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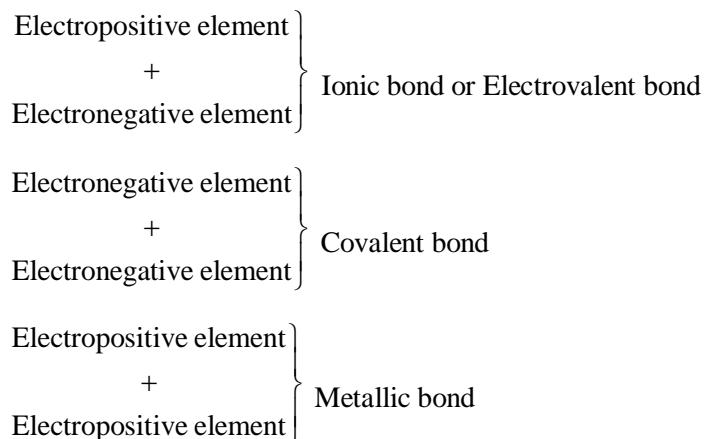


CHEMICAL BONDING

CHEMICAL BONDING & MOLECULAR STRUCTURE

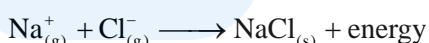
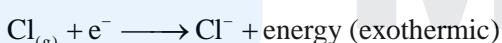
Chemical Bond

It is a type of very strong force of attraction that binds the two atoms (either similar or dissimilar) or ions together.



Electrovalent or Ionic Bond

The bond formed by the transfer of electron from electropositive element towards electronegative element is called electrovalent or Ionic bond. e.g.,



Factors favouring the formation ionic Bond

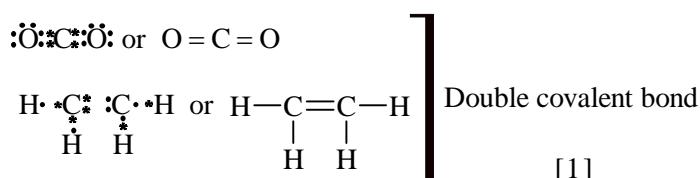
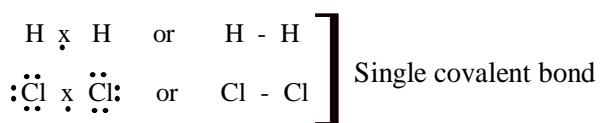
- (i) One of the atom (the metal) must have a low ionization energy
- (ii) The other atom (non metal) must have high electron affinity.
- (iii) The electrostatic attraction between charged ion in the crystal i.e. lattice energy should be high.

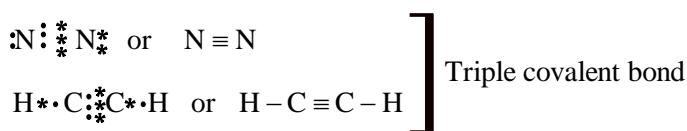
Characteristics of Ionic Compounds

- | | |
|--------------------------------|-----------------------------|
| (i) Ionic crystalline geometry | (ii) Generally solid |
| (iii) Soluble in polar solvent | (iv) Conductor in solution |
| (v) High B.P and M.P. | (vi) Non directional nature |

Covalent Bond

Bond formed by the sharing of equal no. of electrons between the two concerned atoms is called covalent. Bond.





CHARACTERISTICS OF COVALENT BOND

- (i) Low M.P and B.P.
- (ii) Molecular geometry
- (iii) Bad conductor
- (iv) Soluble in non polar solvent
- (v) Directional nature

Co-ordinate Covalent, or Dative bond

The co-ordinate bond formation involves one sided sharing of a lone pair of electrons. The atoms that donates the electron pair is known as donor and the atom which accepts the electron pair is called acceptor. e.g.



Odd Electron Bond

There are very small no. of stable compounds and ions which unpaired electron. e.g. NO , NO_2 , ClO_2

BOND CHARACTERISTICS

- (A) Bond length: It is the average distance between the centres of nuclei of the two bonded atoms
 - (i) The bond length increases with increasing in the size of the atoms. e.g. H–X bond length has the order $\text{H}-\text{I} > \text{H}-\text{Br} > \text{H}-\text{Cl} > \text{H}-\text{F}$.
 - (ii) A multiple bond (= or =) is always shorter than the corresponding single bond.
 - (iii) Bond length decreases with the increase in s-character since an s-orbital is smaller than a p-orbital.
- (B) Bond Energy of Bond Strength: If bond is formed it involves release of certain amount of energy and an equivalent amount of energy is absorbed by breaking the bond.

Remembering facts

- Most of the covalent bonds have energy between 50 to 100 k.cal mol⁻¹.
- Bond energy increases from single to triple bond. i.e., $\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$
- The strength of s bond is more than that of p bond
- The bond energy decreases with the increase in no of lone pair in bonded atom. This is due to electrostatic repulsion between the lone pair of electrons on the two bonded atoms.

Polarisation of Ionic Bond

Cation pulls electron cloud slightly from anion and that's why its ionic character is decreased, i.e, the bond is polarised.

Fajarr's rule :- Smaller cation, larger anion and high charge over both, will polarise the ionic bond largest.

Note :- Greater the polarisation of ionic bond. Lesser is its ionic character.

Order of Polarisation :-

$$(a) \text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$$

$$(b) \text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl}$$

Polarisation of covalent bond : Due to electronegativity difference between the bonded atom shared electrons, slightly shifts towards more electrons, slightly shifts towards more electronegative atom, that's why bond become polarised.

Note : Greater the polarisation of covalent bond greater is its ionic character.

(C) Dipole Moment : It is defined as the product of the net positive or negative charge and distance between the two charged ends (i.e. the bond length).

$$\text{Dipole moment (m)} = \text{Electronic charge} \times \text{Distance}$$

Unit → Debye

$$1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u cm} = 3.33 \times 10^{-30} \text{ Cm}$$

Dipole moment is vector quantity whose direction is from positive to negative charge.

Net dipole moment of any molecule is vector sum of all the individual dipole moments of that molecule.

BeF_2 and CS_2 are also linear molecules. Their net dipole moment will be zero.

APPLICATION OF DIPOLE MOMENT

- In determining the polarity of bonds: As $m = q \times d$, obviously, greater is the magnitude of dipole moment, higher will be the polarity of the bond.
- In the calculation of percentage ionic character : Taking the example of HCl, its dipole moment is 1.03 D. If HCl were 100% ionic, each end would carry charge equal to one unit viz 4.8×10^{-10} e.s.u. As bond length of HCl is 1.275\AA its dipole moment for 100% ionic character would be

$$\mu_{\text{ionic}} = q \times d$$

$$= 4.8 \times 10^{-10} \text{ e.s.u.} \times 1.275 \times 10^{-8} \text{ Cm}$$

$$= 6.12 \text{ D}$$

$$\therefore \% \text{ ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100 \\ = \frac{1.03}{6.12} \times 100 = 16.83\%$$

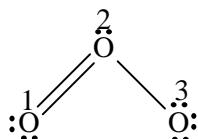
Formal Charge of an Atom in a Molecule

The formal charge on an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in the free state and the number of electrons of that atom in the free state and the number of electrons assigned to that atom in the Lewis structure assuming that in each shared pair of electrons, the atom has one electron of its own and the lone pair on it belongs to it completely. Thus it can be calculated as follows:

$$\begin{aligned} & \left[\begin{array}{l} \text{Formal charge (F.C.)on} \\ \text{an atom in a molecule/ion} \end{array} \right] \\ & = \left[\begin{array}{l} \text{Total no. of valence electrons} \\ \text{in the free atom} \end{array} \right] - \left[\begin{array}{l} \text{Total no. of electrons of lone pair} \\ \text{(non-bonding electrons)} \end{array} \right] \\ & \quad - \frac{1}{2} \left[\begin{array}{l} \text{Total no. of shared electrons} \\ \text{(bonding electrons)} \end{array} \right] \end{aligned}$$

Example 1: Calculate formal charge on each O-atom of O_3 molecule.

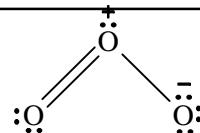
Solution: Lewis structure of O_3 is as follows:



The atoms have been numbered as 1, 2 and 3. Formal charge on end O-atom numbered 1 = $6 - 4 - \frac{1}{2}(4) = 0$.

Formal charge on central O-atom numbered 2 = $6 - 2 - \frac{1}{2}(6) = +1$

Formal charge on end O-atom numbered 3 = $6 - 6 - \frac{1}{2}(2) = -1$



Hence we represent O_3 along with formal charges as follows:

HYBRIDISATION

The phenomenon of mixing up of two or more atomic orbitals of nearly the same energies to form new type of orbitals called hybrid orbitals, is called hybridisation.

Rules of hybridization

- (i) Only orbitals of nearly the same energies and belonging to the same atom or ion undergo hybridization.
- (ii) The no. of hybrid orbitals produced is equal to the number of atomic orbitals mixed during hybridization.
- (iii) Most of the hybrid orbitals are similar.
- (iv) The hybrid orbitals are distributed in space as far as possible.
- (v) Hybrid orbital leads to the formation of sigma bonds only.
- (vi) It is only a theoretical concept to explain the structure and shape of compounds.

Table: Geometry (Shape) of molecules/ion containing bond and lone pair

No. of b.p. of Electron	Hybridisation	Lone pair	Bond angle	expected geometry	Shape of compound	Example compound
2	sp 0	180°	Linear	Linear	BeF ₂ , BeCl ₂ , CO ₂ , HgCl ₂ , HCN, MgCl ₂ , C ₂ H ₂ , [Ag(NH ₃) ₂] ⁺	
3	sp ² 0	120°	Trigonal planar	Trigonal	BF ₃ , BCl ₃ , BH ₃ , AlCl ₃ , SO ₃ , C ₂ H ₄ , NO ₃ ⁻ , CO ₃ ²⁻ , C ₆ H ₆	
2	sp ² 1	—	Trigonal Planar	V-shaped	SO ₂ , SnCl ₂ , NO ₂ ⁻	
4	sp ³ 0	109°28'	Tetrahedral	Tetrahedral	SiCl ₄ , SnCl ₄ , CH ₄ , SO ₄ ²⁻ , ClO ₄ ⁻ , PO ₄ ³⁻	
3	sp ³ 1	≈107°	Tetrahedral	Pyramidal	NH ₃ , NF ₃ , PCl ₃ , PH ₃	
2 4	sp ³ 2 dsp ² 0	≈105° 90°	Tetrahedral Square planar	V-shaped Square planar	H ₂ O, H ₂ S, PbCl ₂ , OF ₂ , [Ni(CN) ₄] ²⁻ , [PtCl ₄] ²⁻ , [Cu(NH ₃) ₄] ²⁺	
5	sp ³ d 0	90°, 120°	TBP	TBP	PCl ₅ , SbCl ₅	
4	sp ³ d 1	109°28	TBP	Triangular pyramidal	SF ₄	
3	sp ³ d 2	90°	TBP	T-shape	ICl ₃ , ClF ₃	
2	sp ³ d 3	180°	TBP	Linear	XeF ₂	
6	sp ³ d ² 0	90°	Octahedral	Octahedral	SF ₆ , SeF ₆ , PF ₆ ⁻ , SnCl ₆ ²⁻	
5	sp ³ d ² 1	90°	Octahedral	Square Pyramidal	Icl ₅	
4	sp ³ d ² 2	90°	Octahedral	Square planar	XeF ₄ , ICl ₄ ⁻	
7	sp ² d ³ 0	72°, 90°	Pentagonal	PBP bipyramidal	IF ₇	

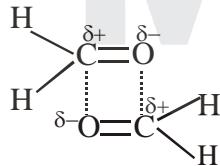
TBP=Trigonal Bypyramidal

Sigma (σ) and pi (π) bonds

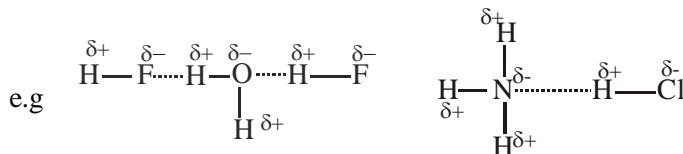
σ bond	π bond
<ul style="list-style-type: none"> (i) It results from the end to end overlapping of orbital (ii) The bond orbital consists of a single electron cloud symmetrically about internuclear axes. (iii) The σ electron are reformed as localized (iv) Provided the groups or atoms are smaller in size, they can undergo torsional rotation about single bonds. (v) The shape of molecule is determined by the σ-bond present in the molecule. (vi) σ-bond can have independent existence 	<ul style="list-style-type: none"> (i) Its results from the side ways overlapping of two p-orbitals. (ii) Its bond orbital consists of two electron clouds one above and other below the Plane of participating atoms. (iii) In π-bond the electron are held less firmly and can be more easily dissociated or polarized. (iv) Due to resistance to rotation around the π bond the group attached to it or not Free to rotate. (v) π-bonding does not affect the shape of the molecule in which it occurs. (vi) π-bond always exist along with s-bond.

Inter Molecular attraction :

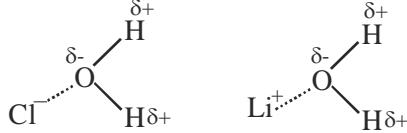
- (i) Dipole-dipole attraction
 (ii) H-Bonding
 (iii) London forces
 (iv) Ion-dipole attraction
 (i) Force acting between opposite poles of two permanent electric dipoles



- (ii) It is extremely powerful dipole-dipole attraction acting between H which is bonded to highly electronegative atom like, F, O and either of F, O or N.



- (iii) It is force attraction between instantaneous dipole-induced dipole or between two induced dipole or between permanent and induced dipole.
 (iv) It is attraction between any ion and opposite pole of any dipole.

MOLECULAR ORBITAL THEORY

- (a) There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by Mulliken (1932) and Hund. Which explains the bonding characteristic in a better way.

- (b) The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecular.
- (c) This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

Important Features of M.O.T

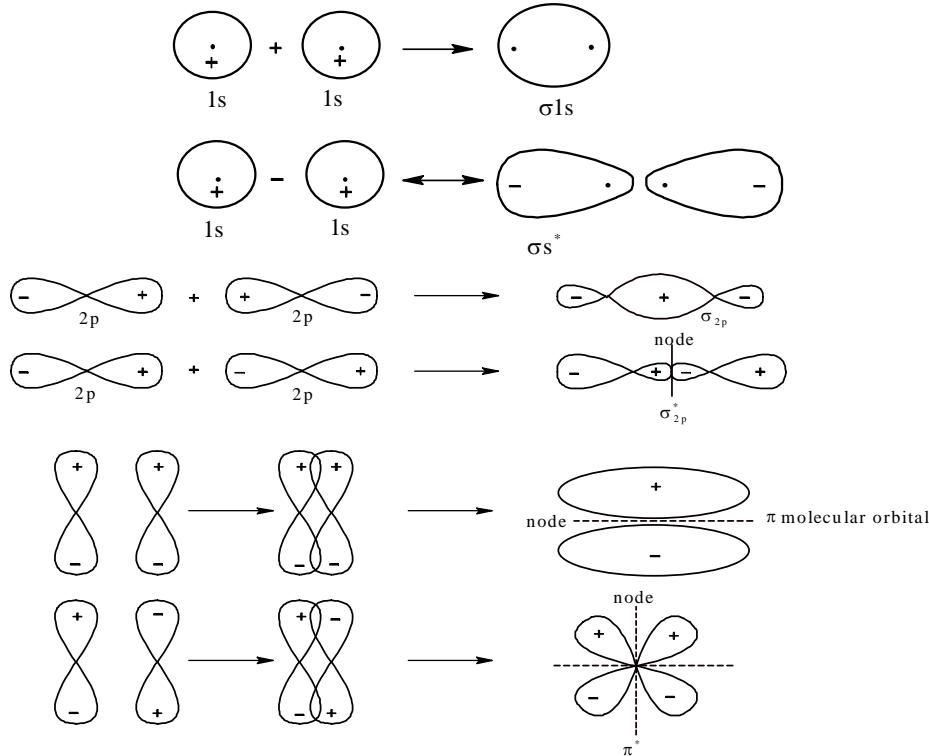
1. Like an A.O. (atomic orbital) which is around the nucleus of an atom there are M.O. (Molecular orbital) which are around the nuclei of a molecule.
2. The molecular orbitals possess different energy levels like atomic orbitals from which they are formed.
3. The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.
4. The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.
5. Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.
6. The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.
7. Like atomic orbitals, the filling of electron in molecular orbitals is governed by the three principles such as Aufbau principle, Hund's rule and Pauli's exclusion principle.

CONDITIONS FOR ATOMIC ORBITALS TO FORM M.O.

1. The combining A.O. should be a comparable energy
2. The combining atomic orbitals must overlap to a large extent greater the overlap, stable is the molecule formed.

Formation of Bonding and Antibonding Molecular Orbitals (LCAO method)

- (a) An electron in an atom is described by a wave function, ψ called an atomic orbitals. Similarly, the behavior of an electron in a molecule is described by a molecular wave function called molecular orbitals.
- (b) Quantum mechanics shows that linear combination of two functions gives, not one but two combination and hence two molecular orbitals are formed a bonding orbital and another an anti-bonding orbital.
- (c) A sigma (σ) M.O. is one that has cylindrical symmetry around the inter nuclear axis.



(A) Aufbau's order of increasing energy for

$\text{H}_2, \text{He}_2, \text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2$ etc.

$$\sigma(1s) \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \pi^*(2p_z)$$

(B) Aufbau's order of increasing energy for

$\text{O}_2, \text{F}_2, \text{Ne}_2, \text{NO}$ etc.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$$

STABILITY OF MOLECULES

(a) Stability of molecules in terms of bonding and antibonding electrons:

- (i) If $N_b > N_a$, the molecule is stable
- (ii) If $N_b < N_a$, the molecule is unstable.

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

- (a) Larger the bond order, smaller is the bond length and larger is the bond strength
- (b) Molecule having negative or zero bond order does not exist.

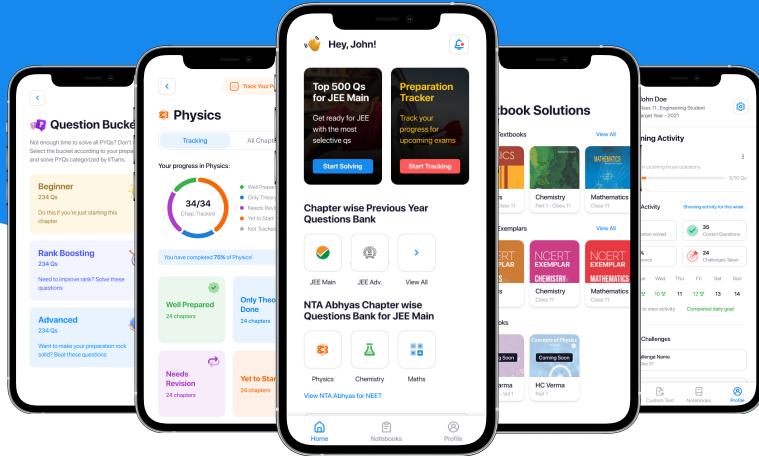
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