Dr. Kumud Kumari
Professor, deptt. of chemistry
H.D. Jain college, Ara.

VALENCE BOND THEORY

This theory was proposed by 'Linus Pauling', who was awarded the Noble Prize for chemistry in 1954. The theory was very widely used in the period (1940-1960)

Atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way unpaired electrons are paired up and the atoms involved all attain a stable electronic arrangement i.e a noble gas configuration. Two electrons shared between two atoms constitute a bond. The nuber of bond formed by an atom is usually same as the number of unpaired electrons in the ground state i.e the lowest energy state. However in some cases the atom may form more bonds. This occurs by excitation of the electron (i.e providing it with energy). when electrons which were paired in the ground state are unpaired and promotted into suitable empty orbitals. This increase the number of unpaired electrons and hence the number of bonds which can formed.

The shape of the molecule determined primarily by the direction in which the orbital point. Electrons in the valence shell of the original atom which are paired are called lone pair.

A covalent bond results from the pairing of electrons. The spin of the two electrons must be opposite because of the pauli exclusion Principle that no two electrons can have all four quantum numbers the same. The Pauling-Slater's theory suggests that:

(a) The atoms which unit to form a molecule completely retain their identity in the resulting molecule.

(b) A covalent molecule is formed due to the overlapping of atomic orbitals. If there are two atoms each having unpaired electrons overlap resulting in the formation of a covalent bond between these two atoms in which the spin of two electrons get mutually neutralised. If these atomic orbitals having parallel spins, repulsion will take place and no molecule will formed.

(c) If the atomic orbitals are having more than one unpaired electron, multiple bond formation is possible. For example in nitroge molecule three bonds are possible because N-atom has three unpaired electrons.

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

(e) The strength of the covalent bond is proportional to the extent of the overlapping of the two atomic orbitals. The greater the overlap between the atomic orbitals, the greater is the strength of the resulting covalent bond. The extent of overlap two atomic orbitals of wave function ψ_A and ψ_B is represented by overlap integral, S, which is as follow:

$$S = \int \psi_A \psi_B \, d\tau$$

From the this relation it is evident that:

(i) If $S = 0$, there is no overlap i.e there is neither attraction nor repulsion between the combinig atoms. Thus no bonds formation is possible.

(ii) If S = Positive, there is an increase in the electron density between two nuclei which result in an increase in attraction between the two combining atoms, forming a covalent bond.

(iii) If S = negative, there occurs decrease in electron density between the nuclei of two combining atoms. Thus repulsion between them is increased and hence no bond formation is possible.

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

(g) Between two orbitals of the same energy content, the overlapping axially will form a stronger bond.

(h) A spherically symmetrical orbital i.e ~~s orbit~~ s-orbital does not show any directional preference whereas non-spherical orbitals, p, d or f, tend to form a bond a bond in the direction of maximum electron density within the orbital i.e. along their axes. For example:

(i) As the charge density of s-orbital is spherical, the two s-orbital will overlap to the same extent in all directions.

(ii) The three p-orbitals lie on mutually perpendicular axes having neucleus at the centre. Whenever p-orbitals overlap, they tend to form a stronger bond in the direction of their maximum electron density.

(iii) When a s-orbital overlap with p-orbitals bond is formed but it is weaker than p-p bond but stronger than s-s bond.