

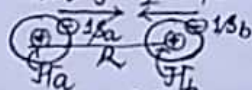
⇒ Valence bond theory of Covalent compounds:

Valence bond theory was put forward by Heitler & London in 1927 and modified later in 1935 by Pauling & Slater. It explains the nature of covalent bonds/compounds.

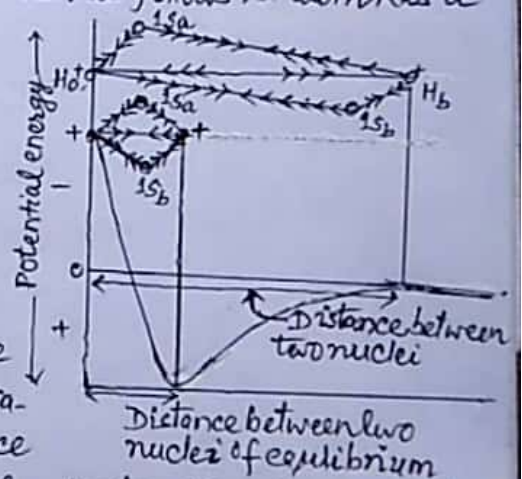
The main postulates of this theory are—

1. The atom which go to enter into chemical combination/bonding must possess one or more unpaired electrons.
2. A covalent bond is formed by sharing or pairing of two electrons with opposite spins. If more than one unpaired electrons are present, multiple (double or triple) bond is formed.
3. In the formation of covalent bond, overlapping of atomic orbitals take place. This can be done in two ways and so there are two types of covalent bond, sigma (σ) & pi (π) bonds.
4. Sigma (σ) bond is formed by coaxial/head to head overlap of two atomic orbitals while pi (π) bond is formed by lateral/sidewise overlap of two atomic orbitals. s-s, s-p, s-d overlapping always give a σ -bond but p-p overlapping give σ or π bond.
5. In the formation of covalent bond only valence electrons are involved. The atoms unite retain their identity.
6. Nature of atomic orbitals determines the bond length. Thus, HCl bond length is smaller than that of H-Br, since former involves 3p-orbital of Cl atom, while latter 4p-orbital of Br atom in overlapping with 1st orbital of H atom.
7. Overlapping determines the strength of the bond. The greater the overlapping of atomic orbitals, greater will be the strength or stronger will be the bond. Thus, stability decreases $\sigma_{s-s} > \sigma_{p-p} > \sigma_{s-p}$, and sigma (σ) bond is stronger than pi (π) bond.

Explanation of VBT: Formation of H_2 molecule can be shown as follows: H-atom has a single electron in 1s-orbital.



When two hydrogen atoms approaching each other to a close distance (R), two electrostatic forces acted. firstly, the attractive force, which acts between the nucleus (H_a) and the electron associated with $1s_a$ & $1s_b$ as well as that between the nucleus H_b and the electron associated with it. secondly, the repulsive force between H_a & H_b as well as between $1s_a$ & $1s_b$. The attractive forces are more important at a large H_a-H_b distance but, short range repulsive force becomes effective when the two atoms come much closer. The repulsive forces increase, much more rapidly when the internuclear distance becomes very short. The change in potential energy with respect to interatomic distance is shown in Fig. 1. When two atoms are far apart, the potential energy of each is independent of other and is arbitrarily at 0. As the two H-atoms approach, there is an attraction between them and the potential energy decreases. The potential energy



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decreases to a minimum value beyond which it shoots up sharply. The energy increase corresponds to short range repulsive forces between like charges when two atoms are brought to very close distances. The position of the minimum corresponds to the bond length (i.e., average distance between the nuclei in the H_2 molecule). Because the potential energy is lowest at this distance the two H atoms tend to favour this spacing.

It is noted, if the net result is attraction, the total energy of the system decreases & a chemical bond (covalent) results. If the net result is repulsion, total energy of the system increases and no chemical bond is possible.

⇒ Sidgwick-Powell theory:

In 1940, Sidgwick & Powell pointed out that the shape of a ^{covalent} molecule was related to the number of electron pairs in the valence shell of the central atom. Pairs of electrons occupy orbitals and since the occupied orbitals repel each other they are oriented in space as far apart as possible. This applies irrespective of whether the electron pair is shared (bond pair) or is not shared (lone pair). If the distribution of orbitals about the central atom can be predicted, the shape of the molecules/ions and bond angles can also be predicted.

Later on, this theory was extended by Gillespie & Nyholm to explain the molecular geometries/structures of compounds/ions on account of bond pairs & lone pair interaction. So called Gillespie-Nyholm theory or Valence shell electron pair repulsion (VSEPR) theory.

Electron pairs (bond pairs or lone pairs) tend to occupy position in space that minimize repulsion and thus maximize distance between them in order to attain stable.

Main features/postulates of this theory are:

1. Electron pairs present on a particular atom are of two types:

(i) Bond pair (b.p.): Electron pair distributed between two atoms (say A & B).

(ii) Lone pair (l.p.): Electron pair present on only one atom (say A).

If a molecule/ion has only bond pairs of electrons, it has regular geometry. The geometry/structure depends upon number of bond pairs, and hence type of hybridisation. Types of hybridisation, shapes, geometries and bond angles of different types of covalent molecules/ions are shown in Table-1.

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Table-1

Type of Compd.	No. of b.p.	Type of hybridisation	Geometry	Bond angle	Shape	Example
AB_2	2	sp		180°	Linear	$BeCl_2, CO_2$ etc.
AB_3	3	sp^2		120°	Triangular Planar	BF_3, NO_3^- etc.
AB_4	4	sp^3		$109^\circ 28'$	Tetrahedral	CCl_4, SO_4^{2-} etc.
AB_5	5	sp^3d		$120^\circ, 90^\circ$	Trigonal bipyramidal	PCl_5
AB_6	6	sp^3d^2		90°	Octahedral	SF_6, PF_6^- etc.
AB_7	7	sp^3d^3		$72^\circ, 90^\circ$	Pentagonal bipyramidal	IF_7

2. If a molecule or ion has one or more than one lone pair of electrons, shape is different from geometry (by hybridisation) due to unbalance electron pair repulsions. Order of repulsions: $l-p-l-p > l-p-b-p > b-p-b-p$ since lone pair (l.p) electron density more spreaded than bond pair (b.p). $l-p-l-p$ & $l-p-b-p$ repulsions decrease the bond angle, and $b-p-b-p$ repulsion increases bond angle (Table-2)

Table-2

Type of Compd.	No. of b.p.	No. of l.p.	Total no. of orbitals	Hybridisation	Geometry as hybridisation	Actual shape	Bond angle as hybrid.	Actual bond angle	Examples	Structure Geometry
ABL	1	1	2	sp	Linear	Linear	180°	180°	HCl	
AB_2L	2	1	3	sp^2	Trigonal planar	Bent	120	$< 120^\circ$	$SnCl_2$	
AB_3L	3	1	4	sp^3	Tetrahedral	pyramidal	$109^\circ 28'$	$\approx 107^\circ$	NH_3	
AB_2L_2	2	2	4	sp^3	"	Bent/V-shaped	$109^\circ 28'$	$\approx 104^\circ$	H_2O	
AB_4L	4	1	5	sp^3d	Trigonal bipyramidal	Seesaw	$120^\circ, 90^\circ$	less than $90^\circ + 120^\circ$	SF_4	
AB_3L_2	3	2	5	sp^3d	"	T-shaped	$90^\circ, 120^\circ$	90°	ClF_3	
AB_2L_3	2	3	5	sp^3d	"	Linear	$90^\circ, 120^\circ$	180°	I_3^-	
AB_5L	5	1	6	sp^3d^2	Octahedral	Square pyramidal	90°	90°	IF_5	
AB_4L_2	4	2	6	sp^3d^2	so	Square planar	90°	90°	XeF_4	
AB_6L	6	1	7	sp^3d^3	Pentagonal bipyramidal	Octahedral	$90^\circ, 72^\circ$	90°	XeF_6	

→ Prediction of shape & structure of compounds/ions:

(i) BF_3 : Central atom of BF_3 is B. Outer electronic conf of B = $2s^2 2p^1$ (G state); F = $2s^2 2p^5$ (G state)

Outer electronic conf of other atom (F) = $2s^2 2p_x^2 2p_y^2 2p_z^1$

Valence electrons (VE) of B = 3, Valence electrons of F = 7

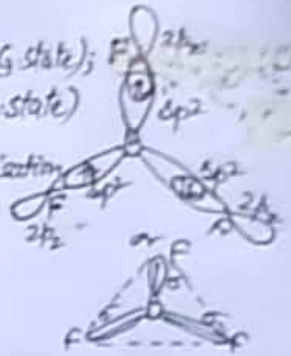
Total valence electrons (TVE) = $3 + 3 \times 7 = 24$

No. of octets = No. of bond pairs = Quotient of TVE ÷ 8 = $\frac{24}{8} = 3$

No. of lone pairs (l.p.) = $\frac{\text{Remainder}}{2} = \frac{0}{2} = 0$

Orbitals needed for hybridisation = $3 + 0 = 3$. Type of hybridisation = sp^2

Geometry & Shape = Triangular planar, Bond angle: 120°



(ii) NH_3 : Central atom of NH_3 is N. Outer electronic configuration of N = $2s^2 2p_x^2 2p_y^2 2p_z^1$

Outer ele. conf of other atom (H) = $1s^1$, Valence electrons of N = 5

Valence electron of H = 1, Total valence electrons = $5 + 3 \times 1 = 8$

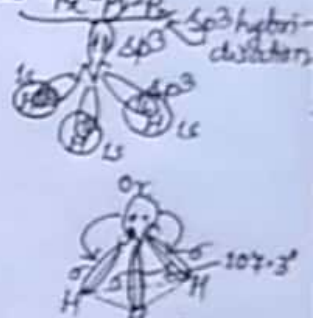
No. of duets = $\frac{TVE}{2} = \frac{8}{2} = 4$, No. of b. ps. = No. of H atoms = 3

No. of l. ps. = No. of duets - No. of b. ps. = $4 - 3 = 1$

Total no. of orbitals needed to N for hybridisation = $3 + 1 = 4$

Type of hybridisation = sp^3 , Geometry = Tetrahedral

Shape - Pyramidal, Bond angle $< 109^\circ 28'$, due to presence of a lone pair of electrons suppress the bond angle ($H-N-H$) as $l.p-b.p$ repulsion $>$ $b.p-b.p$ repulsion.



(iii) H_2O : Central atom of H_2O is O. Outer electronic conf of O = $2s^2 2p_x^2 2p_y^2 2p_z^2$

Outer electronic conf of other atom (H) = $1s^1$, Valence electrons of O = 6

Valence electron of H = 1, Total valence electrons = $6 + 2 \times 1 = 8$

No. of Duets = $\frac{TVE}{2} = \frac{8}{2} = 4$, No. of b. ps. = No. of H atoms = 2

No. of l. ps. = No. of duets - No. of b. ps. = $4 - 2 = 2$

Total number of orbitals needed to O for hybridisation = $2 + 2 = 4$

Type of hybridisation = sp^3 , Geometry = Tetrahedral, Bond angle $< 109^\circ 28'$

Due to presence of two l. ps. of electrons on O-atom, bond angle ($H-O-H$) suppresses more from tetrahedral angle ($109^\circ 28'$), and shape results 'Angular' ($l.p-l.p > l.p-b.p > b.p-b.p$ repulsion).



(iv) SO_4^{2-} : Central atom of SO_4^{2-} is 'S'. Outer electronic conf. of S = $3s^2 3p_x^2 3p_y^2 3p_z^1$

Outer ele. conf. of O-atom = $2s^2 2p_x^2 2p_y^2 2p_z^1$, Outer ele. conf. of O ion = $2s^2 2p_x^2 2p_y^2 2p_z^1$

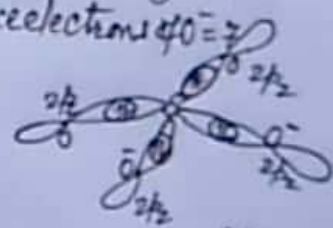
Valence electrons of S = 6, valence electrons of O = 6, Valence electrons of O- = 7

Total valence electrons (TVE) = $6 + 2 \times 6 + 2 \times 7 = 32$

No. of octets = $\frac{TVE}{8} = \frac{32}{8} = 4 = \text{No. of b. ps}$

No. of lone pair = 0. Total number of orbitals needed by S-atom for hybridisation = $4 + 0 = 4$, Type of hybridisation = sp^3

Geometry/shape = Tetrahedral, Bond angle = $109^\circ 28'$



→ Exercise: Predict the shape & structure of following compds/ions: $PCl_5, ClF_3, SF_4, IF_7, NO_3^-$