Drago'S rule

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

(i) Belongs to third or lower period in periodic table

(ii) Contain atleast one lone pair of electron, and

(iii) Electronegativity of surrounding atom is $\leqslant 2.5$

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactorily if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals.

In such molecules bond angle is approximately 90°.

follow Drago's Rule

↓

No Hybridization

Chemical Bonding

Group 15	Bond angle	Group 16	Bond angle
NH_3	107°48'	H_2O	104°28'
PH_3	93°36'	H_2S	92°
AsH_3	91°48'	H_2Se	91°
SbH_3	91°18'	H_2Te	90.5°

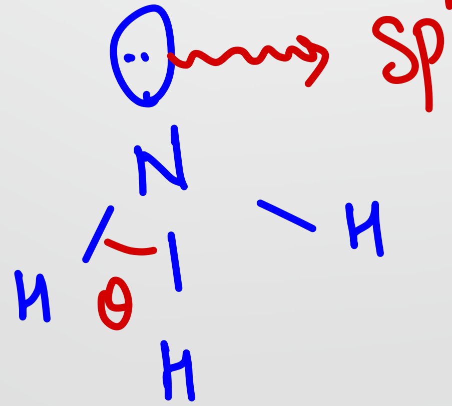
Hybridisation

No hybridisation

Right order of bond angle.

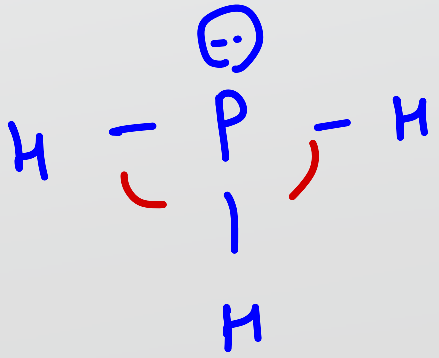
(a) $H_2O > H_2S > H_2Se > H_2Te$ (b) $NH_3 > PH_3 > AsH_3 > SbH_3$

sp3 hybrid orbital



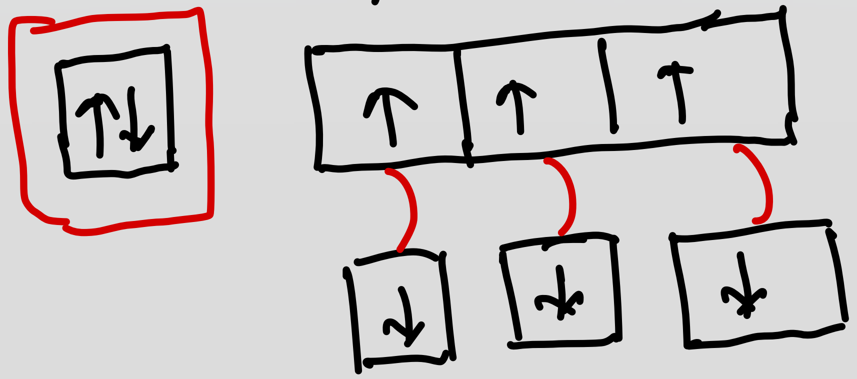
Hyb: sp^3

θ : 107°



Hyb: sp^3

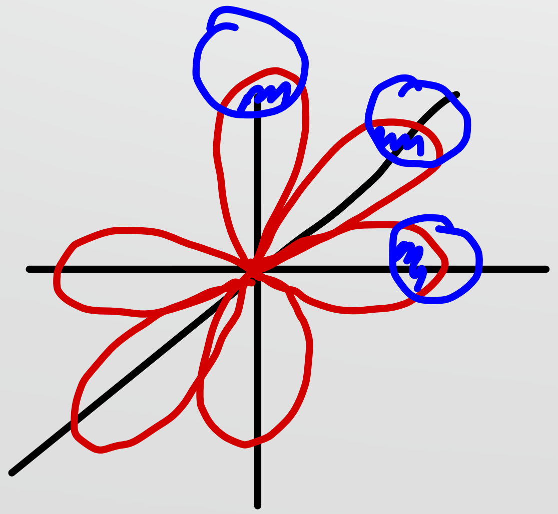
$_{15}P$ [Ne] $3s^2$ $3p^3$



$1s^1$ H

$1s^1$ H

$1s^1$ H



$\cos\theta = \frac{p-1}{p}$

The decreasing values of bond angles from NH_3 (106°) to SbH_3 (91°) down group-15 of the periodic table is due to

(1) decreasing lp – bp repulsion

(2) increasing electronegativity

(3) increasing bp – bp repulsion

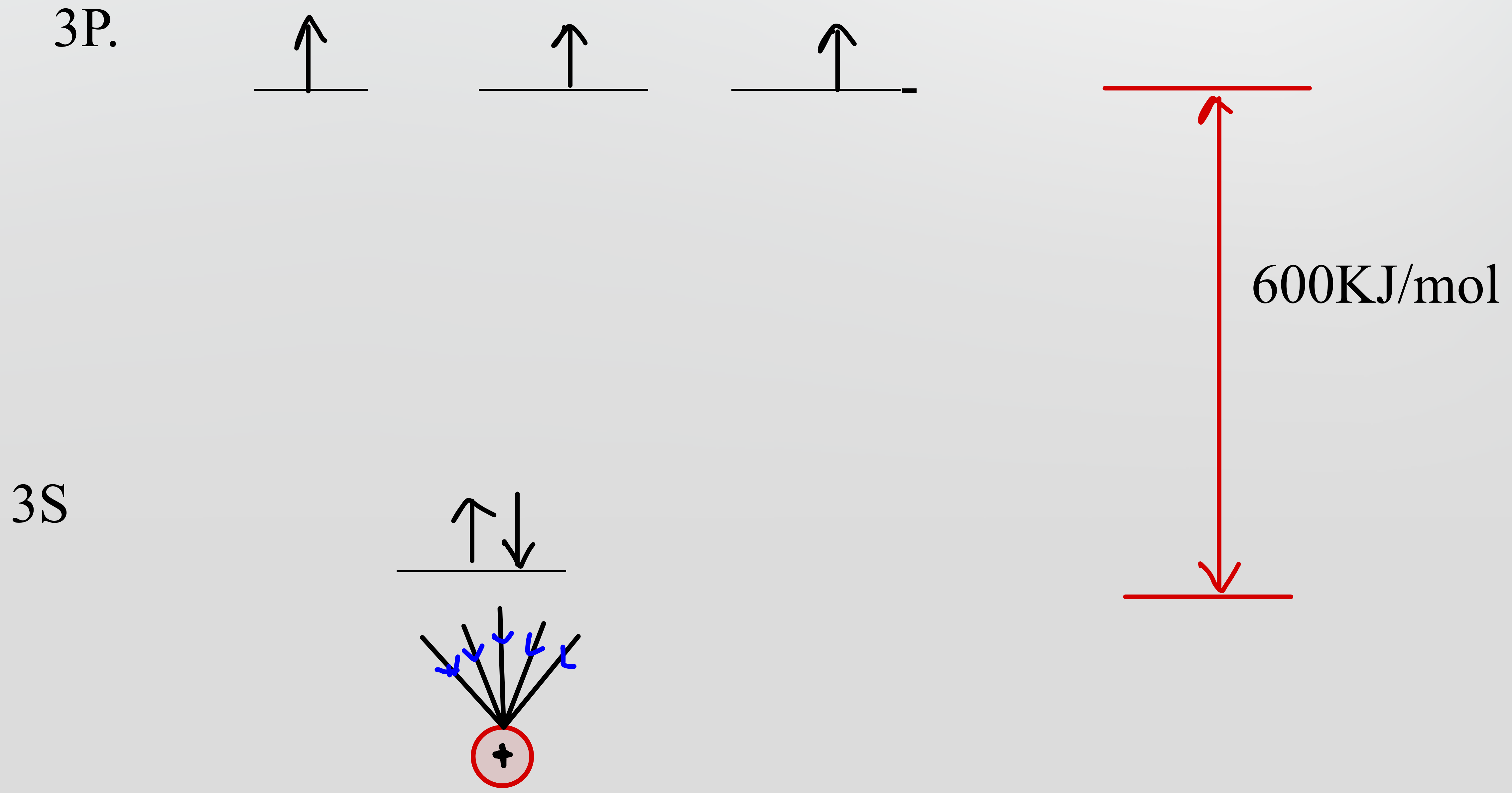
(4) increasing p-orbital character in sp^3

Chemical Bonding

Drago's Rule

" According to dragos rule if central atom of molecule is of third period or below this then lobe pair is present in stereochemically inactive S orbital and boding will take place through pure p orbital .In such case there is no hybridisation and BA is nearly 90 but EN of surrounding atom is less than or equal to 2.5"

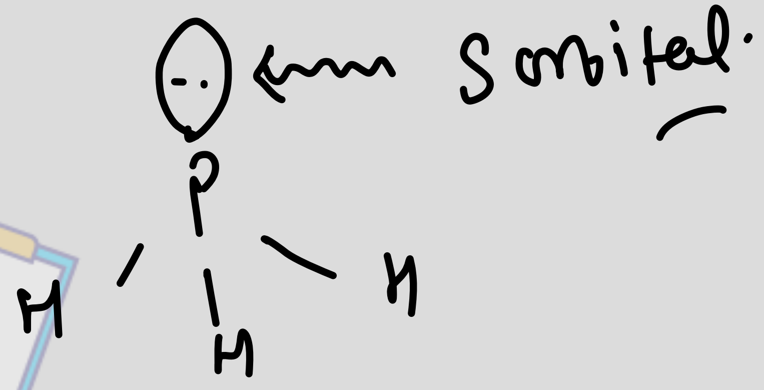
Example : PH3



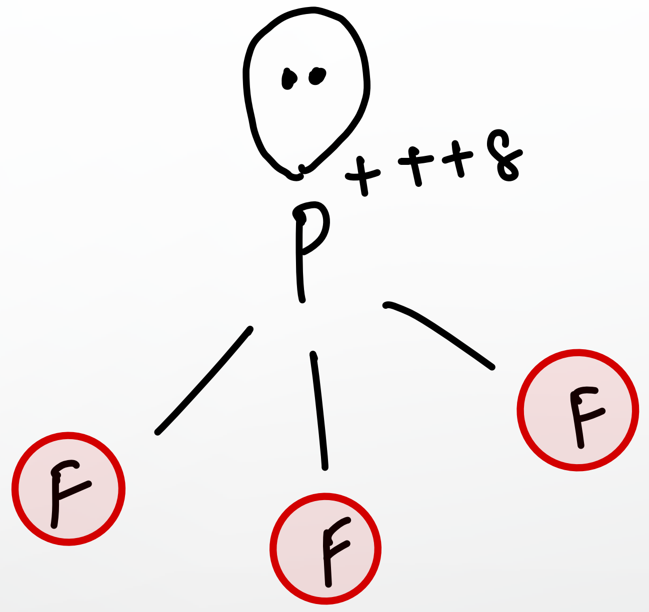
600KJ/mol > 3(P-H) Bond Energy

Hence hybridisation does not occur in PH3

P [Ne] $3S^2$ $3P^3$



Note : In PF3 and PCl3 hybridisation occur because E.N of S.A > 2.5

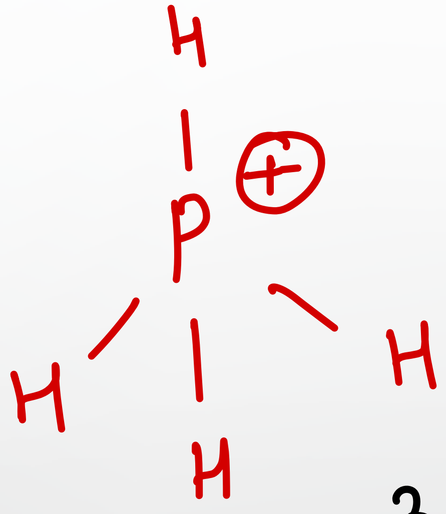


Hyb: sp^3

"3P is pulled near the nucleus hence hybridisation Energy decreases and hybridisation Occur

Chemical Bonding

* Note : In PH_4^+ ——— SP3 hybridisation occur because 600 KJ/ mol < 4(P-H) bond



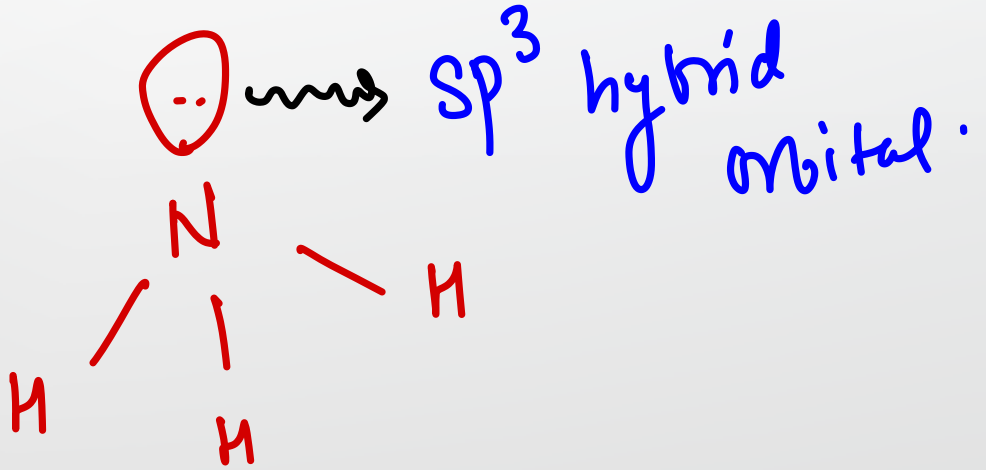
Hyb: sp^3

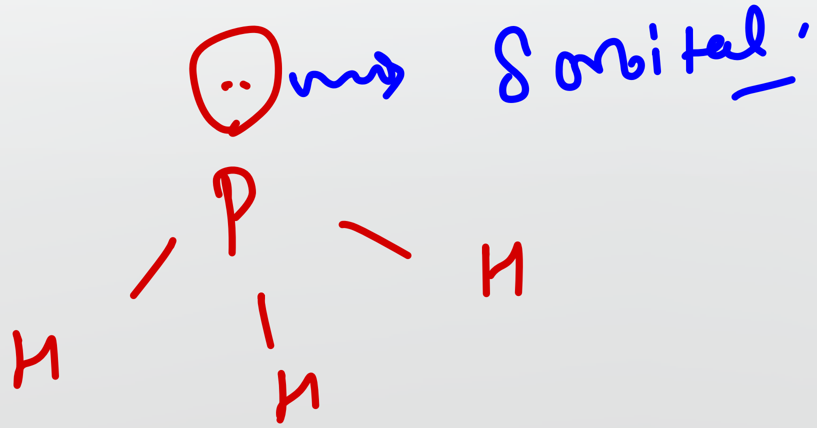
Hyb : sp^3

Effect on property

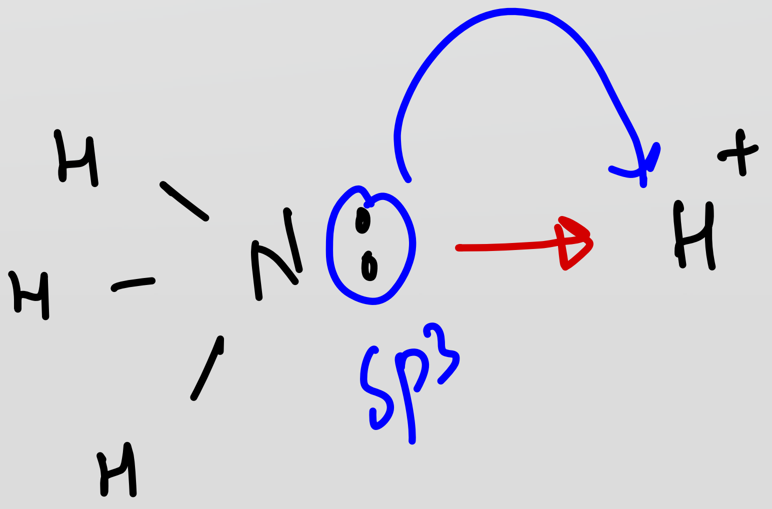
1. Lone pair donation tendency

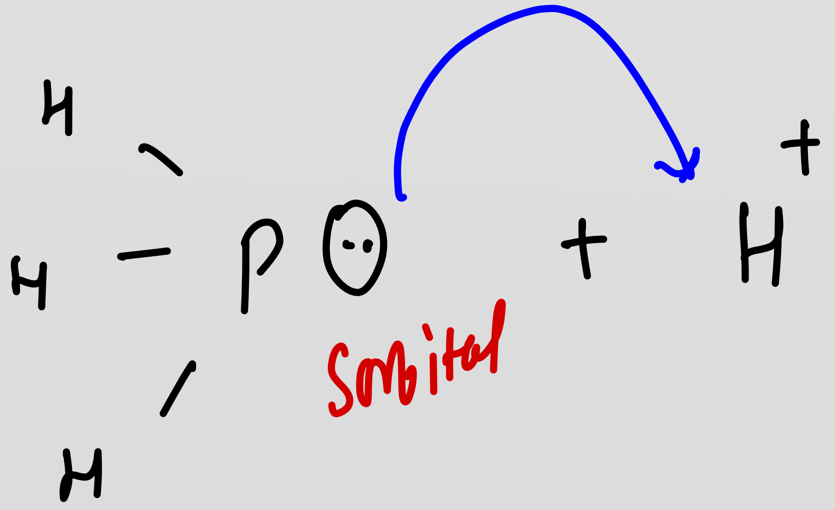
$NH_3 > PH_3$





Hyb: sp^3





Co-ordination compounds

* NH_3 is SFL (Strong field ligand) & PH_3 is WFL (weak feild Ligand)

2. Formation of ions

$NH_3 > PH_3$

$NH_3 + H^{+} \longrightarrow NH_4^{+}$ {fast}

$PH_3 + H^{+} \longrightarrow PH_4^{+}$ {slow}

3. Solubility in H2O

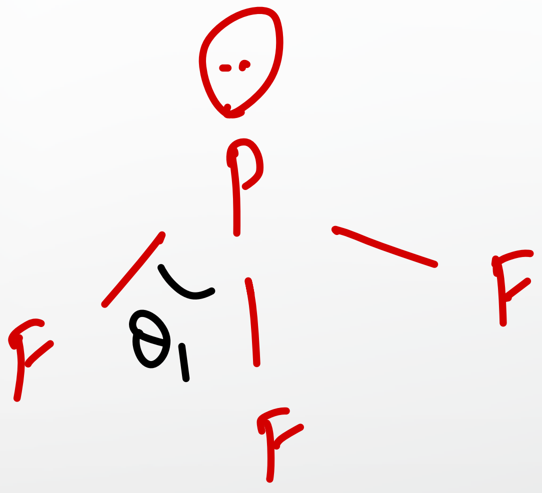
$NH_3 > PH_3$

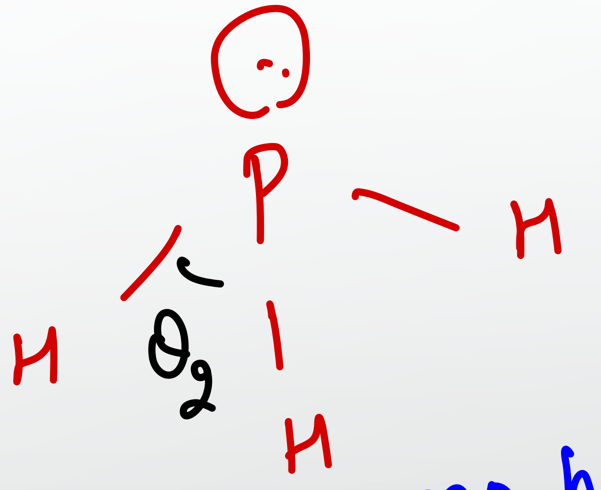
(a) $\ddot{N}H_3 + H-OH \longrightarrow \overset{\oplus}{N}H_4 \ \overset{\ominus}{O}H$

(b) $\ddot{P}H_3 + H-OH \longrightarrow \overset{\oplus}{P}H_4 \ \overset{\ominus}{O}H$

$\boxed{\text{Solubility} \quad \ddot{N}H_3 > \ddot{P}H_3}$

(Q) Compare bond angle in PF_3 and PH_3





Hybridization

(no hybridization)

$$\boxed{\theta_1 > \theta_2}$$

(Q)
Among the following, the correct statement is :

(A) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

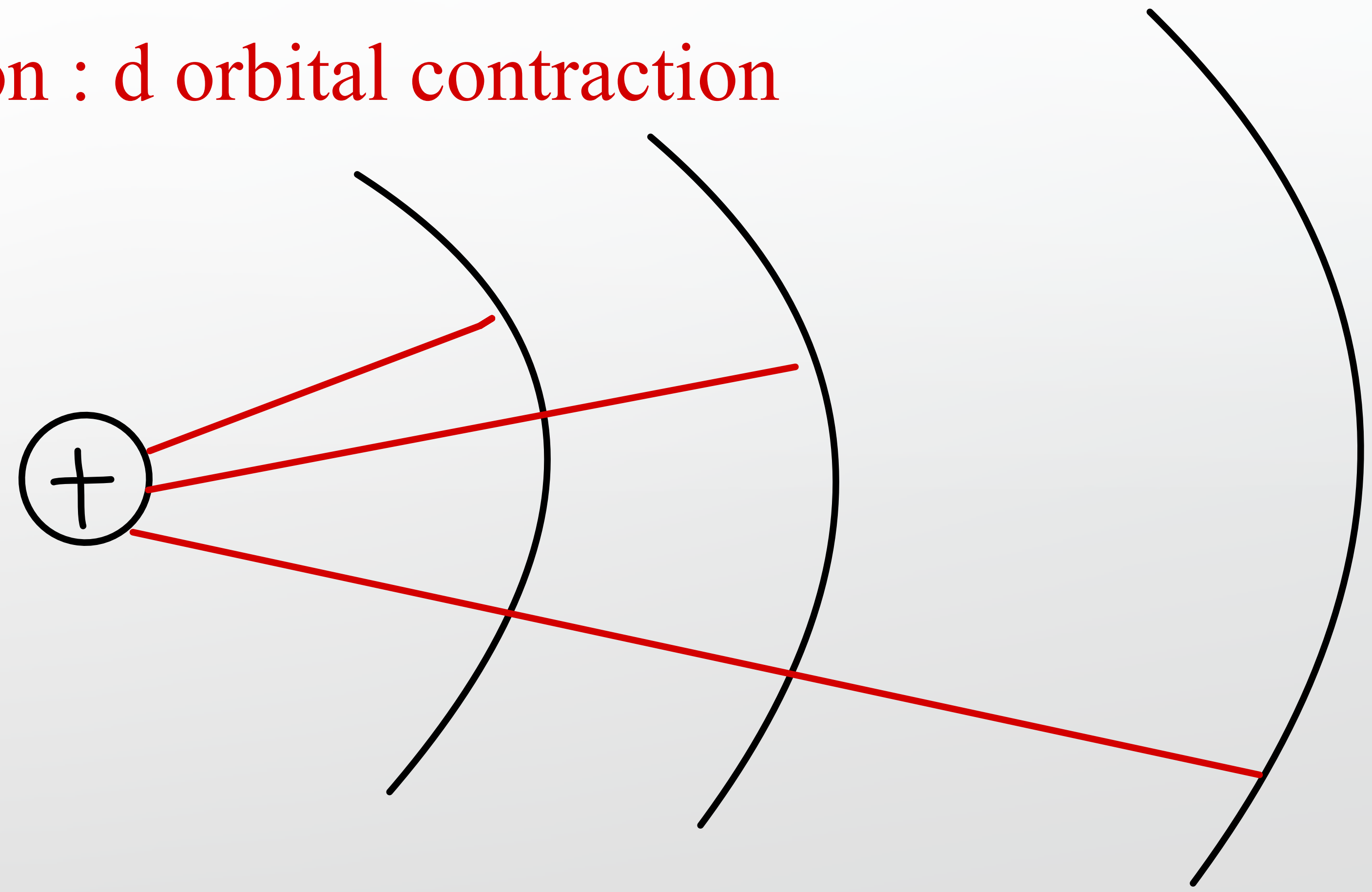
(B) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional

(C) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional

(D) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

(Q) Explain why PH_5 doesn't exist but PF_5 Exist ?

Reason : d orbital contraction



3S. 3P. 3d

Higher energy difference

PH_5	PH_4F.	PH_3F_2.	PH_2F_3.	PHF_4.	PF_5
✗	✗	✓	✓	✓	✓

Find out the % p-character in the orbital occupied by lone pairs in H_2O.

[$\widehat{HOH}$ = 104º5 and cos (104.5) = –0.25]

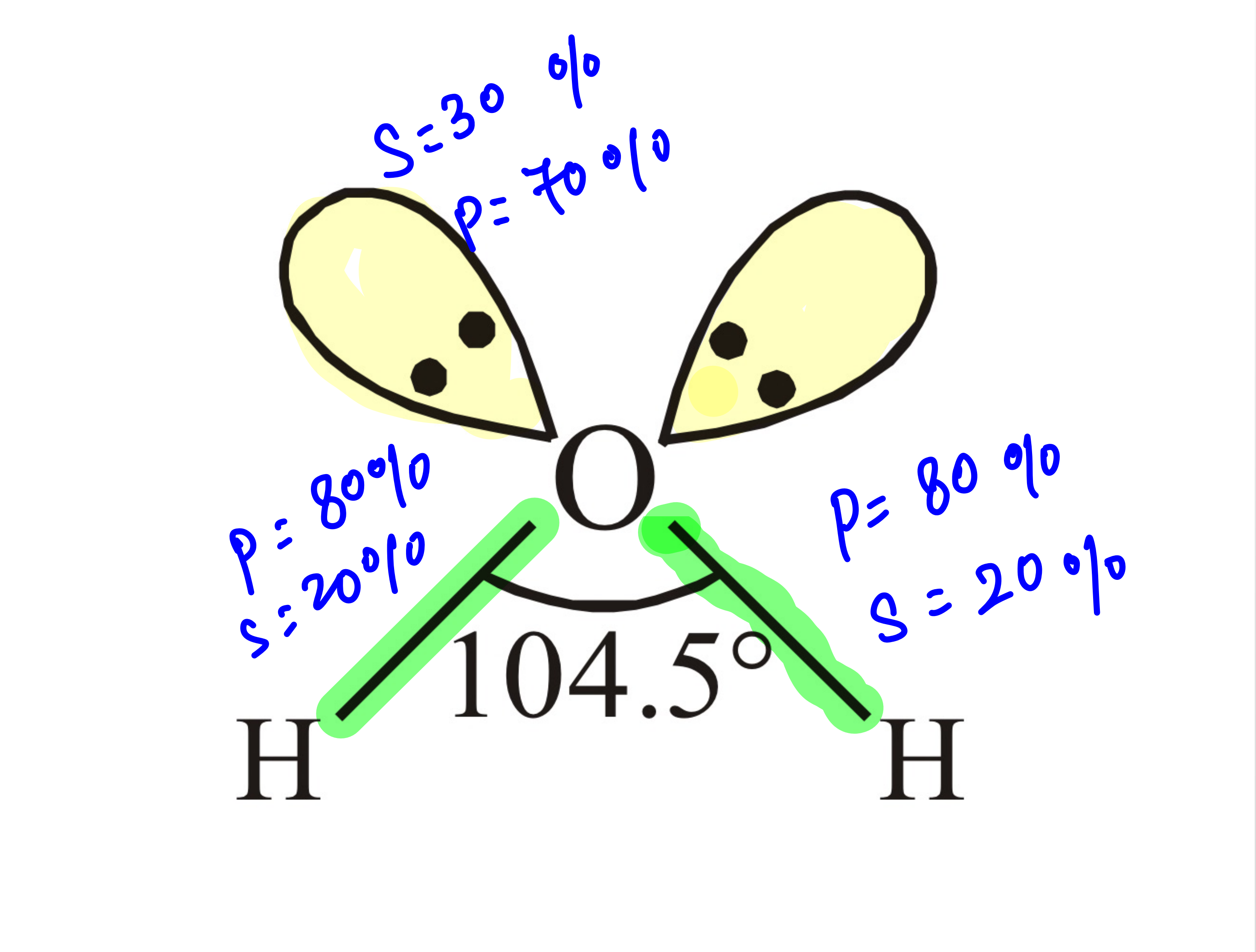
(A) 80 % (B) 20 % (C) 70 % (D) 75 %

$\cos\theta = \frac{p-1}{p}$ $\{-(O-H)\}$

$\cos(104.5) = \frac{p-1}{p}$

$-0.25 = \frac{p-1}{p}$

$p = \frac{4}{5} = 80\%$

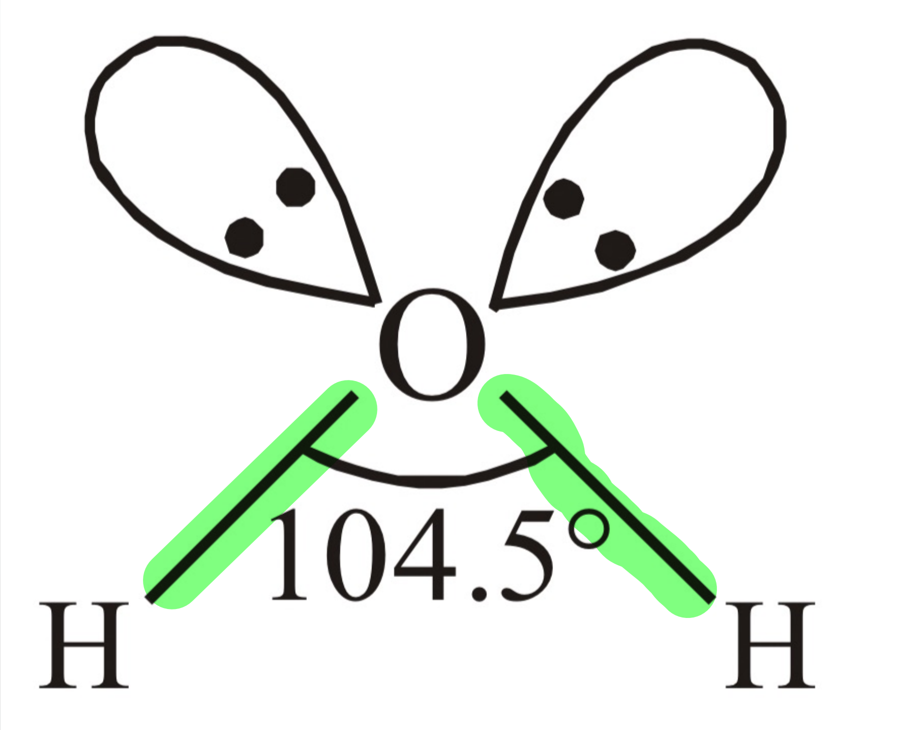


Bond parameters:

Comparison of Bond angle.

Bond Angle

The angle between two bonds is known as bond angle.



Factors affecting bond angle

(a) State of Hybridisation

(b) Presence of lone pair

(c) Electronegativity of central atom

(d) Electronegativity of surrounding atom

(e) Size of surrounding atom

(f) Lone pairs may sometimes be transferred from a filled shell of one atom to an unfilled shell of another bonded atom, causing less repulsion.

(g) Multiple bond orbital repel other orbitals more strongly than single bond orbitals.

Chemical Bonding

Steps to compare bond angle

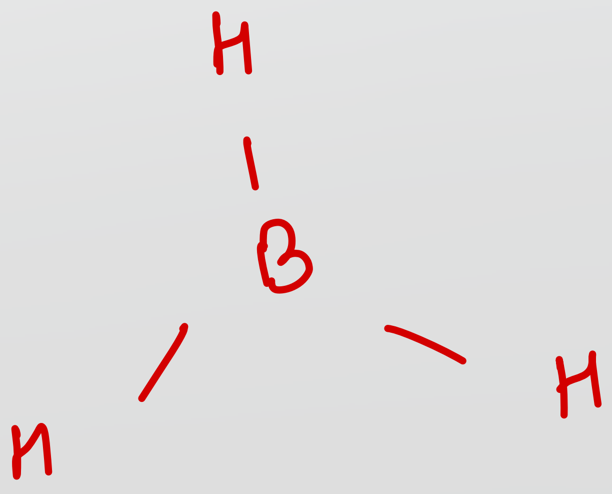
Check the hybridisation of C.A

STEP1

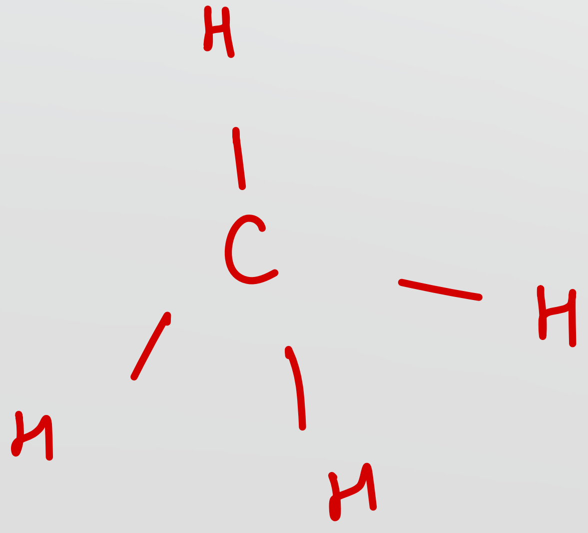
Hybridisation state of central atom: Compounds having different hybridisation have diferent bond angle.

Ex.	BeH_2	BH_3	CH_4
Hybridisation	sp	sp^2	sp^3
Bond angle	180º	120º	109º28'

>



>



Hyb: sp

B. A : 180°

Hyb: sp^2

B A = 120°

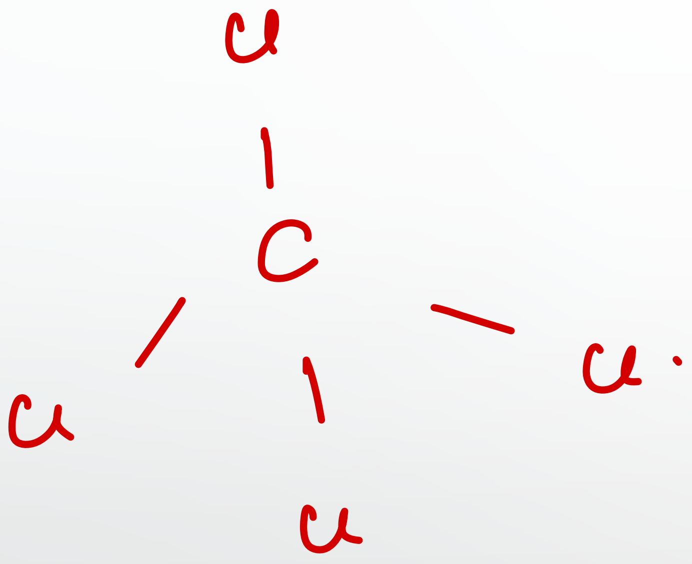
Hyb: sp^3

B . A : $109^{\circ}\,28'$

(Q) compare bond angle of the given molecule (a) $BeCl_2$ (b) BF_3. (C) CCl_4

$Cl - Be - Cl$ $>$

$>$



Hyb : Sp.

B.A = 180^0

Hyb : Sp^2

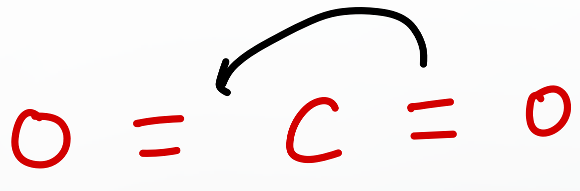
B.A : 120^0

Hyb : Sp^3

B.A = $109^0\ 28'$

(Q) compare bond angle between (a) CO_2 (b) SO_3.   (C). XeO_4

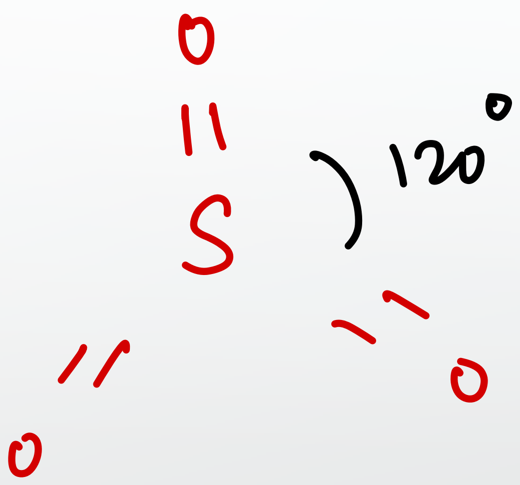
180°



Hyb: sp

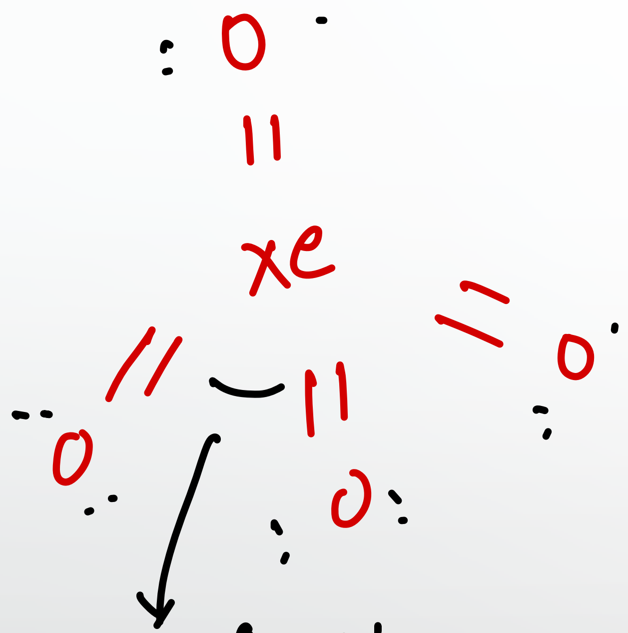
$>$

120°



Hyb: sp^2

$>$



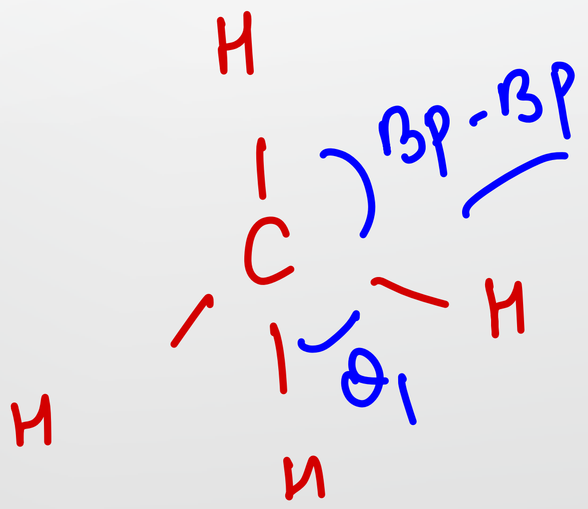
$109^\circ 28'$ Hyb: sp^3.

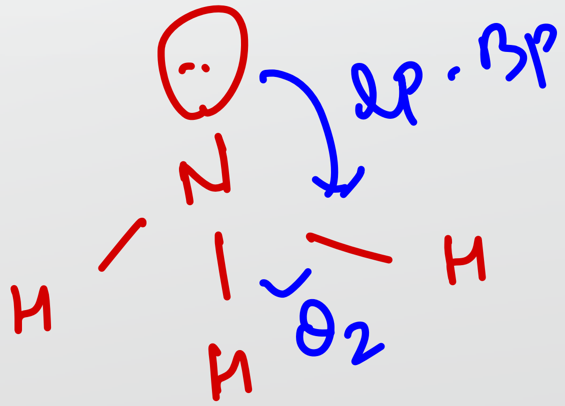
** what if the hybridisation is same for all the molecule ?

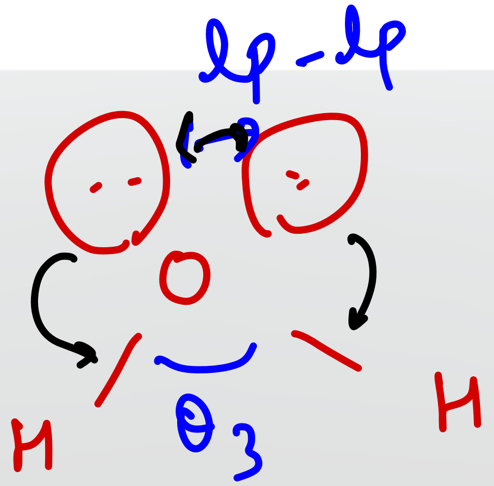
STEP 2

Lone pair of electron: If compounds have same hybridisation states then bond angle depends on lone pair of electron.

Ex.	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
Lone pair e^-	zero	one	two
Bond angle	109°28'	107°	105°







$\boxed{\theta_1 > \theta_2 > \theta_3}$

The different in bond angle is explained on the basis of following repulaion sequence

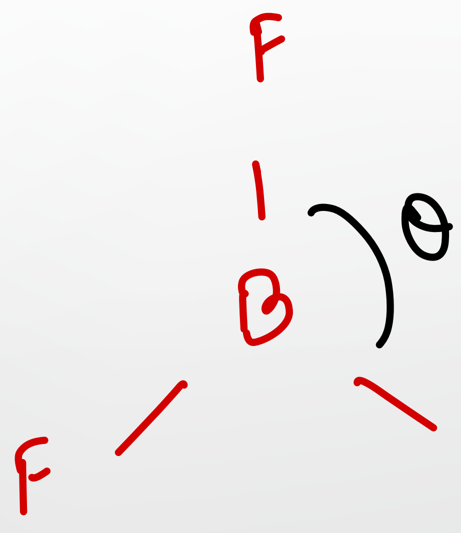
The repulsion between

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair

ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

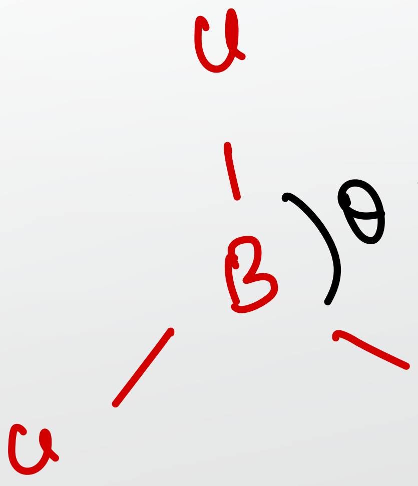
(Q) How to compare bond angle if hybridisation is same and there is no lone pair on central atom.?

Compare bond angle in BF_3 , BCl_3 , BBr_3 , BI_3



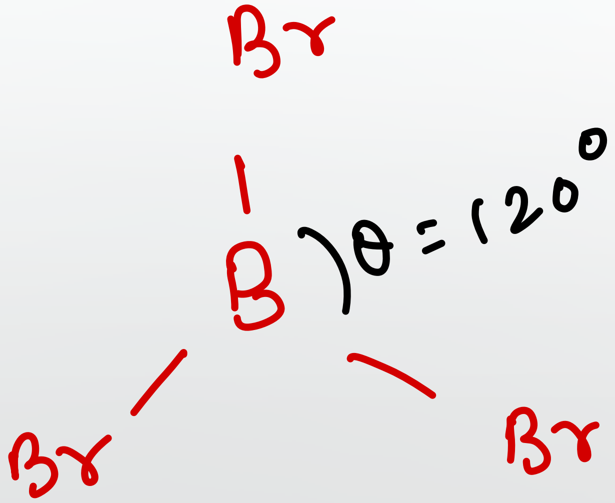
$\theta = 120^\circ$

Hyb: sp^2



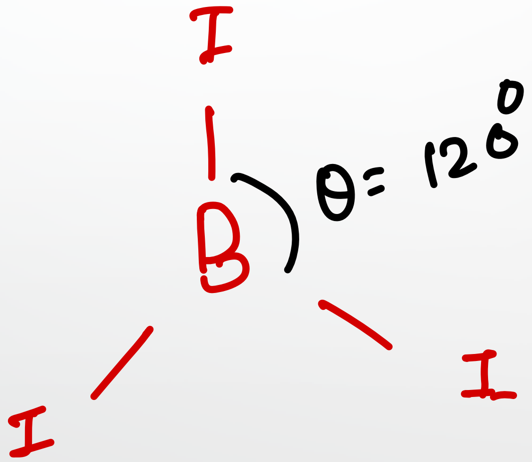
$\theta = 120^\circ$

Hyb: sp^2



$\theta = 120^\circ$

Hyb: sp^2



$\theta = 120^\circ$

Hyb: sp^2

(Q) How to compare bond angle when hybridisation is same and number of lone pair on central atom is also same?

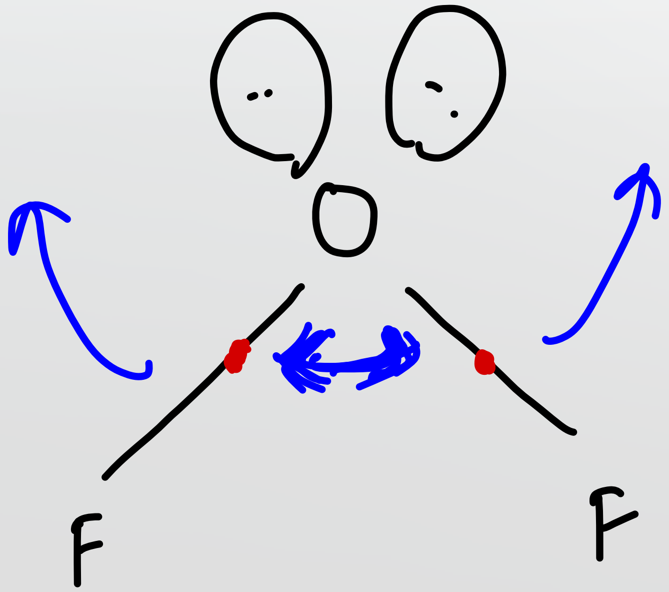
Chemical Bonding

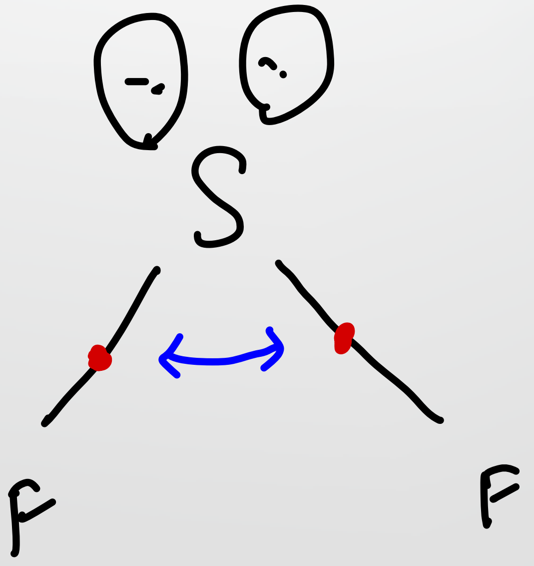
Step 3:

Electronegativity: When compounds having same hybridisation state of central atom and same number of lone pair of electrons, then bond angle depends on electronegativity.

Bond angle ∝ electronegativity of central atom

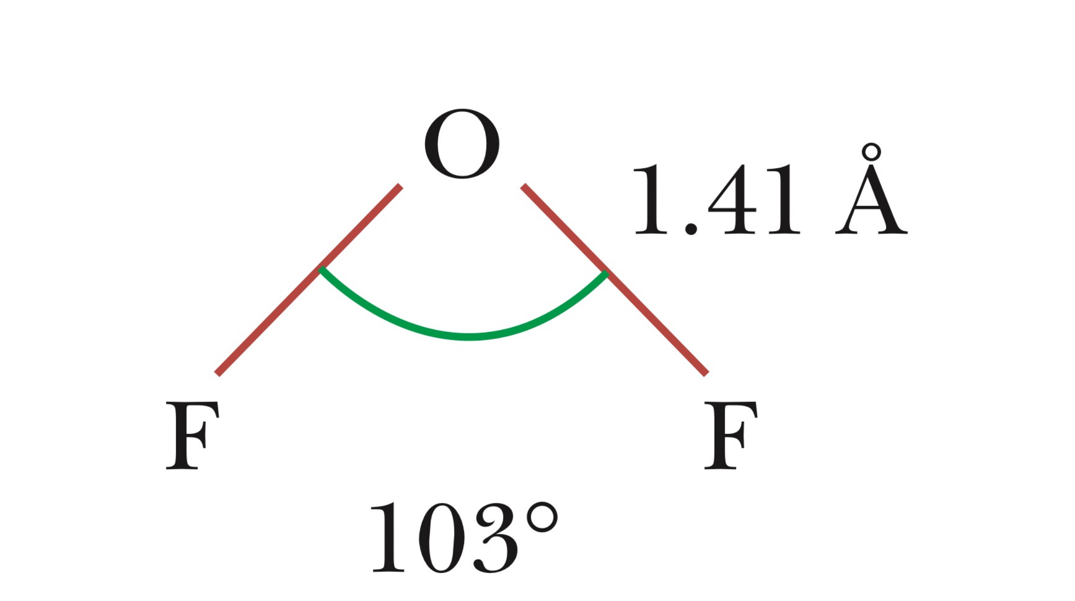
Compare bond angle in (a) OF_2 and (b) SF_2

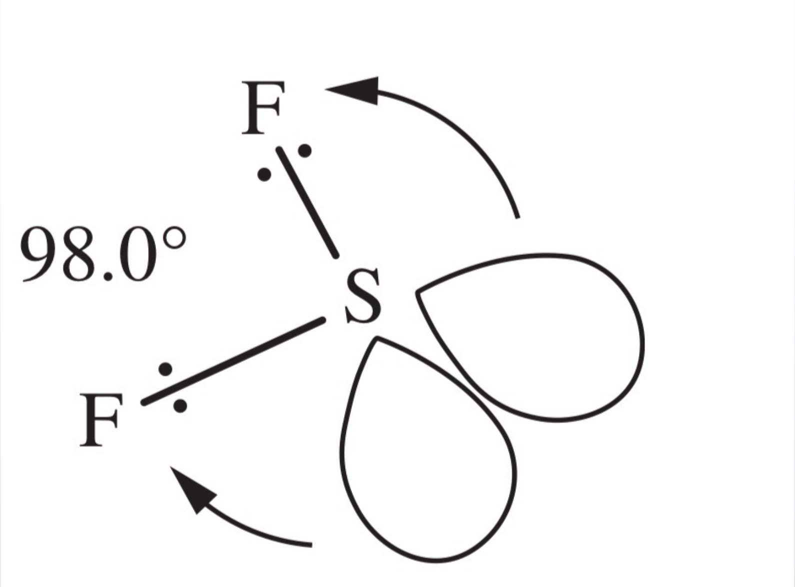




* Hyb: sp^3 Hyb: sp^3

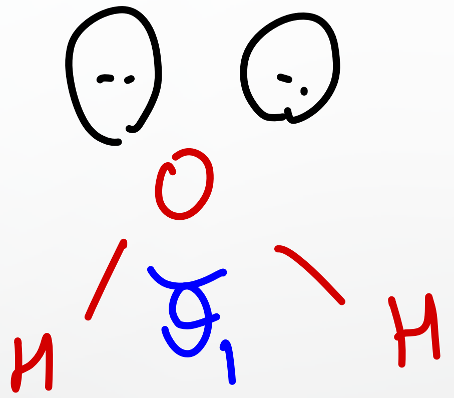
* no of lone pair = 2 (same)


O
1.41 Å
F
F
103°

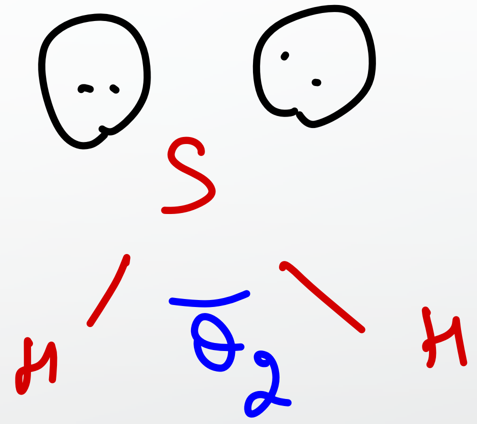

F
98.0°
S
F

Chemical Bonding

(Q) Compare bond angle in (a) H_2O and H_2S
(b) NH_3 and PH_3



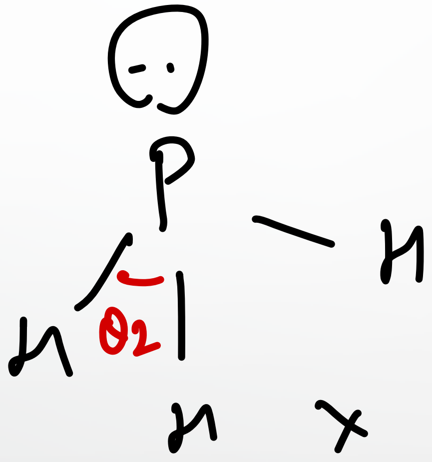
Hyb: sp^3



Hyb: ✗

$\boxed{\theta_1 > \theta_2}$

Hyb: sp^3



$\boxed{\theta_1 > \theta_2}$

Drago's rule

(Q) How to compare bond angle if hybridisation is same ,number of lone pair is same and Central atom is also same