

CHEMICAL BONDING, MOLECULAR STRUCTURE- I PUC

Chemical Bonding Chemical bond is sort of force that keeps atoms , ions or molecules of a substance together .After the formation of a bond between

- they acquire 8 electrons in their outer most shells by transfer or sharing of electrons
- they acquire the electronic configuration of the nearest noble gas , which are chemically least reactive.
- the system acquire minimum possible energy
- the force of attraction and repulsion , between nuclei and electrons, balance each other.

Lewis symbols of elements:

- G.N. Lewis introduced simple symbol to denote the valence shell electrons in an atom.
- To write Lewis symbol for an element, we write down its symbol surrounded by a number of dots or cross equal to the number of valency electrons.
- These symbols ignore the inner shell electrons.

Significance of Lewis symbols:

The number of dots around the symbol gives information of the number of electrons present in the outer most shell. This number of electrons helps to calculate the common valency of the element (X).

- If dots are ≤ 4 : the common valency of the element = No. of dots in lewis symbol.
- If dots are > 4 : the common valency of the element = $8 - \text{no. of dots}$.

Formation of bond:

The electrons in the incomplete outer shell of an atom, called the valence shell, play the major role in the bond formation. These electrons, called valence electrons, involved in bond formation, may be transferred from one atom to another, or may be shared equally or unequally between two atoms.

When atoms of elements enter into chemical reaction, they gain, lose or share electrons in their valence shell to attain stable inert gas configuration.

2. Cause for chemical bonding:

a) Tendency to obtain octet structure:

During bonding, each atom tries to attain the stable electronic configuration of the nearest inert gas containing 8 electrons in the outermost shell. ($ns^2 np^6$). Both ns and np orbitals are completely filled in the octet structure.

b) To attain minimum energy:

Atoms try to attain minimum energy after the bond formation

Exceptions to the Octet Rule

- Incomplete octet:** Examples are BeCl_2 , BF_3 , diborane etc.
- Expanded octet:** Examples are PCl_5 , ClF_3 , SF_6 etc. P(in PCl_5) and Cl (in ClF_3) have 10 electrons and S (in SF_6) have 12 electrons.
- Odd electron bonds:** Examples of compounds having unpaired electron(s) are NO , NO_2 , ClO_2 , O_2 , O_2^- etc.

Bond Characteristics

Bond length: The average distance between the nuclei of two atoms bonded to each other is called bond length.

Bond energy: The enthalpy change required to break a particular bond in 1 mole of gaseous molecule is called bond energy.

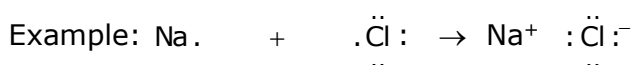
Bond angle: The angle between the orbitals containing the bonding electrons is called the bond angle.

3. Types of bonds

- 1] Ionic or electrovalent bond
- 2] Covalent bond
- 3] Coordinate bond or dative bond
- 4] Hydrogen bond

4. Ionic Bond

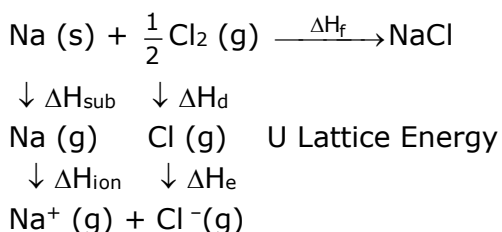
Ionic bond is formed between two atoms by complete transfer of one or more valence electrons from one atom to the other. Ions formed are held together by electrostatic forces of attraction. Ionic bond is non-directional.



Factors affecting ionic bond formation

- Atom forming cation should have low ionisation potential like Na, K, Mg and Al
- Atoms forming the anion should have high electron affinity like F, Cl and Br
- Lattice Energy:
Lattice energy is the energy evolved when one mole of ionic crystal is formed from its gaseous ions
- Lattice energy can be calculated using Born Haber's cycle

Example: Formation of NaCl crystals



Where ΔH_f , ΔH_s , ΔH_i , ΔH_d , ΔH_e are the enthalpies of formation, sublimation, ionisation, dissociation and electron affinity respectively

$$\text{Then: } \Delta H_f = \Delta H_s + \Delta H_i + \frac{1}{2} \Delta H_d + \Delta H_e + U$$

Fajan Rule

Covalent character is introduced in an ionic bond because of attraction of cation on electron cloud of anion.

The power of cation to attract electron cloud of negative ion is called its **polarising power** which is directly proportional to its charge and inversely proportional to its size.

The shift of electron cloud of negative ion towards cation is called its **polarisation** which is directly proportional to its charge and size both.

A cation with pseudo noble gas electronic configuration ($ns^2 np^6 nd^{10}$) has higher polarising power than a cation having noble gas electronic configuration, if the two cations have similar size.

Some examples of increasing covalent character are

- (i) $\text{FeCl}_2 < \text{FeCl}_3$
- (ii) $\text{CsCl} < \text{RbCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$
- (iii) $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$
- (iv) $\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3 < \text{SiCl}_4$

More about Ionic Bond:

Partial covalent character of Ionic Bond (Fajan's Rules)

1. **Partial covalent character of an ionic bond.** Although in an ionic compound, the bond is considered to be 100% ionic, actually it has some covalent character. Thus, just as covalent bond has some ionic character, ionic bonds have some covalent character.
2. **Explanation of partial covalent character.** This was explained by Fajan as follows:
When a cation approaches an anion, the electron cloud of the anion is attracted towards the cation and hence gets distorted. The effect is called **polarisation** of the anion. The power of the cation to polarize the anion is called its **polarising power** and the tendency of the anion to get polarised is called its **polarisability**. The greater is the polarisation produced, more is the neutralisation of the charges (i.e., charge of the cation by the electron cloud of the anion) and hence the ionic character decreases or the covalent character increases. The properties like melting point, heat of sublimation, solubility in water or non-polar solvents change accordingly.
3. **Factors affecting polarising power and polarisability (Fajan's Rules).** The polarising power of the cation, the polarisability of the anion and the development of covalent character is favoured by the following factors:
 - i) **Small size of the cation.** Smaller the cation, greater is its polarising power and hence greater is its tendency to form covalent compounds. For example, LiCl is more covalent than KCl.
 - ii) **Large size of the anion.** Larger the anion, greater is its polarisability and hence greater is its tendency to form covalent compounds. For example, the covalent character of lithium halides decreases as the size of the anion decreases from I^- to F^-
 $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$
 And hence their melting points increasing in the order
 $\text{LiI} < \text{LiBr} < \text{LiCl} < \text{LiF}$
 $(446^\circ\text{C}) \quad (547^\circ\text{C}) \quad (613^\circ\text{C}) \quad (870^\circ\text{C})$
 - iii) **Large charge on the cation or anion.** Larger the charge on the cation, greater is its polarising power and hence greater is its tendency to form covalent compounds. For example, covalent character of the chloride increases as the charge on the cation increases.
 $\text{Na}^+ \text{Cl}^- < \text{Mg}^{2+} \text{Cl}_2 < \text{Al}^{3+} \text{Cl}_3$
 - iv) **Electronic configuration of the cation.** If two cations have the same size and charge, then the one with pseudo noble gas configuration (with 18 electrons in the outermost shell) has greater polarising power than the other with noble gas configuration (with 8 electrons in the outermost shell). This explains why $\text{Cu}^+ \text{Cl}^-$ is more covalent than $\text{Na}^+ \text{Cl}^-$.

Remember

- i) FeCl_3 is more covalent than FeCl_2 because polarising power of Fe^{2+} . Similarly SnCl_4 is more covalent than SnCl_2
- ii) The solubility of aluminium halides decreases from AlF_3 to AlCl_3 due to increase in covalent character in accordance with Fajan rules.

5. Covalent Bond:

When a half filled orbital of one atom overlaps with the half filled orbital of another atom a new orbital called a molecular orbital is formed. This type of bonding is called covalent bonding.

Depending upon the nature of overlap, two types of covalent bonds are defined:

- Sigma (σ) bond
- pi (π) bond

Sigma σ Bond

Sigma bond is formed between two atoms by the overlapping of their orbitals along their axis. Maximum overlapping takes place during σ bond formation and hence σ bond is strong

(s-s) σ bond

It is formed when s orbitals of two different atoms overlap axially.

This bond is non-directional.

(s - p) σ bond

This type of a bond is formed when s orbital of one atom and p orbital of another atom, both containing unpaired electrons overlap axially.

The bond formed is directional

(p - p) σ bond

This type of bond is formed when p orbitals of two atoms containing unpaired electrons overlap axially.

This is a directional bond.

π Bond

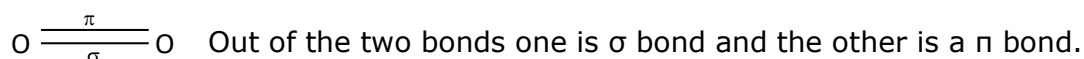
π bond is formed between two atoms by the side way overlapping of two half filled p orbitals.

π bond is weaker than σ bond since side way overlapping is less efficient than axial overlapping.

When two or more bonds are formed between two atoms, the first one is a σ bond and all the rest are π bonds.

Oxygen molecule

Oxygen molecule contains a double bond and the two bonds are perpendicular to each other.



In the case of nitrogen molecule, the triple bond ($\text{N} \equiv \text{N}$) consists of one σ bond and two π bonds and all the three bonds are perpendicular to each other.

Covalency:

The number of electrons contributed by an atom of the element for sharing to form a covalent bond is called covalency of the element.

Covalency of IA, IIA, IIIA group elements = group number.

Covalency of IVA, VA, VIA & VIIA group elements = 8 - group no.

e.g.

- Covalency of hydrogen in water = 1
- Covalency of oxygen in water = 2

- c) Covalency of nitrogen in ammonia = 3
 d) Covalency of C in methane = 4

Variable Covalency:

The variable covalency is shown by elements having vacant d orbitals in their valency shell. The unpairing of the s and p electrons is possible by promoting them to higher orbitals.

e.g.,

- (i) Phosphorous shows 3 and 5 covalencies.
 (ii) S atoms shows 2, 4 and 6 covalencies
 (iii) Chlorine shows 1, 3, 5 & 7 covalencies

6. Hybridisation and shapes of molecules/ions

1. Limitations of VSEPR Theory. (i) It is unable to explain the exact shape in a number of cases. (ii) Taking the direction of electron pairs does not seem to be very rational.

2. Hybridisation. To explain the shapes of molecules in a better way, the concept of hybridisation was put forward. It involves the intermixing of two or more atomic orbitals of slightly different energies but of the same atom so that a redistribution of energy takes place between them resulting in the formation of an equal number of new orbitals (called **hybrid orbitals**) having same energy, size and shape.

It may be noted that:

- Both half-filled and completely filled orbitals as well as empty orbitals can participate in hybridization.
 - Number of hybrid orbitals formed is equal to the number of atomic orbitals mixed
 - Hybridization never takes place in isolated atoms but occurs only at the time of bond formation.
 - Hybrid orbitals form strong bonds than pure atomic orbitals.
- 3. Types of hybridization and shapes of molecules/ions.** Depending upon the number and type of atomic orbitals involved, the hybridization may be divided into the following categories:

| Types of Hybridization | Orbitals mixed | Shape of the molecule/ion | Examples |
|--------------------------------------|--|---------------------------|--|
| (i) sp | One s + one p | Linear | BeF ₂ , BeH ₂ , C ₂ H ₂ , HgCl ₂ |
| (ii) sp ² | One s + two p | Triangular planar | BF ₃ , C ₂ H ₄ , NO ₃ ⁻ , CO ₃ ²⁻ |
| (iii) sp ³ | One s + three p | Tetrahedral | CH ₄ , CCl ₄ , SnCl ₄ , NH ₄ ⁺ , Ni(CO) ₄] |
| (iv) dsp ² | One d (d _{x²-y²}) + one s + two p | Square planar | [Ni(CN) ₄] ²⁻ , [PtCl ₄] ²⁻ |
| (v) sp ³ d | One s + three p + one d (d _{z²}) | Trigonal bipyramidal | PF ₅ , PCl ₅ |
| (vi) sp ³ d ² | One s + three p + two d (d _{x²-y²} , d _{z²}) | Octahedral | SF ₆ , [CrF ₆] ³⁻ , [Co(NH ₃) ₆] ³⁺ |
| (vii) sp ³ d ³ | One s + three p + three d (d _{xy} , d _{yz} , d _{xz}) | Pentagonal bipyramidal | IF ₇ |

4. Predicting hybridisation of central atom and shape of molecule/ion:

a) **Predicting hybridisation.** Calculate the number of hybrid orbitals (X) to be formed by the central atom as follows:

$$X = \frac{1}{2} \left[\left\{ \begin{array}{l} \text{No. of valence electrons} \\ \text{of the central atom} \end{array} \right\} + \left\{ \begin{array}{l} \text{No. of monovalent atoms / groups} \\ \text{surrounding the central atom} \end{array} \right\} - \left\{ \begin{array}{l} \text{Charge on the cation} \\ \text{if the given species is} \\ \text{a polyatomic cation} \end{array} \right\} + \left\{ \begin{array}{l} \text{Charge on the anion} \\ \text{if the given species} \\ \text{is a polyatomic anion} \end{array} \right\} \right]$$

i.e., $X = \frac{1}{2} [VE + MA - c + a]$

Note that only monovalent atoms (MA) or groups are to be considered. For divalent ions, MA = 0. If X = 2, it means two hybrid orbitals are formed. Hence, hybridization is sp. If X = 3, it means three hybrid orbitals are formed. Hence, hybridisation is sp² and so on, as given in the following table:

| | | | | | | |
|-----------------------|----|-----------------|-----------------|-------------------|--------------------------------|--------------------------------|
| Value of X | 2 | 3 | 4 | 5 | 6 | 7 |
| Type of hybridisation | sp | sp ² | sp ³ | sp ³ d | sp ³ d ² | sp ³ d ³ |

b) **Predicting shape:** If number of hybrid orbitals is equal to the number of surrounding atoms/groups (monovalent or divalent etc) the molecules/ion has a regular geometry and the shape is same as that predicted by hybridisation. However, if number of surrounding atoms/groups is less than the number of hybrid orbitals, the difference gives the number of lone pairs present on the central atom and the species is said to have irregular geometry and the shape is predicted by leaving the hybrid orbitals containing the lone pairs.

Note that in predicting the shape, only number of atoms or groups are to be considered irrespective of the fact that they are monovalent or divalent etc.

A few examples to predict the hybridisation of the central atom and shape of the molecule/ion are given below:

| Molecule/Ion | $X = \frac{1}{2} [VE + MA - c + a]$ | Hybridisation | Hybrid orbitals Containing lone pairs | Shape |
|---|--|-----------------|---------------------------------------|-------------------|
| CO ₂ (₆ C = 2, 4) | $X = \frac{1}{2} [4+0-0+0] = 2$ (MA=0 as oxygen is divalent) c = 0, a = 0, as it is neutral molecule) | sp | 0 | Linear |
| BF ₃ (₅ B = 2, 3) | $X = \frac{1}{2} [3+3-0+0] = 3$ (MA = 3 as three F's are monovalent) | sp ² | 0 | Planar triangular |
| SiF ₄ (₁₄ Si = 2, 8, 4) | $X = \frac{1}{2} [4+4-0+0] = 4$ | sp ³ | 0 | Tetrahedral |

| | | | | |
|--|--|--------------------------------|---|------------------------|
| PCl ₅ (₁₅ P = 2, 8, 5) | $X = \frac{1}{2}[5+5-0+0] = 5$ | sp ³ d | 0 | Trigonal bipyramidal |
| SF ₆ (₁₆ S = 2, 8, 6) | $X = \frac{1}{2}[6+6-0+0] = 6$ | sp ³ d ² | 0 | Octahedral |
| NH ₃ (₇ N = 2, 5) | $X = \frac{1}{2}[5+3-0+0] = 4$ (MA = 3 as three H's are monovalent) | sp ³ | 1 | Pyramidal |
| PCl ₃ (₁₅ P = 2, 8, 5) | $X = \frac{1}{2}[5+3-0+0]=4$ (MA = 3 as three Cl's are monovalent) | sp ³ | 1 | Pyramidal |
| IF ₅ | $X = \frac{1}{2}[7+5-0+0] = 6$ | sp ³ d ² | 1 | Square pyramidal |
| IF ₇ | $X = \frac{1}{2}[7+7-0+0] = 7$ | sp ³ d ³ | 0 | Pentagonal bipyramidal |
| H ₂ O (₈ O = 2, 6) | $X = \frac{1}{2}[6+2-0+0] = 4$ | sp ³ | 2 | Bent (V-shaped) |

| Molecule/Ion | $X = \frac{1}{2} [VE + MA - c + a]$ | Hybridisation | Hybrid orbitals Containing lone pairs | Shape |
|---|---|-----------------|---------------------------------------|-------------------|
| NH ₄ ⁺ (₇ N = 2, 5) | $X = \frac{1}{2}[5+4-1+0] = 4$ (c = 1 as charge on cation = 1) | sp ³ | 0 | Tetrahedral |
| H ₃ O ⁺ (₈ O = 2, 6) | $X = \frac{1}{2}[6+3-1+0] = 4$ | sp ³ | 1 | Pyramidal |
| CH ₃ ⁺ (Carbocation) | $X = \frac{1}{2}[4+3-1+0] = 3$ | sp ² | 0 | Triangular planar |
| NO ₃ ⁻ (₇ N = 2, 5) | $X = \frac{1}{2}[5+0-0+1] = 3$ (a = 1 as charge on anion = 1) | sp ² | 0 | Triangular planar |
| CO ₃ ²⁻ (₆ C = 2, 4) | $X = \frac{1}{2}[4+0-0+2] = 3$ (a = 2 as charge on anion = 2) | sp ² | 0 | Triangular Planar |
| SO ₄ ²⁻ (₁₆ S = 2, 8, 6) | $X = \frac{1}{2}[6+0-0+2] = 4$ (MA = 0 as oxygen is divalent) | sp ³ | 0 | Tetrahedral |

| | | | | |
|--|--------------------------------|-----------------|---|-------------|
| ClO ₄ ⁻ (Perchlorate ion) | $X = \frac{1}{2}[7+0-0+1] = 4$ | sp ³ | 0 | Tetrahedral |
| CH ₃ ⁻ (Carbanion) | $X = \frac{1}{2}[4+3-0+1] = 4$ | sp ³ | 1 | Pyramidal |

Alternate:

| Simple molecule | Polyatomic Anion | Polyatomic cation |
|--------------------------|------------------------------|------------------------------|
| $X = \frac{1}{2}[V + G]$ | $X = \frac{1}{2}[V + G + a]$ | $X = \frac{1}{2}[V + G - c]$ |

In the above formulae,

V = Number of monovalent atoms or groups attached to the central atom

G = Number of outer shell electrons in ground state of the central atom

a = Magnitude of charge on anion

c = Magnitude of charge on cation

Calculate the value of X and decide the hybrid state of central atom as follows:

| X | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------|----|-----------------|-----------------|-------------------|--------------------------------|--------------------------------|
| Hybrid state | sp | sp ² | sp ³ | sp ³ d | sp ³ d ² | sp ³ d ³ |

Decrease in angle at central atom decreases percentage 's' character in hybridisation.

| Molecule | Angle | Hybridisation | % s-character |
|-------------------|----------|-----------------|---------------|
| BeCl ₂ | 180° | sp | 50% |
| BCl ₃ | 120° | sp ² | 33% |
| CH ₄ | 109°28' | sp ³ | 25% |
| NH ₃ | ≈ 107° | sp ³ | ≈ 23% |
| H ₂ O | ≈ 104.5° | sp ³ | ≈ 21.4% |

8. Polar molecules

- When two atoms differ with respect to their electronegative values, the bond between them will be a polar bond and the molecule is polar molecule

Example: H₂O, HCl are polar molecules

9. Formal charge:

The formal charge of an atom in a polyatomic molecule or ion is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure.
 Formula charge = Total no. Of valence electrons in the free atom – Total no. of lone pair electrons – (1/2) total number of bonding electrons.

For example formal charge on 'S' in $\text{HSO}_4^- = 6 - 0 - \frac{1}{2}(8) = +2$.

Formal charge on 'Cl' in $\text{HClO}_4 = 7 - 0 - \frac{1}{2}(8) = +3$

10. Valence Bond Theory (VBT) or Atomic Orbital Overlapping

This theory was proposed by Heitler and London in 1927 and later it was modified by Pauling and Slater in 1931.

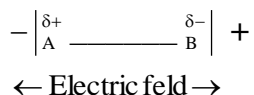
According to this theory,

- Half filled orbitals having electrons of opposite spins, overlap to form a covalent bond.
- Greater the overlapping, stronger is the bond. The extent of overlapping of orbitals is
 $s - s > s - p > p - p$
- Formation of a covalent bond results in decreasing the energy of the system to the minimum and balancing forces of attraction and repulsion among nuclei and electrons.
- Overlapping along the axis is stronger than sideways overlapping.

11. Polar molecules and dipole moment

Dipole moment

The unsymmetrical distribution of electron pair or cloud in a covalent bond results in the separation of charges within a molecule. Due to which, the molecule acquires a tendency to line up along the direction of electrostatic field eg: if B is more electronegative than A in AB molecule, then

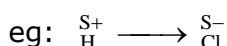


Hence such molecules are dipolar in nature. The degree of polarity of a molecule is expressed in dipole moment. The dipole moment (μ) of a molecule is the product of charge (e) and the distance (d) of separation of charges in the molecule

$$\mu = e \times d$$

The charges is of the order of 10^{-10} e.s.u and the internuclear distance is of the order of 10^{-8} cm, hence the dipole moment is expressed in debye (D): hence
 $1\text{D} = 10^{-10} \text{esu} \times 10^{-8} \text{cm} = 10^{-18} \text{esu} \cdot \text{cm}$

The dipole moment is a vector quantity and directed from positive to negative charge



How to find out whether $\mu = 0$ or $\mu \neq 0$

If the central atom is surrounded by elements having same electronegativity and the molecule is in its real geometry ie., having no lone pair of electrons then $\mu = 0$.

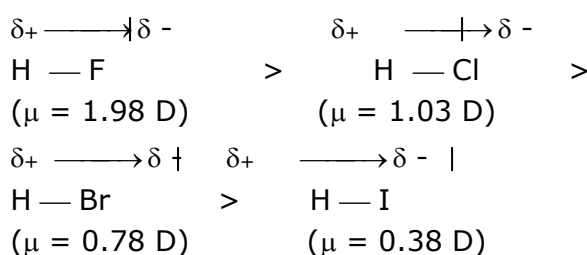
eg : $\text{CO}_2, \text{CS}_2, \text{BF}_3, \text{C}_2\text{H}_4, \text{H}_2, \text{CCl}_4, \text{SnCl}_4, \text{CH}_4$ etc.

If the central atom is either surrounded by elements having different electronegativity or having lone pair of electrons then $\mu \neq 0$.

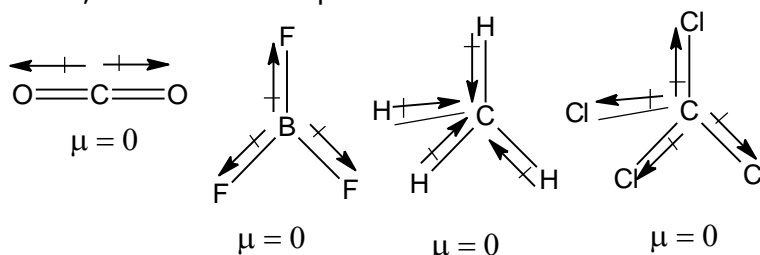
eg : CH_3Cl , CH_2Cl_2 , CHCl_3 , $\ddot{\text{N}}\text{H}_3$, $\text{H}_2\ddot{\text{O}}$: etc.

- In CO_2 and methane, the bonds are polar but because of the molecular symmetry the molecule as a whole is non polar
- Dipole moment of a molecule is defined as the product of charge of the positive or negative centres and the distance between the charges.
- Dipole moment = charge \times distance of separation
- Dipole moment is expressed in term of Debye unit
- 1 Debye = 3.336×10^{-30} cm
- N_2 , H_2 , O_2 are non polar molecules. Hence dipole moment = 0
- CO_2 has a linear structure and has zero dipole moment
- Dipole moment of water is 1.85 D. Hence it has a bent structure
- NH_3 molecule has dipole moment of 1.46 D and the molecule is pyramidal
- **Applications of Dipole Moment**

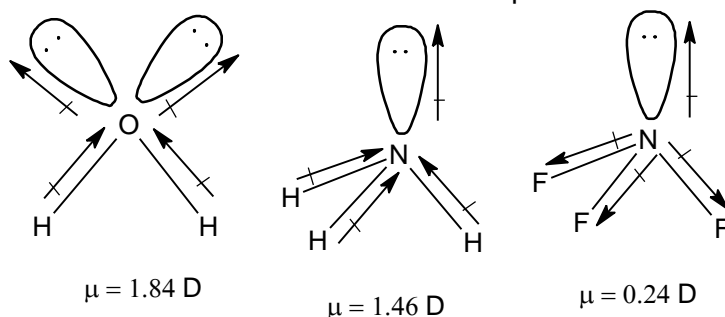
i) **In predicting the polarity of bonds.** The dipole moment helps to predict whether the molecule is polar or non-polar. Greater the dipole moment, greater is the polar character. Thus, polar character of hydrogen halides is in the order:



ii) **In predicting the symmetry of molecules.** For polyatomic molecules, the dipole moment is the vector sum of the dipole moments of various bonds. If the molecule is symmetrical, the resultant dipole moment of the molecule is zero. For example,

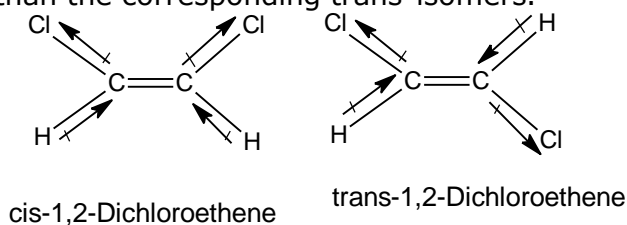


Unsymmetrical molecules have a resultant dipole moment. For example,

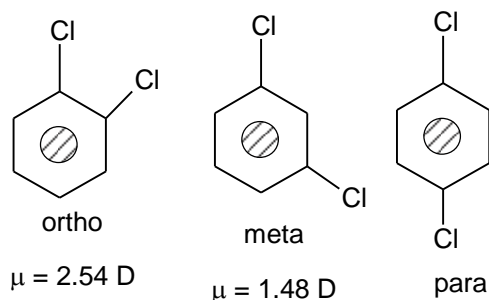


Note that dipole also exists from atom to lone pair.

iii) **In distinguishing between cis and trans isomers.** Usually cis-isomers have higher dipole moments than the corresponding trans-isomers.



iv) **In distinguishing between ortho, meta and para isomers.** For example among isomeric dichlorobenzenes, the dipole moment decreases in the order: o > m > p



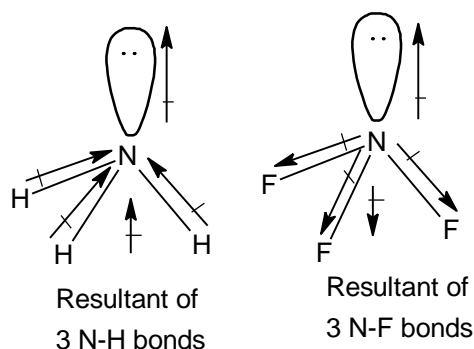
v) **In calculation of percent ionic character of covalent bond.**

• **Comparison of dipole moments of NH_3 , NF_3 , NCl_3 , NBr_3 and NI_3 . In such cases,**

- i) dipole formed between N and lone pair has to be taken into consideration which is in the direction of the lone pair,
- ii) electronegativity difference between N and the other atom is to be considered and the direction taken is towards the more electronegative atom.

a) **Comparison of NH_3 and NF_3**

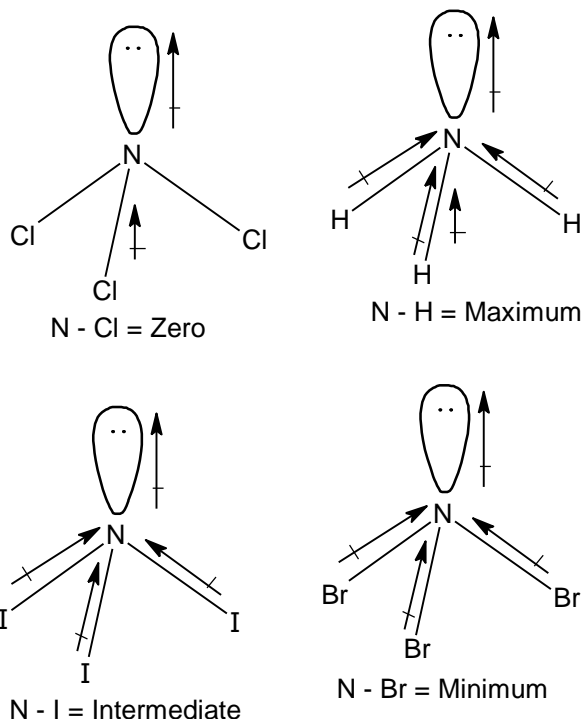
EN difference between N and H ($3.0 - 2.1 = 0.9$) is nearly same as between N and F ($4.0 - 3.0 = 1.0$). However, the direction of their dipoles are opposite as shown below:



Hence, dipole moment of NH_3 (1.46 D) > dipole moment of NF_3 (0.24 D)

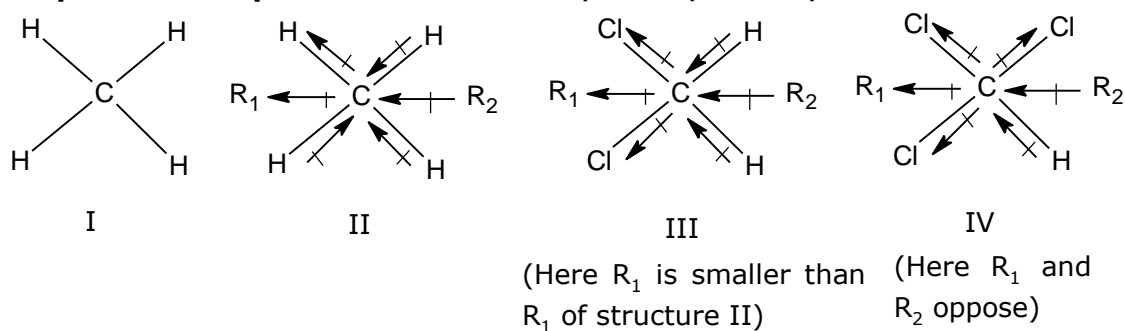
- b) Comparison of other molecules.** EN difference between N (3.0) and Cl (3.0) is zero. Hence, N - Cl bonds are non-polar. Further N is more electronegative than H, Br or I. Hence, their bonds are polar and contribute towards dipole moment. The extent of contribution will depend upon EN difference (N - H = 3.0 - 2.1 = 0.9, N - Br = 3.0 - 2.8 = 0.2, N - I = 3.0 - 2.5 = 0.5)

Thus, we have (contribution of N - X bond is given below each structure)



Hence their dipole moments will be in the order: $\text{NH}_3 > \text{NI}_3 > \text{NBr}_3 > \text{NCl}_3 > \text{NF}_3$

- Comparison of dipole moments of CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4**



[R_1 and R_2 represent the resultants as shown above]

- Partial/Percent ionic character of covalent bond.** Every polar covalent bond has some ionic character. It is calculated as follows:

- a) From Electronegativity difference:**

Higher the electronegativity different between the two atoms forming the covalent bond, higher is the percentage of ionic character. For example,

| Electronegativity difference | Percentage ionic character | Nature of bond |
|------------------------------|----------------------------|----------------|
| 0.2 | 1 | |
| 0.6 | 10 | |
| 0.8 | 15 | |
| 1.2 | 30 | |
| 1.9 | 50 | |
| 2.2 | 70 | |
| 2.8 | 80 | |
| 3.2 | 92 | |

Several empirical equations have been proposed to calculate the percentage ionic character from the electronegativity difference of the bonding atoms. Two such equations are:

Pauling Equation:

$$\% \text{ Ionic character} = [1 - e^{-1/4(x_A - x_B)}] \times 100$$

Hannay and Smith equation:

$$\% \text{ Ionic character} = 16 (x_A - x_B) + 3.5 (x_A - x_B)^2$$

Here, x_A and x_B are the electronegativities of the two atoms forming a bond.

It may be mentioned here that both these equations, however, give approximate values.

b) From Dipole moment: Higher the dipole moment of a covalent bond, higher is its percent ionic character. It can be calculated by the following equation:

$$\% \text{ Ionic character} = \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of a pure ionic bond}} \times 100$$

$$= \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

The dipole moment of a pure ionic bond is obtained by multiplying the electronic charge by the distance between the two atoms, i.e., $\mu = q \times d$ where $q = 4.8 \times 10^{-10}$ esu or 1.602×10^{-19} C and distance d is in \AA , i.e., of the order of 10^{-8} cm or 10^{-10} m.

Valence shell electron pair repulsion theory (VSEPR Theory)

The postulates of the theory are

- 1) The geometry of the molecule or ion depends upon the number of electron pairs in the valence shell of its central atom.
- 2) The electron pairs tend to remain as far as possible in order to acquire a state of minimum energy
- 3) The repulsion between lone pair and lone pair of electrons is different from lone pair and bond pair or two bond pairs of electrons. These repulsive interactions decrease in the following order $lp - lp > lp - bp > bp - bp$
- 4) Repulsive interactions decrease sharply with increase in bond angles between electron pairs.

Ammonia molecule:

Nitrogen atom is sp^3 hybridised. The bond angle in NH_3 is 107° . This is because, nitrogen contains a lone pair of electrons and lone pair and bond pair repulsion is greater than bond pair and bond pair repulsion. NH_3 molecule is pyramidal in shape.

Water molecule:

Oxygen atom is sp^3 hybridised. The bond angle in water is 104.5° . This is because, oxygen contains two lone pairs of electrons and l.p – l.p repulsion is greater than l.p – b.p repulsion. Which is greater than b.p – b.p repulsion. Hence H_2O has V shaped structure.

Valence shell electron pair repulsion (VSEPR) theory and shapes of molecules

- 1. Limitation of Lewis-Langmuir concept of covalent bond.** The main limitation was that it could not explain the shapes of covalent molecules.
- 2. VSEPR Theory.** This was the first simple theory (put forward by Sidgwick and Powell) to explain the shapes of simple covalent molecules. According to this theory, "The electron pairs (bond pairs as well as lone pairs) present around the central atom repel each other and hence move as far apart as possible so that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability. The direction of the electron pairs gives a definite geometry to the molecule."

If the central atom in a molecule is surrounded by only one kind of atoms and surrounded by bond pairs only, the molecule is said to possess regular geometry. If on the other hand, the central atom in a molecule is linked to different types of atoms or is surrounded by both lone pairs and bond pairs, the geometry of the molecule is distorted to some extent. Such molecules are said to possess irregular geometry. This distortion is due to the reason that: Lone pair-Lone pair repulsion > Lone pair-Bond pair repulsion > Bond pair-Bond pair repulsion (i.e., lp-lp > lp-bp > bp-bp). Depending upon the number of bond pairs and lone pairs, the geometries of various types of molecules are summarized below:

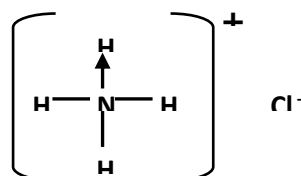
| Total No. of Electron pairs | Geometry of electron pairs | No. of Bond pairs | No. of lone pairs | Type of molecule | Geometry of molecule | Examples |
|-----------------------------|----------------------------|-------------------|-------------------|------------------|------------------------|---|
| 2 | Linear | 2 | 0 | AB_2 | Linear | $BeF_2, [Ag(NH_3)_2]^+, HgCl_2$ |
| 3 | Triangular planar | 3 | 0 | AB_3 | Trigonal planar | $BF_3, AlCl_3, NO_3^-, CO_3^{2-}$ $SnCl_2, PbCl_2$ |
| | | 2 | 1 | AB_2L | V shaped | |
| 4 | Tetrahedral | 4 | 0 | AB_4 | Tetrahedral | $CH_4, SiF_4, NH_4^+, CCl_4$ $NH_3, PX_3 (X = F, Cl, Br, I)$ $H_2O, OF_2, SCl_2, NH_2^-$ |
| | | 3 | 1 | AB_3L | Trigonal pyramidal | |
| | | 2 | 2 | AB_2L_2 | V-shaped | |
| 5 | Trigonal bipyramidal | 5 | 0 | AB_5 | Trigonal bipyramidal | $PF_5, PCl_5, SbCl_5, Fe(CO)_5$ $SF_4, TeBr_4$ $ClF_3, XeOF_2$ XeF_2, ICl_2^-, I_3^- |
| | | 4 | 1 | AB_4L | See saw | |
| | | 3 | 2 | AB_3L_2 | T-shaped | |
| | | 2 | 3 | AB_2L_3 | Linear | |
| 6 | Octahedral | 6 | 0 | AB_6 | Octahedral | $SF_6, [SbF_6]^-$ $IF_5, ClF_5, [SbF_5]^{2-}, XeOF_4$ XeF_4, ICl_4^- |
| | | 5 | 1 | AB_5L | Square pyramidal | |
| | | 4 | 2 | AB_4L_2 | Square planar | |
| 7 | Pentagonal bipyramidal | 7 | 0 | AB_7 | Pentagonal bipyramidal | IF_7 XeF_6 |
| | | 6 | 1 | AB_6L | Distorted octahedral | |

13. Coordinate bonds

- In this, both electrons of the shared pair are donated by one atom to another. The bond is also called dative bond.
- In many molecules in addition to coordinate bonds, covalent or ionic or both the type of bonds may be present.

Illustration: In ammonium chloride, ionic bond is formed between NH_4^+ ion and Cl^- ion.

- In NH_4^+ ion, 3 hydrogen atoms are covalently linked to nitrogen. The coordinate bond is present between NH_3 molecule and H^+ ion.



14. Hydration of Ions

Water is polar solvent having partial positive charge on H-atom and partial negative charge on O-atom. When an ionic solid is dissolved in water, its cation get surrounded by water molecules due to attraction with negatively behaving O-atom and anions too, because of attraction with positively behaving H-atoms. This process is known as **hydration** and is exothermic in nature.

- ❖ An ionic solid will dissolve in water if the hydration energy dominates its lattice energy.
- ❖ The extent of hydration is directly proportional to the charge density of the ion. Charge density of Ca^{2+} is approximately double that of Na^+ . The hydration energy of Ca^{2+} is approximately four times that of Na^+ .
- ❖ For alkali metals,

| | | |
|--|---|--|
| Order of size of ion | : | $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ |
| Order of hydration | : | $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ |
| Mobility of hydrated ion | : | $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ |
| Conductivity of hydrated Ion in aqueous solution | : | $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ |

15. Hydrogen Bond (Latimer and Rodebush)

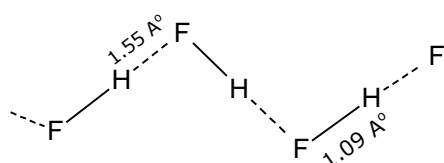
It is the force of attraction between covalently bonded, positively behaving H-atom of a molecule with an electronegative atom of the same or different molecule.

Hydrogen bond is only about 5-10% as strong as a covalent bond.

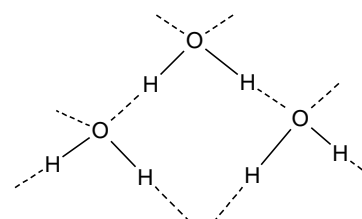
For an H-atom to form H-bond, it must be covalently bonded to a small highly electronegative atom such as N, O or F and the other negative atom should be at a maximum distance of 275 pm. Basically, H-bonding is a strong dipole-dipole interaction.

Types of H-bonds

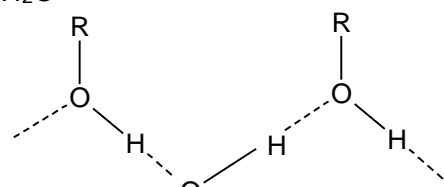
- (I) **Intermolecular hydrogen bond** : It is the H-bond formed between two different molecules of the same or different substances.

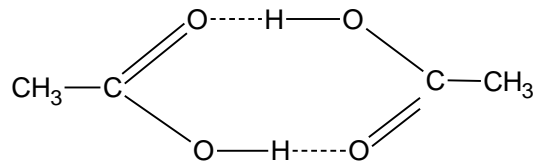


H-bonding in HF molecules
2H-bonds per molecule of HF
 H_2O



H-bonding in H_2O molecules
4H-bonds per molecule of

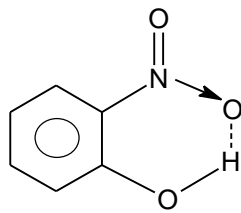




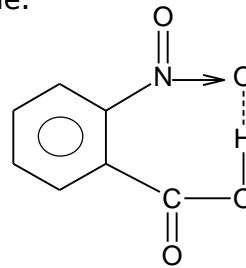
H-bonding between ROH and H₂O

H-bonding in CH₃COOH

(II) Intramolecular hydrogen bond : It is the H-bond formed between H-atom and a highly electronegative atom of the same molecule.

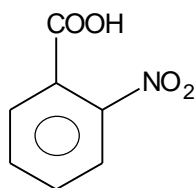


o-Nitrophenol



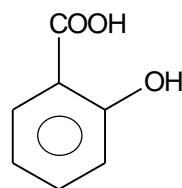
o-Nitrobenzoic acid

- Intermolecular hydrogen bonding** among same type of molecules decreases density (increase in volume) but increases b.p. If it is present among molecules of different compounds, there is slight contraction in the volume.
- Intramolecular hydrogen bonding** decreases solubility and boiling point. At the same time the substance becomes steam volatile and more acidic.
- Boiling points of hydrides :
 - HCl < HBr < HI < HF
 - H₂S < H₂Se < H₂Te < H₂O
 - PH₃ < AsH₃ < NH₃ < SbH₃ < BiH₃
- Acid strength of benzoic acid :



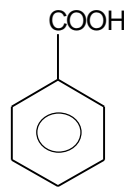
$pK_a = 2.17$

>



$pK_a = 2.98$

>



$pK_a = 4.17$

- One H₂O molecule forms four H-bonds.
- O-atom of H₂O forms two covalent bonds with two H-atoms of the same molecule (usual feature) and two H-bonds with two other H₂O molecules (one-bond with each).
- The rigidity of silk, cotton, synthetic fiber, wool fibers , etc,.. is due to hydrogen bonding.
- Honey and glue are sticky because of hydrogen bonding.

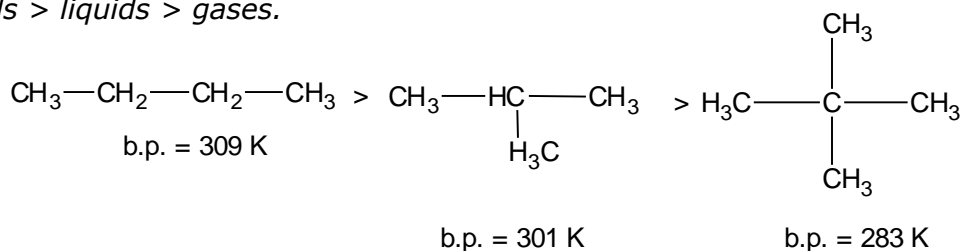
16. Van der Waal's Forces

A weak inter atomic or intermolecular force of attraction which holds the different constituents together. When the molecular mass increases vander Wall's force increases in the following order solids > liquids > gases .

Forces, much weaker than valence bonds that bind non-polar molecules (e.g., H₂, Cl₂, CH₄, etc) and atoms of noble gases, are called van der Waal's forces. These are inversely proportional to the 7th power of the distance between atoms or molecules. These forces are responsible for non-ideal behaviour of gases and for the lattice energy of molecular solids.

Following three factors are responsible for such forces :

- Dipole – dipole interactions** : Such interactions arise among gaseous molecules, such as NH₃, SO₂, HCl, etc, which have permanent dipole moments.
 - Dipole – induced dipole interactions** : Here, the permanent dipole of one molecule polarises a neighbouring non-polar molecule to cause attraction, e.g., the solubility of noble gases in water is due to this factor.
 - Induced dipole-induced dipole interactions** : Non-polar atoms and molecules induce polarity in one another to cause the attraction forces . These forces are also called **London forces**. These forces are present among molecules of oxygen, methane, noble gases, etc.
- ❖ Higher the size of the molecule, higher are the van der Waal's forces and higher are the boiling points.
 - ❖ Higher the molar mass, higher are the van der Waal's forces and higher are the boiling points, in general.
I₂ (b.p. = 456 K) > Br₂ (b.p. = 331 K) > CCl₄ (b.p. = 231 K) > F₂ (b.p. 85 K)
 - ❖ According to *the state of substance, van der Waal's forces are in the order* :
solids > liquids > gases.



Effect of hydrogen bond

Solubility of a compound in water increases if the substance can form hydrogen bonding with water.

Due to the presence of inter molecular hydrogen bonding in water, water has some abnormal properties like high latent heat of fusion of ice, lower density for ice than water, and water to have highest density at 4^oC and abnormally high boiling point (100^o C)

17. Resonance energy: The resonance hybrid is more stable than any of the resonating structure. The difference between the energy of the resonance hybrid and that of the most stable contributing structure is called **resonance energy**.

• Rules for writing Resonating Structures:

- The various resonating structures differ in the position of electrons and not in the relative positions of atoms.
- All the contributing structures should have the same number of unpaired electrons.
- The various canonical structures should not differ much in energy

- iv) Resonance structures in which the negative charge resides on electronegative atom and positive charge resides on electropositive atom contribute more towards the resonance hybrid than the resonance structure in which these charges are reversed.
- v) Resonance structures should be so written that unlike charges reside on adjacent atoms
- vi) Resonance structure with greater number of covalent bonds contributes more towards the resonance hybrid.

18. Salient features of MOT

- 1) A molecular orbital is formed by the linear combination of atomic orbitals
- 2) When two atomic orbitals combine, two molecular orbitals are formed. One with lower energy is called bonding molecular orbital while the other with higher energy is called anti bonding molecular orbital.
- 3) The molecular orbital is represented by a wave function ψ . The probability of finding the electron in this orbital is ψ^2
- 4) The combining atomic orbitals should have comparable energy.
- 5) The shapes of the molecular orbitals depend upon the shapes of the combining atomic orbitals.
- 6) The number of molecular orbitals formed is equal to the number of atomic orbitals taking part in linear combination
- 7) Molecular orbitals are polycentric
- 8) The combining atomic orbitals should have same symmetry
- 9) Electrons are arranged in molecular orbitals according to Auf – bau principle, Pauli's exclusion principle and Hund's rule
- 10) Each molecular orbital has definite amount of energy.

19. Symmetric combination:

Where the wave function of atomic orbitals are added, the molecular orbital obtained is called bonding molecular orbital.

$$\psi_s = \psi_A + \psi_B$$

20. Asymmetric combination:

Where the wave function of atomic orbitals are subtracted, the molecular orbital obtained is called antibonding molecular orbital

$$\psi_a = \psi_A - \psi_B$$

21. Rules governing L. C. A. O:

1. The combining atomic orbitals should have comparable energies
2. The combining atomic orbitals should have same symmetry
3. The atomic orbitals combine only when they overlap by considerable extent. When atomic orbitals overlap axially, a σ molecular orbital is formed, while when atomic orbitals overlap sideways, a π molecular orbital is formed.
4. The sign of the wave functions of overlapping lobes determine the nature of molecular orbital. If the overlapping lobes have similar sign of wave function, (+ and + or – and –), a bonding molecular orbital is formed. If the overlapping lobes have opposite sign of wave function, an antibonding molecular orbital is formed.
5. **Energy level diagram:** The graphical arrangement of various molecular orbitals in the increasing order of their energies is called energy level diagram. The arrangement of various molecular orbitals in the increasing order of their energies is For diatomic molecules with atomic number more than 7

$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$
 For diatomic molecules with atomic number less than 7 the order is
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$

22. Bond Order

Bond order = $\frac{1}{2}$ [Number of electrons in BMO – Number of electrons in ABMO]

Bond order (B.O.) = $\frac{1}{2}(N_b - N_a)$

where N_b = number of electrons in the bonding molecular orbitals

N_a = number of electrons in the antibonding molecular orbitals

Bond order helps to predict:

- Formation of molecule/molecular ions—if bond order is greater than zero, then the molecules exist otherwise not.
- Stability—higher the bond order, greater is the stability.
- Bond dissociation energy—higher the bond order, higher is the bond energy.
- Bond length—higher the bond order, shorter is the bond length.
- If any compound show resonance then effective bond order can be calculated as

Bond order = $\frac{\text{Total no. of bonds between atoms}}{\text{Total no. of resonating structures}}$

Alternate method to calculate Bond order

If total number electrons equal 14 or less than 14

Bond order = $\frac{N-8}{2}$

If total number of electrons equal to 14 to 20

Bond order = $\frac{20-N}{2}$

N = Total number electrons

23. Rules governing electronic configuration:

- Auf –bau principle:** Electrons occupy various molecular orbitals in the increasing order of their energies
- Pauli's Exclusion principle:** A molecular orbital can occupy a maximum of two electrons with opposite spins.
- Hund's rule:** No electron pairing takes place in molecular orbitals of identical energy until each orbital of the given set is singly occupied with parallel spins

24. Magnetic property:

If a molecule contains at least one unpaired electron, it is paramagnetic. If it does not contain any unpaired electron, then it is diamagnetic.

Electronic configuration of H_2 : σ_{1s}^2

Electronic configuration of He_2 : $\sigma_{1s}^2 \sigma_{1s}^{*2}$

Electron configuration of Li_2 : $KK\sigma_{2s}^2$

Electron configuration of O_2 : $KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \pi_{2px}^2 \pi_{2py}^2 \pi_{2px}^{*1} \pi_{2py}^{*1}$

Bond order in oxygen is 2.

Note:

- 1) Higher the bond order, shorter is the bond length
- 2) Higher is the bond order, stronger is the bond.

25. Metallic bond:

It is a force of attraction which holds various metal ions together in a sea of electrons. Metallic bonding can be explained by electron sea model. It was proposed by Drude and Lorentz in 1925. The postulates of this theory are

- a) Metal atoms readily lose their valence electrons forming +vely charged metal ions called Kernel
- b) These electrons are free to move throughout the metal using vacant orbitals
- c) The metal ions are arranged in definite geometric shape
- d) The metal ions are submerged in a sea of electrons. The movement of electrons is similar to the movement of sea water. The strength of a metallic bond depends upon
 - i) number of valence electrons
 - ii) charge on the metal ion
 - iii) size of the metal ion
- e) Transition metals have strong metallic bonding because
 - i) they have several valence electrons
 - ii) they have high +ve charge on the metal ion
 - iii) metal ions are small in size.

Correlation of metallic properties on the basis of electron sea model:

1. **Metallic luster:** Metals have shining surface. The mobile electrons absorb radiation and oscillate. The oscillating electrons lose energy by emitting radiation.
2. Metals are good conductors of heat and electricity. When a metal is heated from one end, the mobile electrons gain energy and transfer energy to the other electrons and the other metal ions. Hence, metals show thermal conductance
3. **Malleability and ductility:** When metal is hammered with force, the positive metal ion layers slide over one another. The mobile electrons move so that the environment around the metal ion layer remains unchanged. Hence, metal can be drawn into thin sheets or wires.
4. **Photoelectric or thermoionic emissions:** When a metal is heated strongly electrons gain energy so that they overcome the attraction by the metal ions. This explains thermoionic emission.

When light falls on the metals like Rb and Cs, the loosely held valence electrons can be removed out of the metal surface. This is called photoelectric effect.
5. Metals show high boiling point, high tensile strength, high melting point due to strong metallic bond between atoms.