Chemical Bonding and Molecular Structure

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The attractive force which holds together the constituent particles (atoms or molecules) in chemical species is known as **chemical bond**.

Tendency of atoms to attain stable configuration of eight electrons in their valence shell is cause of chemical combination.

The principle of attaining a maximum of eight electrons in the valence shell of atoms is known as **octet rule.**

Kössel's first insight into the mechanism of formation of electropositive and electronegative ions related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of electrovalency.

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

The electrostatic force of attraction which holds the oppositely charged ions together is known as **ionic bond** or electrovalent bond. Ionic compounds will be formed more easily between the elements having comparatively low ionization enthalpy and elements having comparatively high negative value of electron gain enthalpy.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the **crystal lattice**. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the enthalpy of lattice formation.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone-pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone-pairs around each atom in a molecule.

The **formal charge of an atom** in a polyatomic ion or molecule is defined as the difference between the number of valence electrons in an isolated or free atom and the number of electrons assigned to that atom in a Lewis structure. Significance of Formal charge: The formal charges help to select lowest energy structure from a number of possible Lewis structures for a given molecule or ion. Lowest energy structure is the one that has lowest formal charges on the atoms.

Co- Ordinate Covalent Bond:

Covalent type bond in which both the electrons in the shared pair come from one atom is called a coordinate covalent bond.

Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance**. The contributing structures or canonical forms taken together constitute the resonance hybrid which represents the molecule or ion.

The **VSEPR model** used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, molecular geometry is determined by repulsions between lone pairs and lone pairs; lone pairs and bonding pairs and bonding pairs and bonding pairs. The order of these repulsions being: $\mathrm{lp} - \mathrm{lp} > \mathrm{lp} - \mathrm{bp} > \mathrm{bp} - \mathrm{bp}$

The **valence bond (VB) approach** to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H2 molecule from two hydrogen atoms involves the overlap of the 1s orbitals of the two H atoms which are singly occupied.

It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of **hybridisation of atomic orbitals**. sp,sp2, sp3 hybridizations of atomic orbitals of Be, B,C, N and O are used to explain the formation and geometrical shapes of molecules like $\mathrm{BeCl_2}$, $\mathrm{BCl_3}$, $\mathrm{CH_4}$, $\mathrm{NH_3}$ and $\mathrm{H_2O}$. They also explain the formation of multiple bonds in molecules like $\mathrm{C_2H_2}$ and $\mathrm{C_2H_4}$.

The **molecular orbital (MO) theory** describes bonding in terms of the combination and arrangement of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals.

The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if the number of electrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.

Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intramolecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds.