VSEPR Theory, Valence Bond Theory, Characteristic of Covalent Compounds

1. VSEPR theory was proposed by Gillespie and Nyholm to explain the shapes of molecules and ions.

2. The orbital which contains the bonded pair of electrons is known as the localised orbital.

3. The orbital which contains the non bonded pair of electrons is known as the delocalised orbital and that electron pair is called delocalised electron pair (or) lone pair. Lone pair occupies more space than bond pair around the nucleus of central atom.

4. The shape of a simple molecule depends on the number of electron pairs present in valence shell of central atom.

5. The lone pairs of electrons and bonded pairs of electrons on central atom are oriented in such a way they feel minimum repulsion and maximum stability.

6. The repulsion between electron pairs is in the order.

7. The number of electron pairs in single bond (or) double bond (or) triple bond (or) dative bond is counted as only one pair because all the electron pairs in the same bond are oriented in the same direction.

8. The molecules without lone pairs have a regular geometry.The presence of lone pairs give an irregular geometry due to unequal repulsive forces.

9. The number of lone pairs of electrons (l.p) and bond pairs of electrons (b.p) on central atom determines the shape of molecule or ion.

No of B.Ps	No of L.Ps	Formula	Molecular shape	Example
2	0	AB_2	Linear	$BeCl_2$ BeF_2 C_2H_2
3	0	AB_3	Planar Triangle	BF_3 BCl_3
4	0	AB_4	Tetrahedral	CH_4 NH_4^+ CCl_4
5	0	AB_5	Trigonal bipyramidal	PCl_5
6	0	AB_6	Octahedral	SF_6
2	1	AB_2E	Bent	SO_2 O_3
3	1	AB_3E	Trigonal Pyramidal	NH_3
2	2	AB_2E_2	Bent	H_2O
4	1	AB_4E	See Saw	SF_4
3	2	AB_3E_2	T-Shape	ClF_3
5	1	AB_5E	Square Pyramidal	BrF_5
4	2	AB_4E_2	Square Planar	XeF_4

A = Central atom in the compound.

B = Atom linked to the central atom.

E = Lone pairs of electron.

Valency Bond Theory (V.B.T)

1. V.B.T was proposed by Heitler and London to explain the shapes of covalent molecules, their bond angles and bond lengths.It was extended by Pauling and Slater to explain the directional nature of covalent bonds.

2. Covalent bond is formed by the overlapping of two orbitals having unpaired electrons. The two orbitals involving in overlapping must belong to two different atoms and the electrons present in them must have opposite spins.

3. The greater the extent of overlapping, the stronger is the bond formed. The overlapping of atomic orbitals follows the order. p-p >s-p > s-s

4. The bond is formed in the direction of overlapping of orbitals.

5. A covalent bond formed due to Axial or Linear overlapping of atomic orbitals results in the formation of sigma bond(σ). Its electron cloud is concentrated symmetrically around the inter nuclear axis.

6. A covalent bond formed by the side wise overlap (Or) Lateral overlapping of atomic orbitals is known as a pi bond(π) .Its electron cloud is present on either side of the inter nuclear axis. 'σ' bond is formed only after the formation of 'π' bond.

7. Any type of orbitals can involve in σ '' bond formation. Only 'p' or 'd' - orbitals can involve in π '' bond formation.

8. Single bond is always 'σ' bond. Double bond contains one 'σ' bond and one 'π' bond.

   Triple bond contains one 'σ' bond and two π '' bonds.

9. 'σ' bond is stronger than 'π' bond due to greater extent of overlapping.

10. Strength of the bonds follows the order $\sigma_{p-p} > \sigma_{s-p} > \sigma_{s-s} > \pi$

11. Strength of the bonds follows the order triple bond > double bond > single bond.

12. i) H_2 contains one 'σ' formed by 1s - 1s axial overlapping

    ii) Cl_2 contains one 'σ' formed by $2p_z$ - $2p_z$ axial overlapping

iii) O_2 contains one 'σ' & 1 π bond i.e. 'σ'is Formed by P_y - P_y axial overlapping and π bond is formed by side wise overlapping

iv) N_2 contains one 'σ'bond and two π bonds

v) HCl contains one 'σ' bond i.e formed by 1s - p_z axial overlappaing

vi) H_2O contains two 'σ' bonds. i.e. formed by axial overlapping of s & p orbitals. In H_2O at '0' centre both P orbitals are present in mutual perpendicular directions. So expected bond angle of H_2O is 90^0. But in H_2O actual Bond angle is $104^0.30^1$.

vii. NH_3 contains three 'σ' bonds i.e formed by axial overlapping of S & P orbitals. In NH_3 at 'N' centre, three 'P' orbitals are present in mutual perpendicular directions. So expected bond angle in NH_3 is 90^0. But actual bond angle in NH_3 is $107^0.14^1$
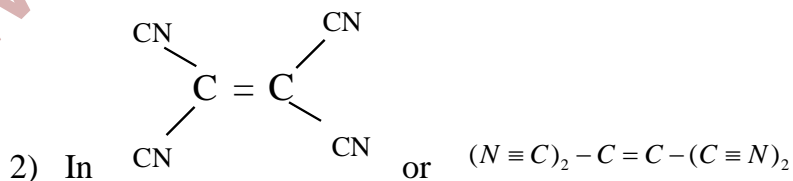
viii) In CH_4, four 'σ' bonds are present i.e one is formed by 1s & 2s orbitals axial overlapping and other three are formed by 1s & 2p orbitals axial overlapping.

14. No.of 'σ'bonds in open chain compounds = atomacity - 1

no.of'σ' bonds in a cyclic compound= atomacity

a. Example: CO_2

No. of 'σ' bonds = 3 - 1 = 2

2) In

or $(N \equiv C)_2 - C = C - (C \equiv N)_2$

No. of 'σ' bonds = 10 - 1 = 9, no.of pi bonds=9

3) In C_2H_4 no. of 'σ' bonds = 6 - 1 = 5

Properties of Covalent Compounds

1. Covalent compounds exist as solids, liquids and gases

2. Covalent compounds have low melting and boiling points as their molecules held of weak vanderwaals forces.

3. Mostly Covalent compounds are soluble in Non polar solvents are Benzene, Carbon disulphide, carbon tetrachloride etc. but not in polar solvents.

4. Covalent compounds are not electrical conductors either in molten state or in aqueous solutions as they do not contain free ions or electrons. Graphite, etc are covalent compounds but their aqueous solutions are good electrical conductors due to free ions.

 *Graphite is a good conductor as it contains free electrons.

5. Covalent compounds involve in chemical reactions very slowly.

6. Covalent compounds exhibit space isomerism because covalent bond is a directional bond.

7. Covalent compounds contain individual molecules.

* Diamond, Graphite, Boron, Silicon, Silica, Boron nitride, Boron Carbide and Silicon carbide etc are po;ymeric covalent substances.

 8. Covalent compounds involve in chemical reactions slowly because molecules take part in the reactions.

Hybridization

1. The intermixing of atomic orbitals of almost same energy and their redistribution into an equal number of identical orbitals is known as hybridisation

2. The orbitals of one and the same atom only involve in hybridisation.

3. The no.of hybrid orbitals formed is numerically equal to no. of orbitals participating in hybridisation.

4. The hybrid orbitals symmetrically arranged around the nucleus such that they have maximum stability.

5. The orbitals involving in the hybridisation have different shapes but almost same energy.

6. The hybrid orbitals have same shape and same energy.

7. The angle between any two hybrid orbitals in an atom is generally same.

8. While filling electrons into hybrid orbitals Hund's rule and Pauli's principle should be followed.

9. The hybrid orbitals involve only in bond formation.

10. The concept of hybridisation was introduced to explain the shapes of molecules, bond angles in the molecules and bond lengths in the molecules.

s.no	Types of hybridisation	Orbitals involve in hybridisation	No of hybrid orbitals formed in hybridization	Shape of hybrid orbitals	B.A	% S character $=\frac{no.of's'orbitals involve}{total no.of orbitals involve}\times100$	% of p charac ter	Maximum no.of planer atoms
1	SP	One s, one P	2 SP	Linear	180^0	50	50	3
2	SP^2	One s, two P	$3SP^2$	Planar triangular	120^0	33.33	66.67	4
3	SP^3	One s , three P	$4SP^3$	Tetrahydral	109^028^1	25	75	3
4	SP^3d	One s, three P & one d	$5sp^3d$	Trigonal bipyramidal	$90^0, 120^0$	20	60	4
5	SP^3d^2	One s, three P & two d	$6SP^3d^2$	Octahydral	90^0	16.67	50	5
6	SP^3d^3	One s, three P & three d	$7SP^3d^3$	Pentagonal Bipyramidal	$72^0, 90^0$	14.28	42%	6
7	dsp^2	One d, one s & two P	$4d\,SP^2$	Square planar	90^0	25	50	5

12. Assigning the type of hybridisation: No.of hybrid orbitals hybridisation

I) Total molecular valency method

Step1: Total number of valence electron in the molecule is calculated by adding the individual valency of all constituent atoms.

Step2: If total electrons are greater than eight, then divided by eight and quotient is eual to hybridised orbitals.

E.g. PCl_5

Total valence electrons = 5+ (5 X 7) =40

40 / 8=5=no.of hybridised orbitals-->sp^3d

*If remainder comes, that remainder should be divided by 2, if still remainder comes then sum of quoitent and final remainder is equal to number of hybridised orbitals. **E.g**. $XeOF_2$

Total valence electrons=8+6+(2 x 7)= 28

      28 / 8 Quotient=3

      Remainder=4

Remainder is divided by 2

      4 / 2Quotient=2

Hence, sum of Quotient = 3+2 = 5 = no. of hybridised orbitals --->sp^3d

Step3: If total valence electrons is either eight or less, dividing by 2, what Quotient appears, should be considered as number of hybridised orbitals. **E.g.,** H_2O

Total valence electrons = 2 + 6 = 8

      8 / 2 = 4 =sp^3

II) Total number of hybridised orbitals (For neutral molecule)_____ = $1/2(V + M)$

V = no.of valence electrons

M = no.of monovalent atom

Total number of Hybridised orbitals (For cationic species) = $1/2(V + M - C)$;

Total number of Hybridised orbitals (For anionic species) = $1/2(V + M + A)$;

      C = +Ve charge.

      A = -Ve charge.

iii) No. of hybrid orbitals = no.of atoms surrounded around central atom + ½ [Group number of central atom - valence charge] here no. of atoms surrounded around central atom indicate 'σ' bond pairs $\frac{1}{2}(G - V \pm ch\arg e)$ indicates no.of lone pairs

Ex: SO$_3$, *No.of hybrid orbitals* $= 3 + \dfrac{1}{2}(6 - 6 \pm 0)$ =3+0=3 i.e sp^2

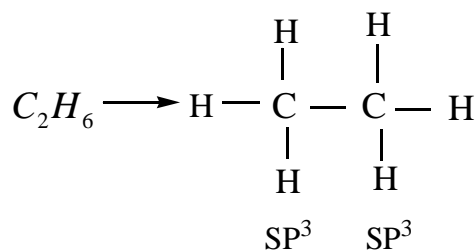| Molecule /ion	No.of hybrid orbitals (calculated by using above relations)	Hybridisution	No of σ bond pairs	No of l.p	shape
CH_4	4	SP^3	4	0	Tetrahydral
$BeCl_2$	2	SP	2	0	Linear
BCl_3	3	SP^2	3	0	Planar triangular
$SnCl_2$	3	SP^2	2	1	Angular
SO_2	3	SP^2	2	1	Angular
SO_3	3	SP^2	3	0	Planar triangular
NH_3	4	SP^3	3	1	Pyramidal
H_2O	4	SP^3	2	2	Angular
NH_4^+	4	SP^3	4	0	Tetrahydral
H_3O^+	4	SP^3	3	1	Pyramidal
PCl_5	5	SP^3d	5	0	Trigonal bipyramidal
I_3	5	SP^3d	2	3	Linear
SCl_4	5	SP^3d	4	1	Distorted trigonal bipyramidal (or) square pyramidal

Hybridisation in Carbon Compounds

The carbon atom in carbon compounds is tetravalent (i.e., carbon atom always form four Covalent bonds)

i. The carbon atom forming four single bonds sp^3 is hybridised.

ii. The carbon atom forming one double bond and two single bonds sp^2 is hybridised

iii. The carbon atom forming two double bonds (or) one triple bond & one single bond is SP hybridised

Hybridizations in carbon compounds & ratio of pure and hybrid orbitals calculations

i. No. of hybrid orbitals = sum of all hybrid orbital on all atoms

ii. No. of pure orbitals = no.of atoms other than carbon atoms +2x no. of Pi bonds
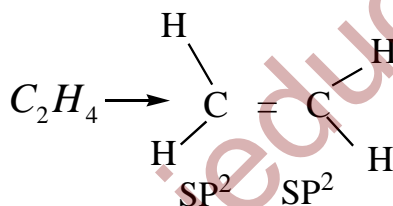
$$C_2H_6 \longrightarrow H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - H$$

$$SP^3 \qquad SP^3$$

Ex1.

No of hybrid orbitals = 4+4=8

No of pure (or) unhybrid orbitals = 6+2x0=6

:. Ratio of pure and hybrid orbitals = 6: 8 = 3: 4

$$C_2H_4 \longrightarrow \underset{H}{\overset{H}{\diagdown}} C = C \underset{H}{\overset{H}{\diagup}}$$

$$SP^2 \qquad SP^2$$
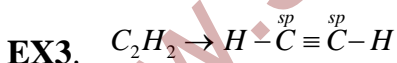
EX 2.

No. of hybrid orbitals = 3 + 3 = 6

No.of pure / unhybrid orbitals = 4+2x1=6

:. Ratio of pure and hybrid orbitals = 6: 6= 1: 1

EX3. $C_2H_2 \rightarrow H - \overset{sp}{C} \equiv \overset{sp}{C} - H$

No.of hybrid orbitals = 2 + 2 = 4

No.of pure orbitals = 2+2x2=6

:. Ratio of pure and hybrid orbitals = 6: 4 = 3: 2

$$C_6H_6$$
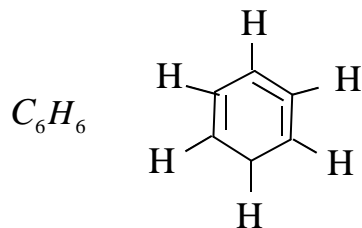
EX4.

In benzene all carbons are SP^2

∴. No.of hybrid orbitals =6x3=18

No. of pure orbitals =6+2x3=12

∴. Ratio of pure and hybrid orbitals = 12: 18 = 2: 3

Note: no.of Linear atoms = no.of atoms in SP hybridisation which are in direct link and their direct attached atoms

Example: In 3 - hexyne, no. of linear carbon atoms are '4'

$$CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$$
∴   SP   SP