4.Chemical bonding and Molecular Structure

Some Important Points and Terms of the Chapter

1. **Lewis dot structures** are shorthand to represent the valence electrons of an atom. The structures are written as the element symbol surrounded by dots that represent the valence electrons.
2. **Covalent Bonds**- The bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets or duplets. When two atoms share one electron pair they are said to be joined by a single covalent bond.e.g H_2 If two atoms share two electron pairs of electrons, the covalent bond between them is called a double bond. e.g O_2 If two atoms share three electron pairs of electrons, the covalent bond between them is called a double bond. e.g N_2
3. **Octet Rule-** Kossel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to attain their octet. This is known as octet rule.
4. **Limitations of octet rule-**

a) Incomplete octet of the central atom: In some compounds the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples- LiCl ,$BeCl_2$, BCl_3

b) Odd-electron molecules: In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, the octet rule is not satisfied for all the atoms.

c) The expanded octet : Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Some of examples of such compounds are: PF_5, SF_6.

d) This theory does not account for the shape of molecules.

5. **Electrovalent bond or Ionic Bond**: The chemical bond as result of transfer of electron from one atom(electropositive) to another atom (electronegative).Ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively

high_negative value of electron gain enthalpy._Most ionic compounds have cations_derived from metallic elements and anions_from non-metallic elements.

6. **Formation of Ionic Bond**

$$M(g) \rightarrow M^+(g) + e^- ; \quad \text{Ionization enthalpy}$$

$$X(g) + e^- \rightarrow X^-(g) ; \quad \text{Electron gain enthalpy}$$

$$M^+(g) + X^-(g) \rightarrow MX(s)$$

7. **Bond length** is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.
8. **Bond Angle:**It is defined as the angle between the orbital containing bonding electron pairs around the central atom in a molecule/complex ion. It gives some idea regarding the distribution of orbital around the central atom in a molecule/complex ion and hence it helps us in determining its shape
9. **Bond enthalpy**: It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}
10. **Bond Order :** The Bond Order is given by the number of bonds between the two atoms in a molecule. E.g.: Bond Order of O_2= 2. With increase in bond order, bond enthalpy increases and bond length decreases.
11. **Resonance**: According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and the non- bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately
12. **Polarity of bonds:** In case of heteronuclear molecules like HCl, the shared pair of electron between the two atoms gets displaced more towards chlorine since the electronegativity of chlorine is far greater than that of hydrogen. The resultant covalent bond is called a polar covalent bond.
13. **Dipole moment**: As a result of polarization, the molecule possesses the dipole moment which can be defined as the product of charge and the distance between the centers of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows:

    Dipole moment (μ) = charge (Q) X distance of separation (r)

14. **VSEPR Theory**

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
- The repulsive interaction of electron pairs decrease in the order: Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) –Bond pair (bp)
- **Geometry of Molecules** on the basis of VSEPR Theory

Bond pair	**Lone pair**	**Shape**	**Examples**
2	0	Linear	$BeCl_2$
3	0	Trigonal Planar	BCl_3
2	1	Bent	SO_2
4	0	Tetrahedral	CH_4
3	1	Pyramidal	NH_3, ,PH_3,
2	2	V-shape	H_2O
5	0	Trigonal bipyramidal	PCl_5
4	1	See saw	SF_4
3	2	T-shaped	CIF_3,
2	3	Linear	XeF_2
5	1	Square pyramidal	CIF_5, IF_5
4	2	Square planar	XeF_4,
6	1	Distorted Octahedral	XeF_6

15. **Hybridization:** It can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formations of new set of orbitals of equivalent energies and shape.

- **Salient Features of hybridization :**
- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement.

16. **Types of Hybridisation**
    - **sp hybridisation**- This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.e.g.$BeCl_2$
    - **sp^2 hybridisation**- In this hybridisation there is involvement of one s and two p-orbitals in order to form there equivalent sp^2 hybridised orbitals. e.g.BCl_3
    - **sp^3 hybridisation**- When there is mixing of one s and three p-orbitals of the valence shell to form four sp^3 hybrid orbitals of equivalent energies and shape. e.g.CH_4

17. **Molecular orbital.** It gives electron probability distribution around a group of nuclei in a molecule. They are filled in the same way as atomic orbitals. Molecular orbitals are formed by linear combination of atomic orbitals.

18. **Bonding molecular orbital.** A molecular orbital that is formed by addition overlap (*i.e.,* when the lobes of atomic orbitals overlap with the same sign) of two atomic orbitals is known as *bonding molecular orbital*. It is represented as

    $\Psi_{MO} = \Psi_A + \Psi_B$ Its energy is lower than the atomic orbitals from which it is formed. It favours bonding.

19. **Anti-bonding molecular orbital.** A molecular orbital that is obtained by the subtraction overlap (*i.e.,* when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals is know as *anti-bonding molecular orbital.* It is represented as

$\Psi^*_{MO} = \Psi_A - \Psi_B$ Its energy is higher than the atomic orbitals from which it is formed. It does not favour bonding.

20. Bond order. It is defined as half of the difference between number of electrons in bonding and anti-bonding orbitals, *i.e.*, B.O. = ½ ($N_b - N_a$) 'where N_b are number of electrons in bonding orbitals' and N_a are number of electrons in anti-bonding orbitals. Bond order helps in estimating stability of atom.

21. Relationship between electronic configuration and molecular behaviour :

(a) If N_b is greater than N_a, the molecule is stable.

(b) The molecule is unstable if N_a is greater than N_b.

(c) The molecule is also unstable if N_a is equal to N_b because anti-bonding effect is stronger than bonding effect.

22. Sigma (σ) molecular orbitals. A molecular orbital which is formed from the overlap of two *s* atomic orbitlas or head to head overlap of one *s* and *p*-atomic orbitals or head to head overlap of two *p*-atomic orbitals, is known as *sigma molecular orbital.*

23. pi (π) molecular orbitals. A molecular orbital which is formed by lateral overlap of two parallel *p*-orbitals is known as *pi(π) molecular orbital.*

24. Conditions for the Combination of Atomic Orbitals. The linear combination of atomic orbitals takes place only if the following conditions are satisfied :

(i) The combining atomic orbitals must have same or nearly same energy.

(ii) The combining atomic orbitals must have the same symmetry about the molecular axis. By convention, z-axis is taken as the molecular axis.

(iii) The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlapping, the greater will be electron density between the nuclei of a molecular orbital.

25. Energy level Diagrams for Molecular Orbitals. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below.

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi 2\overset{*}{p}_x = \pi 2\overset{*}{p}_y < \sigma 2\overset{*}{p}_z$$

However, this sequence of energy levels of molecular orbitals is not correct for remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2 etc., the increasing order of energies of various molecular orbitals is

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi 2\overset{*}{p}_x = \pi 2\overset{*}{p}_y < \sigma 2\overset{*}{p}_z$$

The important characteristic feature of this order is that the energy of $\sigma 2p_z$ **molecular orbital is higher than that of** $\pi 2p_x$ **and** $\pi 2p_y$ **molecular orbitals** in these molecules.