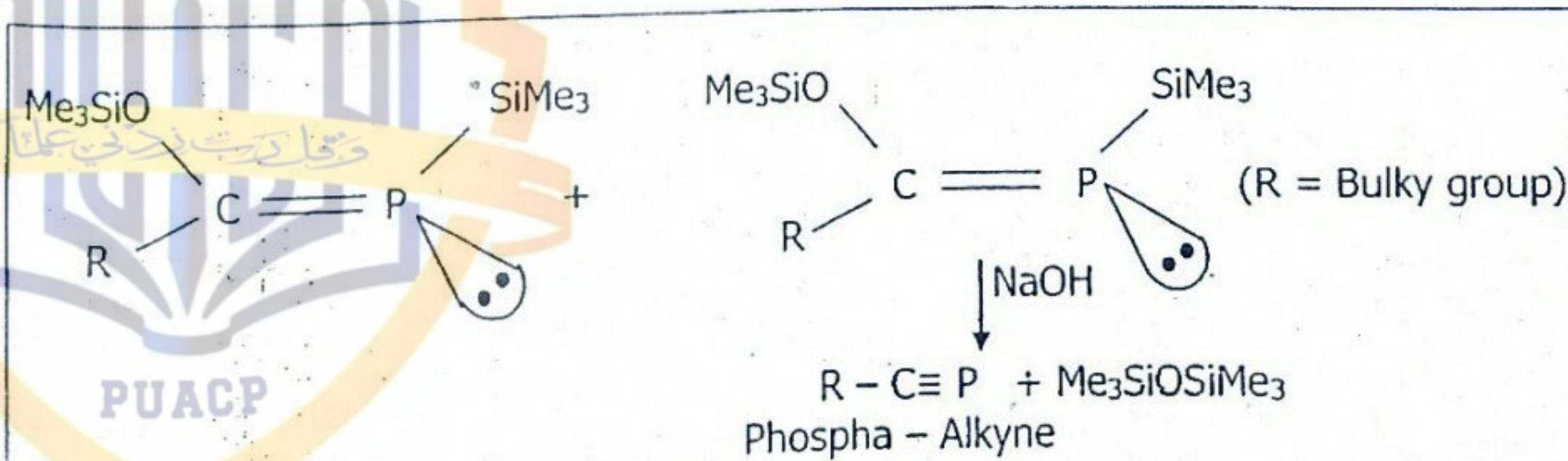
The Ge = Ge and Sn = Sn bonds are not as short as expected for true double bonds. Calculation indicate that $P\pi - P\pi$ bonding is less important and other interaction may become increasingly important. Calculated bond orders are Ge = Ge (1.61) and Sn = Sn (1.46). Remember in heavier elements single bonds are more effective than the multiple bonds.

Group V Elements

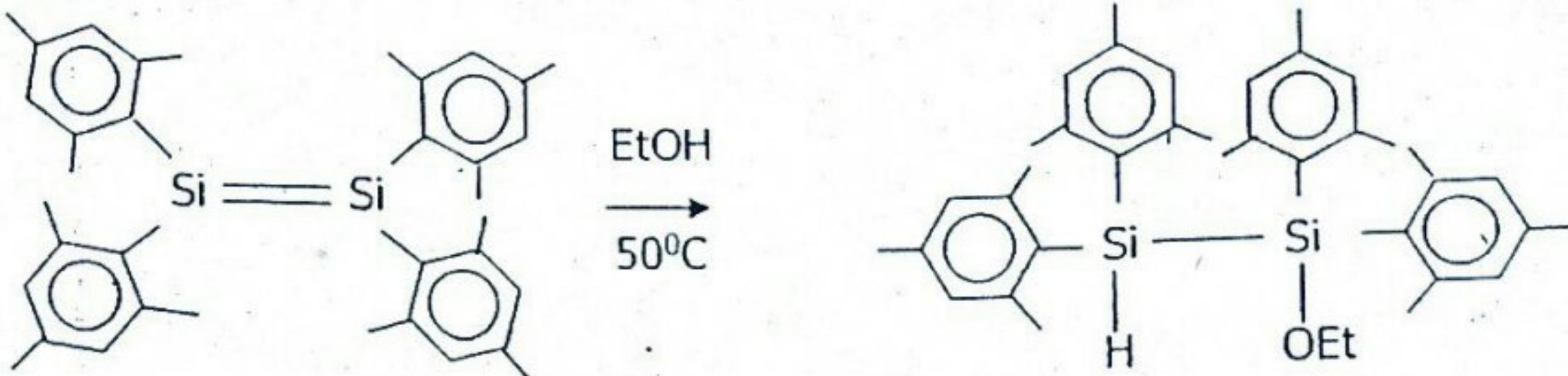
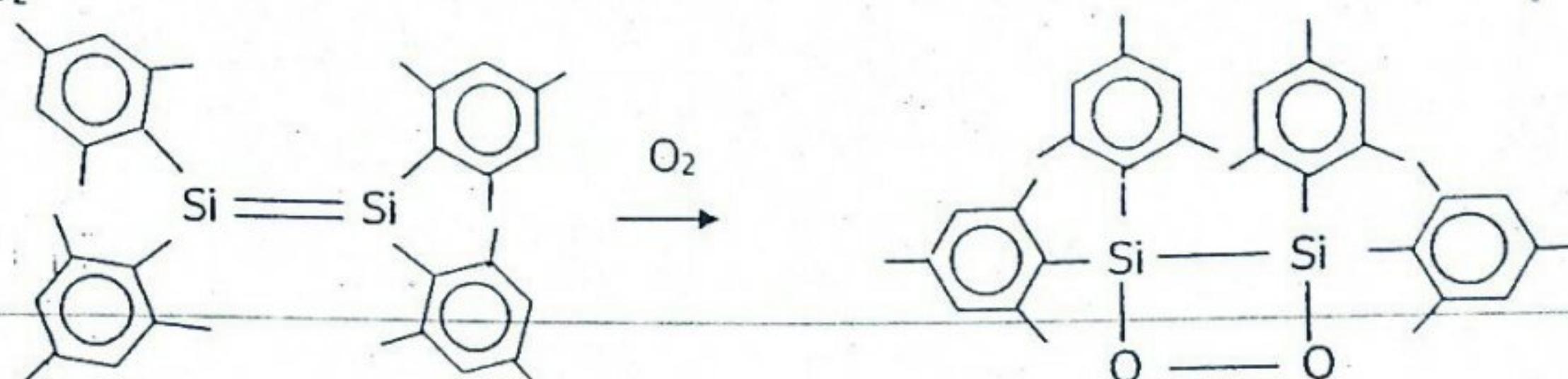
HCN is stable but HCP is highly propionic gas which polymerizes above -130°C .



Kinetically stable phospha-alkynes can be synthesized if a sufficiently bulky substituent (R) is present.



Addition of EtOH

Addition of O₂**Comparison of Strength of P_π – P_π Bond**

The 2p_π – 2p_π bond is stronger than their higher – n – congeners.

Reason

Greater stability of π – bond between smaller atoms. There is better overlap between two '2p' A.Os. The overlap integral is poor in the higher – n – congeners.

Heavier Congeners in Group IVA

Carbon is tetravalent except transient carbene or methylene intermediates. Ge, Sn and Pb give divalent compounds if bulky substituents (R = CH(SiMe₃)₂] are present.

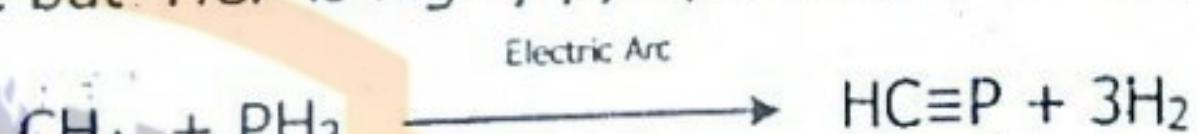
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Remember in heavier elements single bonds are more effective than the multiple bonds.

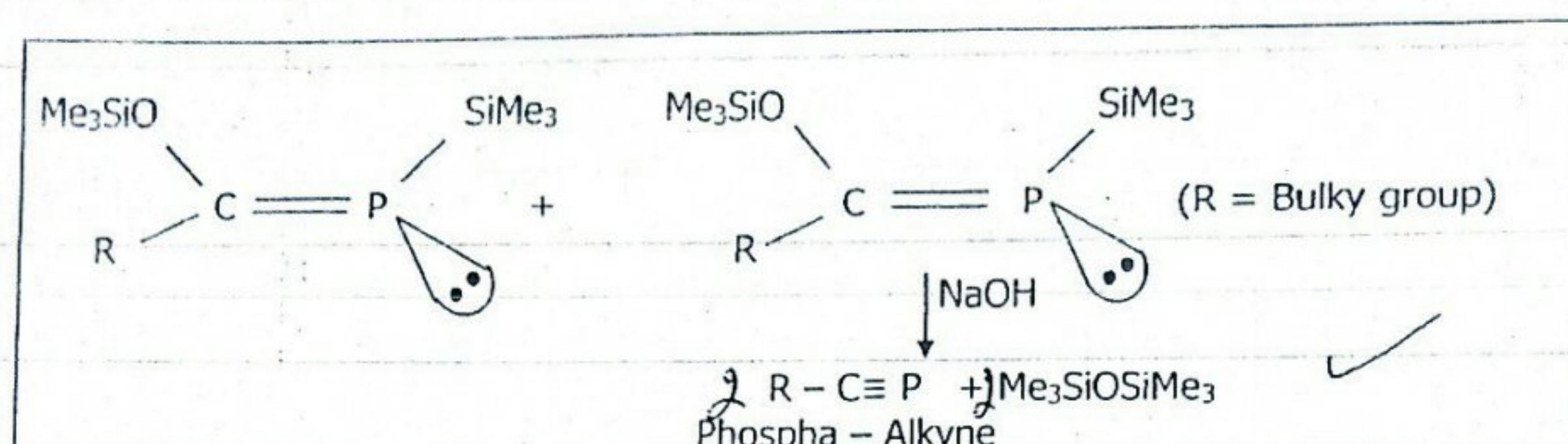
Group V Elements

HCN is stable but HCP is highly pyrophoric gas which polymerizes above – 130°C.

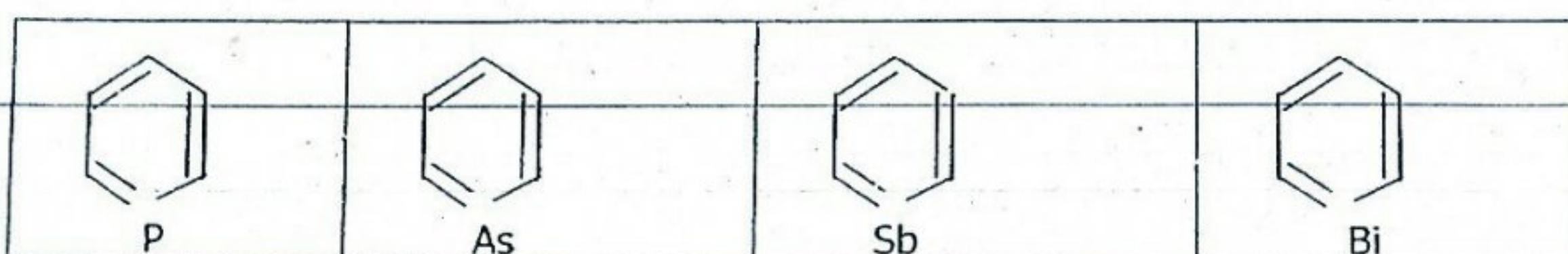


Kinetically stable phospha – alkynes can be synthesized if a sufficiently bulky substituent (R) is present.





All of the elements of Group VA(15) form compounds similar to pyridine.



However these compounds must be considered as the exception rather than the rule for heavier elements.

THE USE (or not) OF d - ORBITALS PARTICIPATION BY NON - METALS

Theoretical arguments against d orbital participation in non - metals

1) Principal Objection

There is large promotion energy required for the $s^2 p^n d^0 \longrightarrow s^1 p^{n-m} d^{m+1}$
Where m = 0 (for P), 1(for S) or 2 (for Cl) to achieve maximum multiplicity and availability of electrons for bonding.

$${}_{15}\text{P} = 1s^2, 2s^2, 2p^6, 3s^2, {}^0 3p_x^1, 3p_y^1, 3p_z^1, 3d_z^2 \text{ (Ground State) (Trivalent)}$$

$${}_{15}\text{P} = 1s^2, 2s^2, 2p^6, 3s^1, {}^1 3p_x^1, 3p_y^1, 3p_z^1, 3d_z^2 \text{ (Excited State) (Pentavalent)}$$

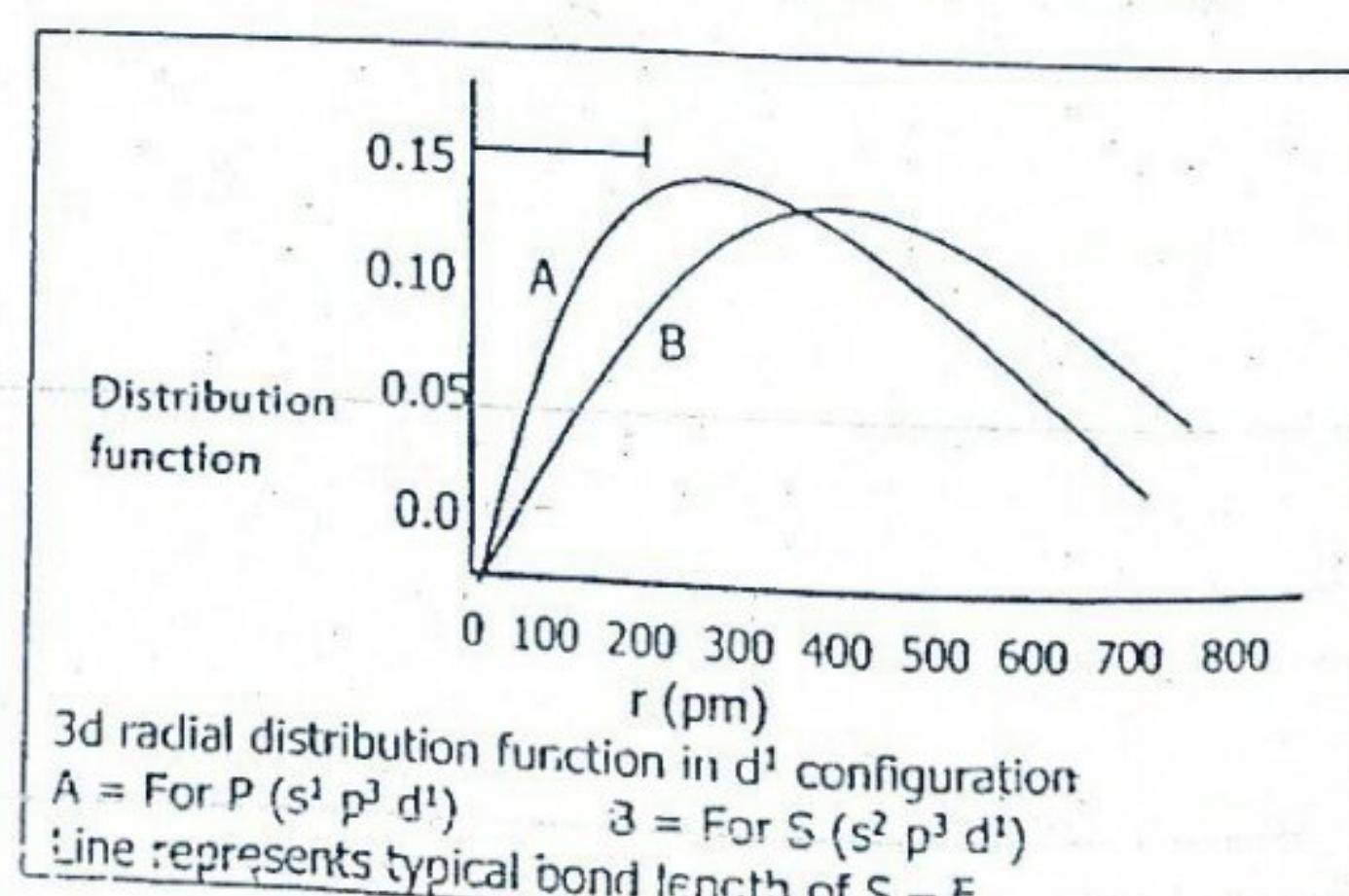
$${}_{16}\text{S} = 1s^2, 2s^2, 2p^6, 3s^1, {}^1 3p_x^1, 3p_y^1, {}^1 3p_z^1, {}^1 3d_{x^2-y^2}, 3d_z^2 \text{ (Excited State) (Hexavalent)}$$

$${}_{17}\text{Cl} = 1s^2, 2s^2, 2p^6, 3s^1, {}^1 3p_x^1, 3p_y^1, {}^1 3p_z^1, {}^1 3d_{xy}, {}^1 3d_{xz}, {}^1 3d_{yz} \text{ (Excited State) (Heptavalent)}$$

2) Second Objection

Poor overlap of d - orbitals does not favour the utilization of d - orbital participation with the neighboring atoms.

Reason: The 3d orbital of the free "S" atoms are shielded completely by the inner electrons. They do not feel nuclear charge as much as felt by "3s" and "3p" electrons. As a result they are extremely diffuse

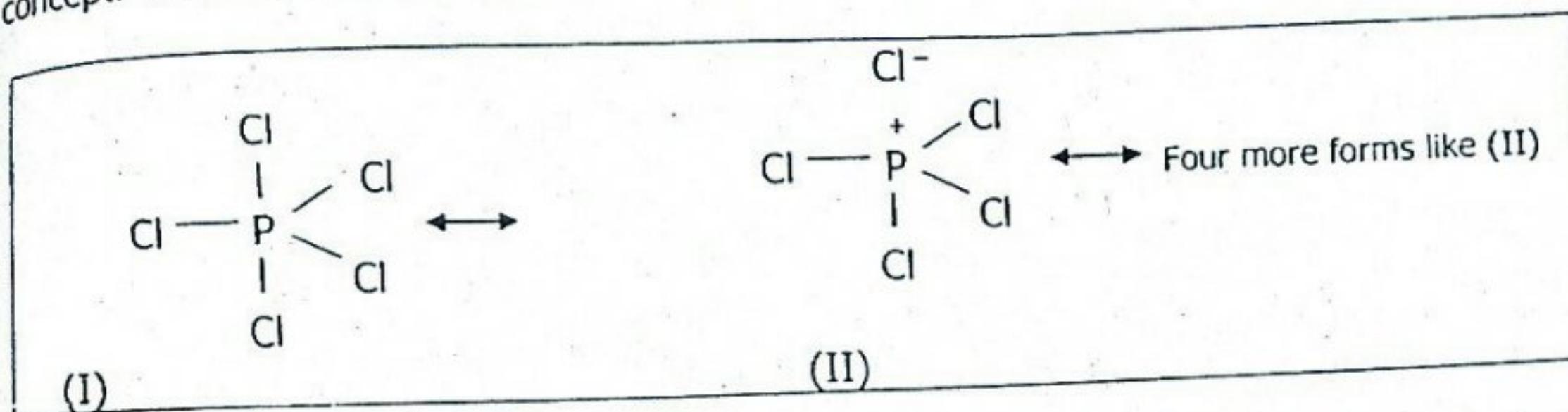


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20. having radial distribution maxima at a distance which is approximately twice the typical bond distance. This results in poor overlap and weak bonding.

1) First Alternative Explanation

In the favour of higher oxidation states of non-metals, Pauling suggested resonance concept. The resonance structures of PCl_5 are:



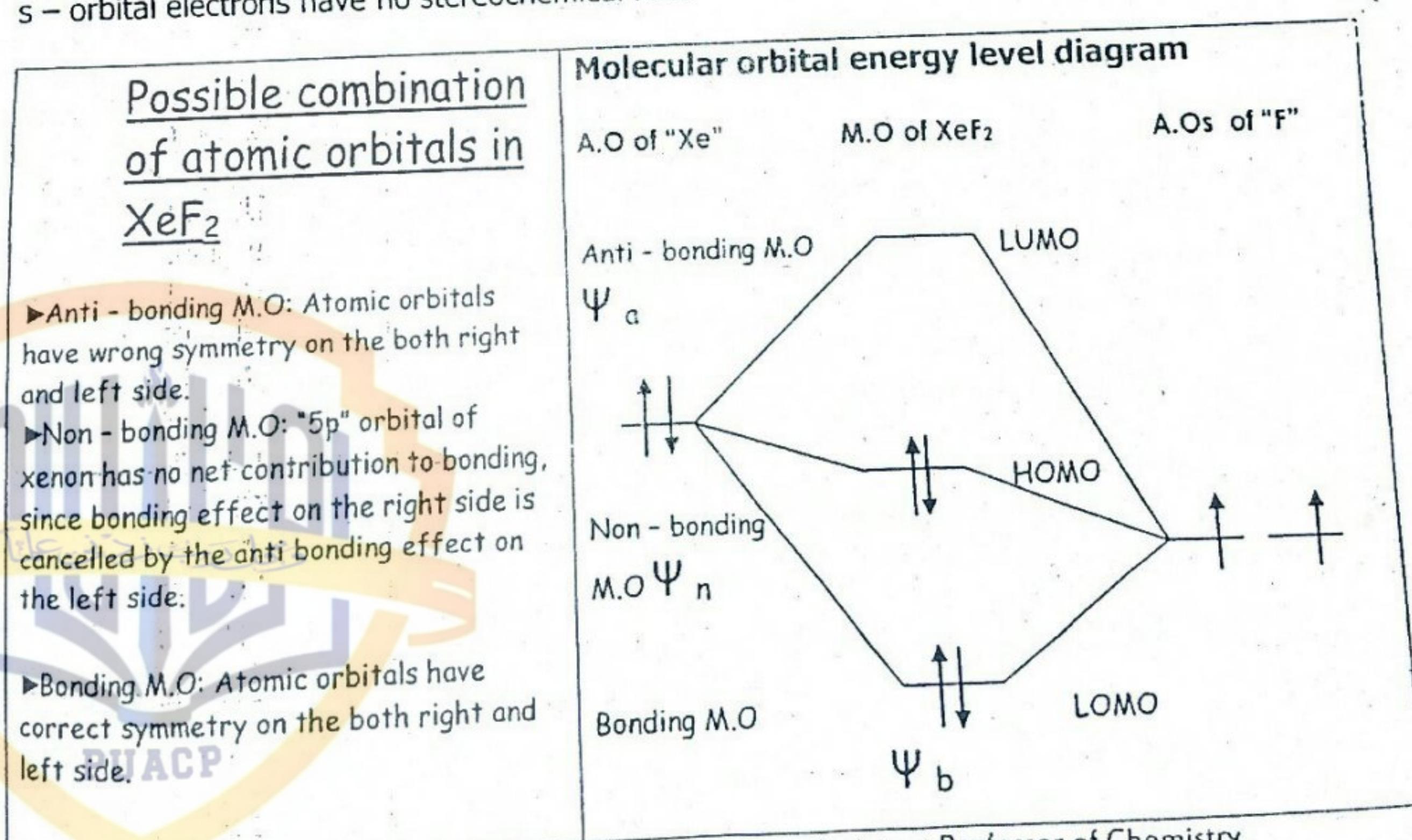
Only structure (I) involves d-orbital and so the "d" character of total hybrid is small. Each P-Cl bond has 20% ionic character and 80% covalent character from structure such as II.

2) Second Alternative Explanation (3c - 4e bond)

A new concept i.e., 3c - 4e bond model was introduced for explaining the properties of hypervalent molecules. It gives ionic properties of bond.

A 3c - 4e bond is axial, polar and multicentre sigma (σ -bond) bond. It is a combination of p-orbital of central atom and two ligand's orbitals i.e., an occupied bonding molecular orbital (LOMO), a non bonding molecular orbital (HOMO) and an unoccupied anti-bonding molecular orbital (LUMO).

The two "2p_z" orbitals of two fluorine atoms and one "2p_z" orbital of xenon atom combine to give three molecular orbitals. The four electrons - two of xenon and two of two fluorine atoms - will occupy the low energy molecular orbitals i.e., bonding M.O and non-bonding M.O. The s-orbital electrons have no stereochemical role.



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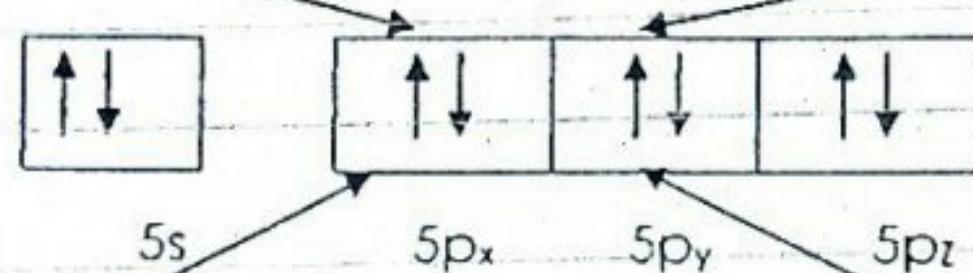
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XENON TETRAFLUORIDE (XeF_4): It has two $3c - 4e$ bonds.

$${}_{54}Xe = [Kr]^{36}, 4d^{10}, 5s^2, 5p_x^2, 5p_y^2, 5p_z^2$$

$${}_{9}F = [He]^2, 2s^2, 2p_x^1, 2p_y^2, 2p_z^2 \quad {}_{9}F = [He]^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^2$$

XENON



$${}_{9}F = [He]^2, 2s^2, 2p_x^1, 2p_y^2, 2p_z^2 \quad {}_{9}F = [He]^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^2$$

Theoretical arguments in the favour of d orbital participation in non-metals

Several workers said that large promotion energy and diffused character of d-orbitals are the properties of the isolated P-atom and S-atom. We should consider the properties of "P" and "S" in SF_5 and SF_6 . The properties have to be approximated in a molecular environment. The "d" orbital participation is formed only in the non-metals in high oxidation states with electronegative substituents.

Partial Charge Induction

The more electronegative substituents induce partial charges on a central "P" or "S" atom (as in PF_5 , OPX_3 , O_2SX_2).

(1) Increase in Effective Nuclear Charge

Increase in effective nuclear charge makes the energy levels to come close to each other. The inductive effect lowers the "d" orbital more than the corresponding "s" and "p" orbitals.

Reason

"d" orbital is more shielded and hence it is more sensitive to changes in electron density. The promotion energy will be lowered.

(2) Large partial charge on the atom results in shrinking of large diffuse "d" orbitals into smaller and more compact orbitals. So they overlap with neighbouring orbitals effectively.

Example

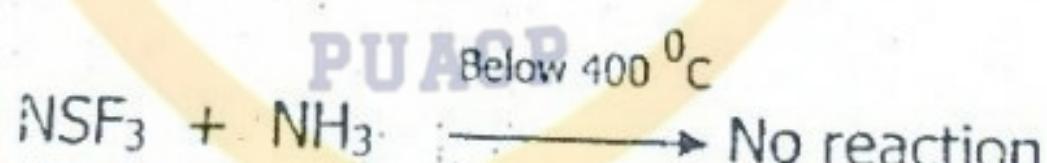
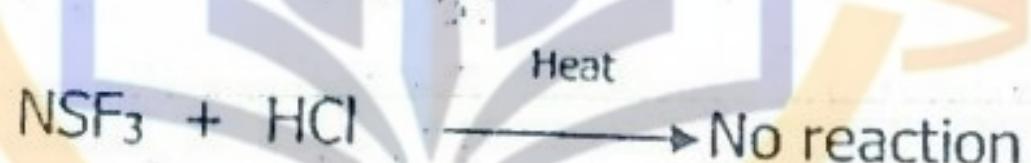
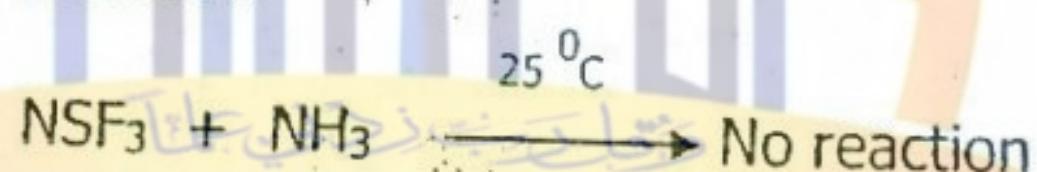
In SF_6 , "d" orbital have been contracted to an extent that the radius of maximum probability is only 130pm compared with the large values of 300 – 400pm in the free sulphur atom.

EXPERIMENTAL EVIDENCE FOR 'd' ORBITAL CONTRACTION AND PARTICIPATION

Consider following molecules as d orbital contraction and participation.

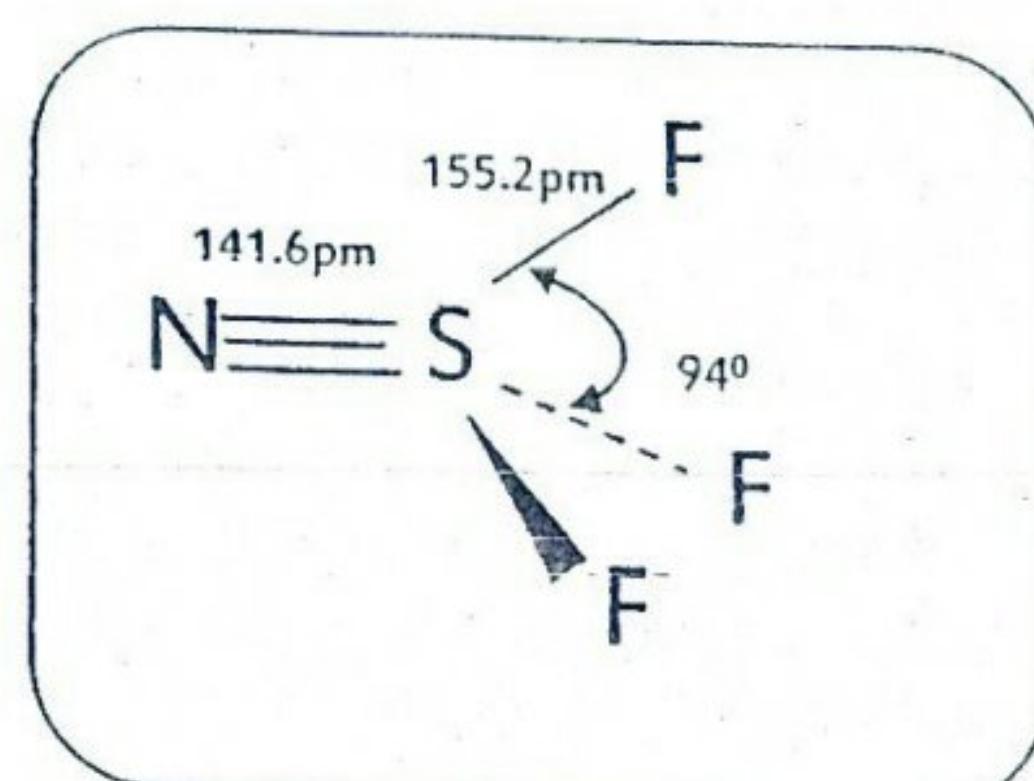
1) Thiacyl Trifluoride NSF_3

It is a stable compound and does not give following reaction.



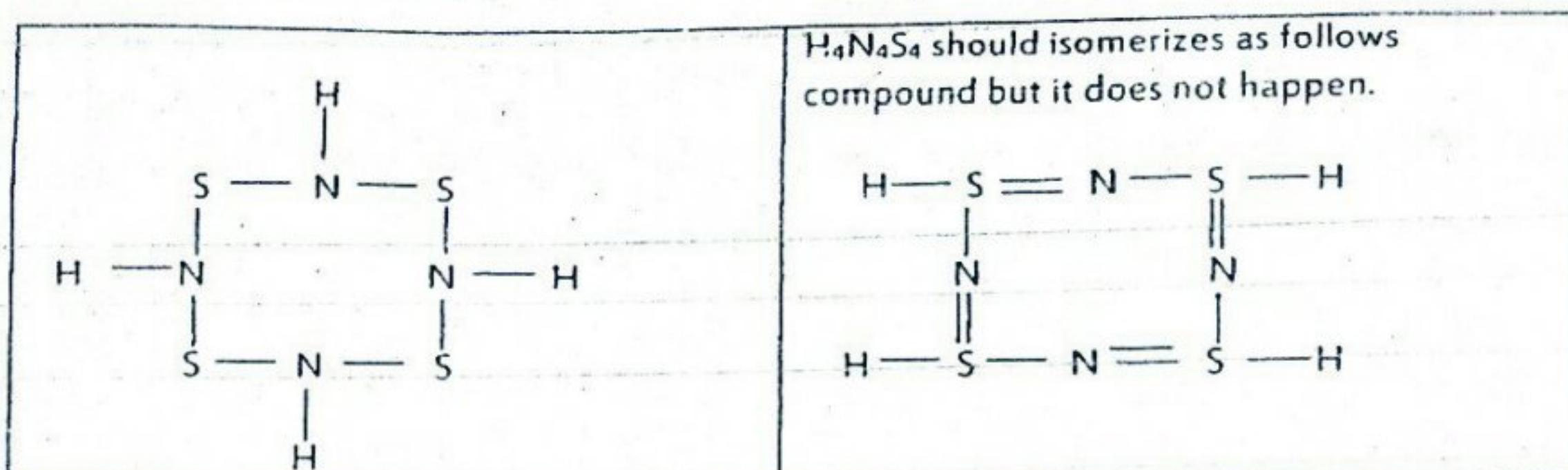
FSF bond angle is comparable to approximate sp^3 bonding. There is presence of sp^3 sigma bond and two

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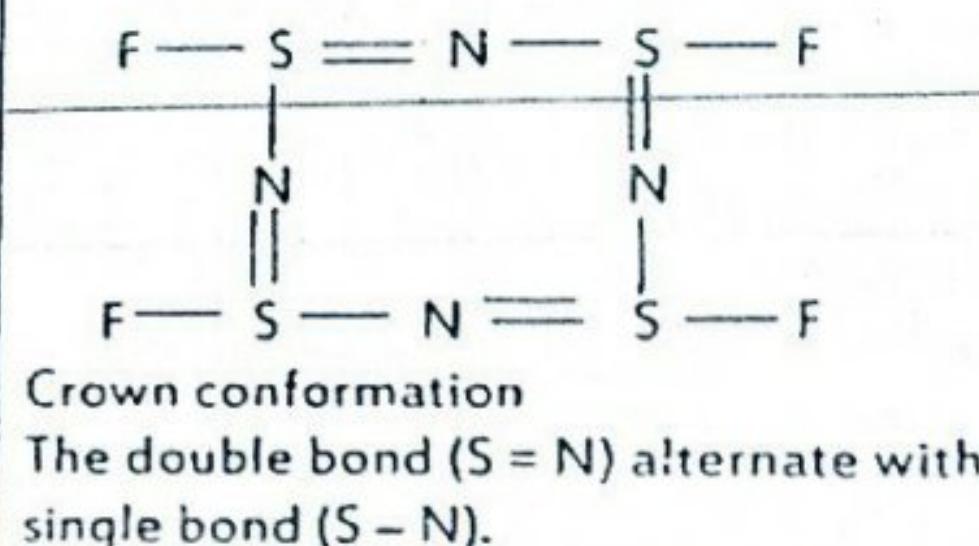
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2) Tetrasulphur tetraimide, $N_4S_4H_4$ Tetrasulphur tetraimide is isoelectronic with S_8



3) Tetrathiaazyil tetrafluoride, $N_4H_4F_4$

The pi bonding is possible in the presence of electronegative atom fluorine. The more electronegative substituents results in the contraction of d orbital and more efficient pi bonding.



Conclusion

Theoretical chemists are not convinced by the solution of problems of promotion energy and poor overlap.

Experimental chemists are involved in synthesis and characterization of compounds are convinced in the participation of d - orbitals.

REACTIVITY AND d - ORBITALS PARTICIPATION

The second row elements Li to F resemble their heavier congeners in formal oxidation states.

They also resemble with lower right diagonal elements in

Charge Size Electronegativity

Example # 1 Both Si and P form hydrides that have properties in common with alkanes, although they are less stable.

Example # 02 Both Si and P differ markedly from that of carbon. Consider reactions
 $\text{CCl}_4 + \text{H}_2\text{O} \longrightarrow$ No reaction



The Si and P have enhanced reactivity in their compound. It is also true for all the heavier nonmetals. But not true for compounds of elements of second row like CCl_4 . This is due to the d orbital participation.

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