

Handwritten Notes On Chemical Bonding



- * Chemical Bond: force of attraction that binds two atoms together.
- * Cause of formation of Chemical Bond:
 - attain the octet state,
 - minimize energy,
 - gain stability,
 - decrease reactivity.
- * Types of bonds: (bond strength - decreasing order).

1. Ionic bond, 2. Covalent bond, 3. Coordinate bond, 4. Metallic bond, 5. Hydrogen bond, 6. Van der Waals bond.

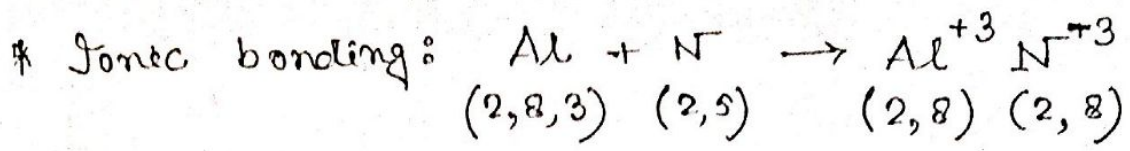
- * Octet rule: Each atom tries to obtain the (Lewis, Kossel) octet state.

- Contraction of Octet State: Central atom is electron deficient or does not have an octet state. eg. $\frac{\text{Be} \times_2}{4}$, $\frac{\text{B} \times_3}{6}$, $\frac{\text{Al} \times_3}{6}$, $\frac{\text{Ge}(\text{CH}_3)_3}{6e^-}$

- Expansion of Octet State: Central atom has more than 8 electrons due to empty d orbitals.

eg. $\frac{\text{PCl}_5}{10}$, $\frac{\text{SF}_6}{12}$, $\frac{\text{OsF}_8}{16}$, $\frac{\text{ICl}_3}{10}$.

- Other exceptions: a) Transition metal ions (Cr^{3+} , Fe^{2+}), b) Pseudo inert gas configuration (Zn^{2+}), c) odd electronic species (NO , NO_2), d) Inter halogen compound (IF_7 , BrF_3), e) Compounds of Xenon (XeF_2 , XeF_4).



- Max number of electrons transferred by a metal to non-metal is three, as is the case of AlF_3 .
- A non directional bond.
- Condition for formation of ionic bond:
 - a) process $\Delta H = -ve$.
 - b) metal must have low ionization energy.
 - c) non metal must have high electron affinity.
 - d) ions must have high lattice energy.
 - e) cation should be large with low electronegativity.
 - f) anion must be small with high electronegativity.
- Ionic compds are hard.

$$\text{hardness} \propto \frac{\text{electrostatic force of attraction} \propto \text{charge on ion}}{\text{ionic radius}}$$
- Ionic compd has high value of bp, mp & density.

BP, MP \propto electrostatic force.

- Ionic compd shows isomorphism; i.e. they have same crystalline structure.
- Conductors in fused, molten, aqueous state.
- Show fast ionic reactions,
- don't show space isomerism.
- U , lattice energy \propto charge on ion.

- In case of univalent & bivalent compounds, lattice energy decreases as follows - $BI-BI > Uni-BI$ or

$$BI - Uni > Uni - Uni$$

$$\text{eg. } HgO > MgCl_2 > NaCl.$$

- Ionic compounds are soluble in polar solvents like water due to the high dielectric constant of these solvents.

o Solubility: $\Delta H(\text{hydration}) > \text{lattice energy}$
- ionic compd soluble

$\Delta H(\text{hydration}) < \text{lattice energy}$
- ionic compd insoluble

$\Delta H(\text{hydration}) = \text{lattice energy}$
- ionic compd at equilibrium

$$\text{solubility} \propto \frac{1}{\text{lattice energy}}$$

o presence of common ions decrease solubility.

* Covalent Bond: Formed by equal sharing of electrons between two atoms.

- One atom can share maximum three electrons with other atom.

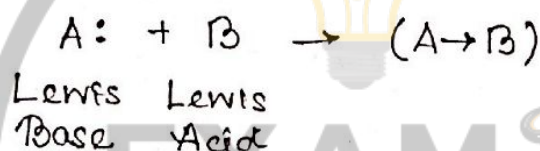
- Solubility of covalent compounds follows the concept - 'like dissolves like', i.e., non polar solute dissolves in non-polar

solvent & polar solute in polar solvent. eg. CCl_4 (non-p) in organic solvents; alcohol, ammonia in water.

- Covalent compounds are non-conductors. (exception - graphite).
- Covalent compounds are directional in covalent bond. They show space isomerisms.

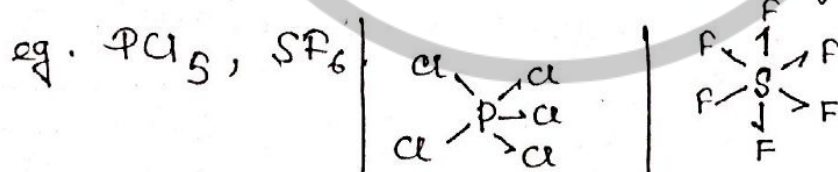
* Coordinate / Dative Semi Polar bond:

Formed by donation of electron pair from donor to receiver.



- Coordinate compounds are more close to covalent compounds.

o Sargent Linkage: Singlet linkage formed by donation of one electron.



* Modern concept of Covalent Bond:

- Valence-Bond Theory: A covalent bond is Heitler-London Theory formed due to half filled atomic orbitals having electrons with opposite spin to each other.

■ Features:

1. The atom should have unpaired electrons. 2. Max. electron density lies between the bonded atoms. 3. The internuclear distance of maximum overlapping is called the bond length.

Limitations: 1. does not explain formation of odd electron molecules (O_3 , NO_2), 2. Can not explain formation of coordinate bond. 3. Can't explain π bond. 4. Can't explain stereochemistry of molecules.

- Pauling & Slater's Theory: a) bond strength depends upon the overlapping & is directly proportional to the extent of overlapping. b) a spherically symmetric orbit, s-orbital will not show any preference in direction whereas non-spherical orbitals, say p- or d-orbitals will tend to form a bond in the direction of maximum electron density with the orbital.

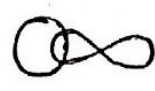
■ i) The overlapping of the orbitals of only those electrons which take part in bond formation. ii) The two orbitals, having similar energy level, the one which is more directionally concentrated, will form


stronger bond. iii) Strongness of overlapping \propto directional nature of orbital. eg.

$$p-p > s-p > s-s$$

Types of Overlapping:

1. s-s : Overlapping between two similar or dissimilar s-s electrons.

2. s-p overlapping  s-p

3. p-p overlapping  p-p

* Bond Length: Average distance between the centers of nuclei of the two bonded atoms. For ionic compound, sum of ionic radius of cation & anion; for covalent compound sum of covalent radius.

• Factors affecting bond length:

- i) bond length \propto size of atom
- ii) bond length $\propto \frac{1}{\text{bond order}}$

eg. $C-C > C=C > C \equiv C$.

iii) bond length $\propto \frac{1}{s\%}$ eg. $sp^3 > sp^2 > sp$.

iv) bond length \propto electronic repulsion.

eg. $H_2^- > H_2^+$

v) Resonance & hyperconjugation also change bond length.

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* **Bond Energy:** Energy needed to break one mole of bonds of a particular type, so as to separate them into gaseous atoms.
Or, the energy released during the formation of one mole of a particular bond.

• Factors affecting bond energy:

i) bond energy \propto bond order

ii) bond energy $\propto \frac{1}{\text{bond length / size of atom}}$

iii) bond energy \propto s%

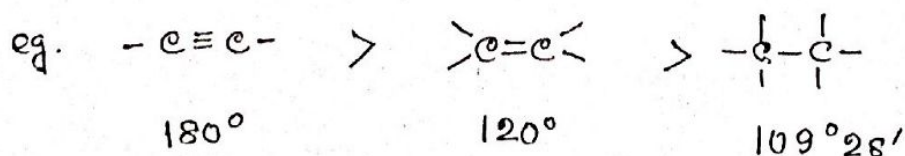
iv) bond energy $\propto \frac{1}{\text{lonc pair of electrons / electronic repulsion}}$

eg.	C-C	>	N-N	>	O-O	>	F-F
lonc pair	0		1		2		3
BE (kJ)	247		163		146		138.8

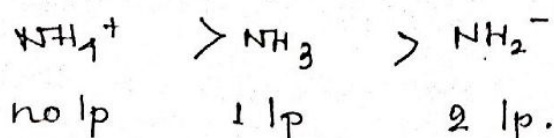
* **Bond angle:** Angle between the lines representing the directions of the bonds or the orbitals having bonding pair of electrons.

• Factors affecting bond angle:

i) bond angle \propto bond order \propto s% $\propto \frac{1}{\text{bond length}}$



ii) affected by electronic repulsion.



iii. bond angle $\propto \frac{1}{(\text{size of terminal atom})^{-1}}$

eg. $\text{I}_2\text{O} > \text{Br}_2\text{O} > \text{Cl}_2\text{O} > \text{OF}_2$.

iv) bond angle $\propto \frac{1}{\text{size of central atom / electronegativity.}}$

eg. $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{BiH}_3$.

v) bond angle \propto electronegativity of terminal atom.

* Polarization & Fajan's Rule: When cation & anion are close to each other, the shape of anion is distorted by the cation, this is called polarisation. Due to this, covalent nature develops in ionic molecule.

Polarization \propto Covalent Nature $\propto \frac{1}{\text{ionic nature}}$

Covalent nature explained by following rules:

a) Charge on cation: Greater the charge on cation greater will be its polarising power & more will be covalent nature.

b) size of cation: When charge is same and anion is common, covalent nature $\propto (1/\text{size of cation})$.

c) size of anion: Covalent nature \propto size of anion (when charges are same, cation is common).

• A cation with 18 valence electrons has more polarising power than a cation with 8

- As the covalent nature increases, the intensity of the colour increases.

* **Dipole Moment**: Dipole moment is used to ($\mu = q \times r$). measure the polarity in a molecule.

Unit of μ : $\mu = (e \times d)$ esu·cm, debye.

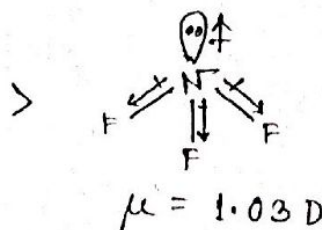
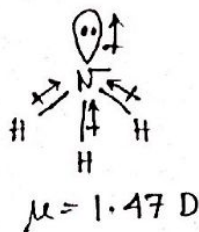
$$1 \text{ debye} = 10^{-18} \text{ esu-cm}$$

Represented by \rightarrow from electropositive to electronegative species or less electronegative to more electronegative species.

$$\mu_{\text{net}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

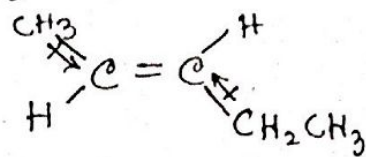
Factors affecting μ :

- $\mu \propto$ electronegativity difference. ($\text{HF} > \text{HCl} > \text{HBr}$)
- $\mu \propto$ number of lp of electrons. ($\frac{\text{HF}}{3} > \frac{\text{H}_2\text{O}}{2} > \frac{\text{NH}_3}{1}$)
- $\mu \propto \frac{1}{\theta}$ (ortho > meta > para).
- homo atomic molecules like N_2, O_2 & molecules having normal shapes according to hybridisation will be non polar.
- molecules having central atom with lone pair or have distorted shapes, like angular, pyramidal, sea-saw will have some value of μ .

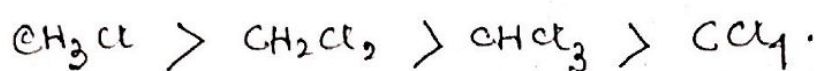


vi) Dipole moment of a cis-alkene is more than trans-alkene. In trans-alkenes, it is zero due to symmetry.

but, unsymmetric alkenes with odd number of carbon has some μ .



• Specific cases of dipole moment:



• Ionic nature (%) = $\frac{\mu_{\text{observed}}}{\mu_{\text{calculated}}} \times 100$.

* σ bonds: Formed by axial or head to head or linear overlapping between two s-s, sp, p-p orbitals.

a) σ bond is stronger, less reactive.

b) min & max number of σ bond between two bonded atoms is one.

c) stability \propto number of σ bonds.

d) reactivity $\propto \frac{1}{\sigma}$.

e) in σ bond, free rotation of atoms is possible.

f) σ bonds determine the shape of a molecule.

* π - bonds: Formed by lateral or sideways of overlapping between two p orbitals.

a) weak bond, more reactive.

b) min & max π bonds between two bonded atoms are 0 and 2.

c) Stability $\propto \frac{1}{\text{number of } \pi \text{ bonds}}$

d) in π bonds, free rotation is not possible.

e) doesn't determine shape of a molecule, but shortens bond length.

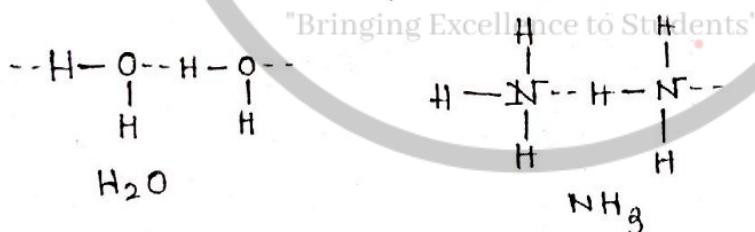
* Finding σ & π bonds:

single bond = 1 σ , double bond = 1 σ , 1 π ,

triple bond = 1 σ , 2 π .

* Hydrogen bond: weak interaction between H and a highly electronegative & small sized atom like F, O & N.

• Intermolecular H bond: Formed between two or more different molecules of the same or different types.



i) due to intermolecular H-bond, the water molecules are closely packed, so water has less volume but more density than ice where an open cage like structure is observed.

ii) Water has max density at 4°C.

iii) two ice cubes when pressed, form one block due to H bonding.

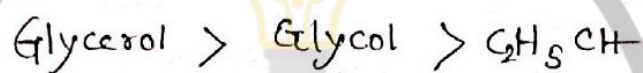
• Effect of intermolecular H bonding:

a) Increase in BP, MP, solubility, thermal stability, viscosity, surface tension & occurrence liquid state is observed as molecules get associated more closely.

b) HF is a liquid having higher BP, than other HX.

c) Alcohols are highly soluble in water & have high BP than others which are less soluble in water.

d) Glycerol is highly viscous with high BP.



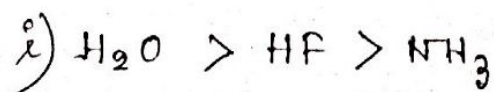
BP, Viscosity.

e) acids have higher BP & solubility than their corresponding acid derivatives.

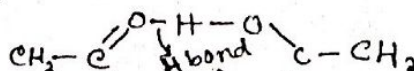
f) In DNA, RNA the complementary strands are held together by H bonds.

g) Nucleic acids & proteins are held together by H bonds.

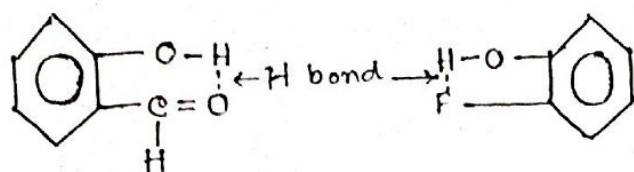
h) KHF_2 or HF_2^- exists due to H bonding, but formation of other HX_2^- (HCl_2) is not possible, due to absence of H bonding.



j) acids can dimerise due to intermolecular H bonding. eg. acetic acid dimerizes in benzene.



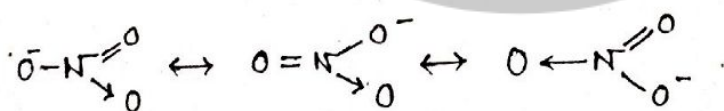
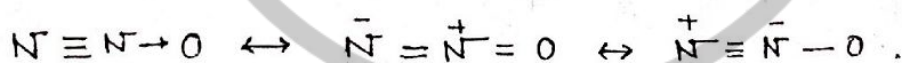
- Intramolecular H bonding: Or Chelation formed within a molecule.



- Effect of intramolecular H bonding:

- a) the BP & acidic nature of molecule decreases but volatile nature increases.
- b) o-nitrophenol has a low BP & reduced acidic nature, but more volatile than p-nitrophenol.

* Resonance: Sometimes, molecules are represented by many structural formulas that are canonical structures or resonating structures. It's observed due to delocalization of π electrons.



* Resonance Energy: Energy of most stable canonical structure - Resonance Hybrid Energy.

- a) $RE \propto$ number of canonical structures
- b) $RE \propto$ stability
- c) $RE \propto \frac{1}{\text{reactivity}}$
- d) $RE = \text{Expected heat of hydrogenation} - \text{Actual heat of hydrogenation}$

e. Due to high RF, benzene is quite stable & undergoes electrophile substitutions. It does not undergo addition reactions, although it has double bonds (due to delocalization of π electrons or resonance).

• Stability of Canonical Structures:

1. A non polar structure is always more stable than a polar structure. $\text{C}_6\text{H}_6 > \text{C}_6\text{H}_5^+ > \text{C}_6\text{H}_7^-$

2. Greater the number of covalent bonds greater will be the stability.



3. The canonical structure in which positive charge on electropositive atom & negative charge on electronegative atom is more stable.



4. The canonical structure in which each atom has a octet state is more stable.



5. If like charges are closer, the structure is unstable.

• Types of resonance:

i) isovalent: canonical structures have same number of bonds & same type of charges.

ii) heterovalent: canonical structures have different number of bonds & charges.

• Bond Order :

$$\frac{\text{Total no. of order b/w two atoms.}}{\text{Total no. of major Canonical structures}}$$

In SO_3 , $\text{BO} = \frac{1}{3} = 1.33$.

* Hybridisation (Pauling & Slater) : Intermixing or redistribution of energy among two or more half filled, fully-filled, incompletely filled or empty orbitals of comparable energy to form same number of hybrid orbitals of identical energy.

a) A hybrid bond is always a sigma bond.

b) A hybrid bond is always stronger than a non-hybrid bond.

c) hybridization \propto overlapping

d) hybridization increases stability.

e) hybridization occurs in the central atom in a molecule.

f) hybridization does not occur in isolated atoms but in bonded atoms.

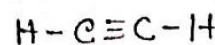
* Types of hybridization:

1. sp - Shape linear

bond angle

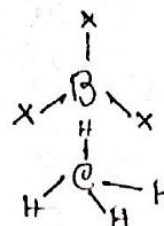
180°

eg.



2. sp^2 - trigonal

120°



3. sp^3 - tetrahedral

$109^\circ 28'$



	Shape	Bond angle	eg.
4. dsp^2 -	Square Planar	90°	$\left[\begin{array}{c} \text{CN}^- \quad \text{CN}^- \\ \quad \\ \text{H} \\ \quad \\ \text{CN}^- \quad \text{CN}^- \end{array} \right]^{2-}$
5. sp^3d -	Trigonal bipyramidal	$90^\circ, 120^\circ$	
6. sp^3d^2 -	Octahedral	90°	
7. sp^3d^3 -	pentagonal bipyramidal	between $90^\circ, 72^\circ$	

* Finding the type of hybridisation:

1. For covalent compounds & ions count the number of valence electrons and (+) charge, to find a particular value (N).

2. Divide N to get quotient X (number of bp electrons) — a) if $N \in (2, 8)$, divide by 2, b) if $N \in (10, 56)$, divide by 8, c) if $N \in (58 \text{ to } \infty)$, divide by 18.

3. If any remainder is left, divide to get quotient Y.

1. If X or $X+Y = 2 = sp$
 $= 3 = sp^2$

$= 4 = sp^3$, $= 5 = sp^3d$, $= 6 = sp^3d^2$, $= 7 = sp^3d^3$.

* Finding geometry of covalent compounds:

a) Total no of electron pair around central atom which gives hybridisation

$$(P) = \frac{1}{2} (V + M - C + A)$$

A → Charge on anion

C → charge on cation

M → no. of monovalent atoms

— no. of electrons in the of central atom.

b) Lone pair = $P - N$

$P \rightarrow$ electron pair around central atom

$N \rightarrow$ number of atoms surrounding central atom or number of bond pair of electrons.

For SO_2 , $P = \frac{1}{2}(6+0-0+0) = 3$ sp^2

$lp = 3 - 2 = 01$

* Hybridization in complexes:

Coordination number of ligand

Hybridization

eg. for $[Fe(CN)_6]^{3-}$
hybridisation is d^2sp^3 .

2

sp

3

sp^2

4

sp^3 or dsp^2

5

sp^3d or dsp^3

6

sp^3d^2 or d^2sp^3

When ligands are weak like H_2O, F, Cl

When ligands are strong like CO, CN, NH_3

* VSEPR Theory (Valence Shell Electron Pair Repulsion Theory): [Nyholm & Gillespie]

a) According to the theory, besides hybridization, the nature of electrons around the central atom also decide the shape of molecule.

b) There may be two types of electrons around the central atom, i.e., bond pair & lone pair.

c) These electrons undergo repulsion & decreasing order of repulsion is $lp-lp > lp-bp > bp-bp$.

d) Due to this repulsion, shape of molecules gets distorted & bond angle changes.

* Molecular Orbital Theory: (Hund & Mulliken).

based on LCAO (Linear combination of atomic orbitals) model.

i) Atomic orbitals undergo linear combination to form same number of molecular orbitals, if they fulfil the following conditions:

a) atomic orbitals must have comparable energies.

b) atomic orbitals must overlap linearly for enough & effective overlapping.

c) atomic orbitals must have same symmetry along with the major molecular axes.

ii) molecular orbitals are formed due to constructive and destructive interference of atomic orbitals.

iii) Constructive interaction of orbitals between orbital lobes having same wave function ψ produces bonding MOs like σ , π , and Δ , these are HOMOs (Highest occupied MOs)

iv. Destructive interaction between atomic orbitals having different sign of Ψ produces antibonding MOs (LUMOs), Lowest unoccupied MOs. eg. σ^* , π^* , d^* .

• Facts related to HOMOs and LUMOs :

a) Energy : LUMOs $>$ HOMOs.

b) Wavelength: LUMOs $<$ HOMOs.

c) LUMOs have nodal planes, HOMOs may or may not have nodal planes.

d) Electrons contribute force of attraction in HOMOs while they contribute repulsion in LUMOs.

e) Like atomic orbitals, MOs also follow Pauli Exclusion Principle, Hund's Rule, Aufbau Principle.

• The MO obtained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals & is called bonding orbital. The MO obtained by subtraction of atomic orbitals is of higher energy & is called an anti-bonding orbital.

• Bond order (B.O.) = $\frac{1}{2} (n_b - n_a)$

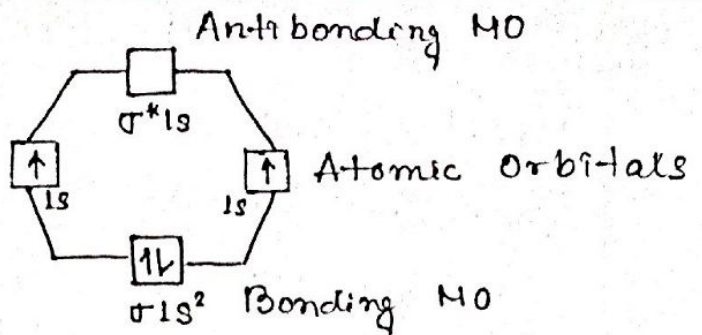
$n_b \rightarrow$ bonding electrons

$n_a \rightarrow$ anti bonding electrons.

- H_2 molecule:

$$BO = \frac{1}{2} (2 - 0) = 1.$$

ENERGY ↑

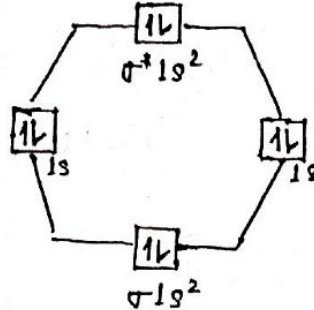


- He_2 molecule:

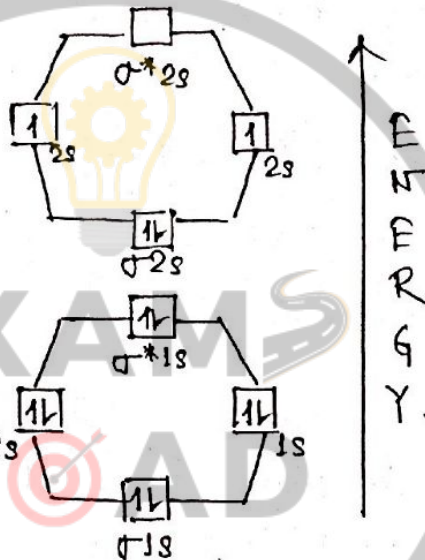
$$BO = \frac{1}{2} (2 - 2) = 0.$$

He_2 doesn't exist, as

$BO = 0$ for He_2 .

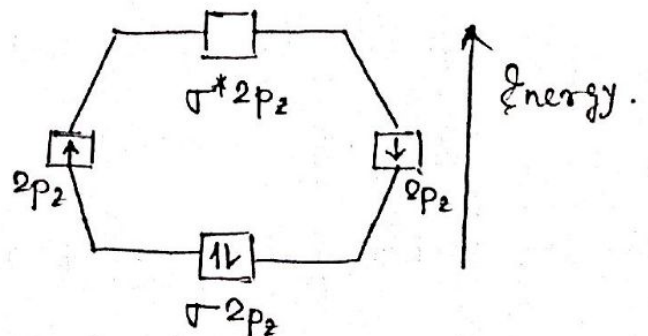


- Li_2 molecule:



• MO Bonding in diatomic molecules of 2nd Period: Atomic orbitals of comparable energies and suitable symmetry (p_z with p_z , p_x with p_x) combine to give MOs.

MO from 2 $2p_z$ orbitals:



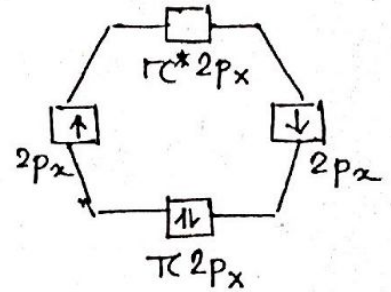
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Chemical Bonding.

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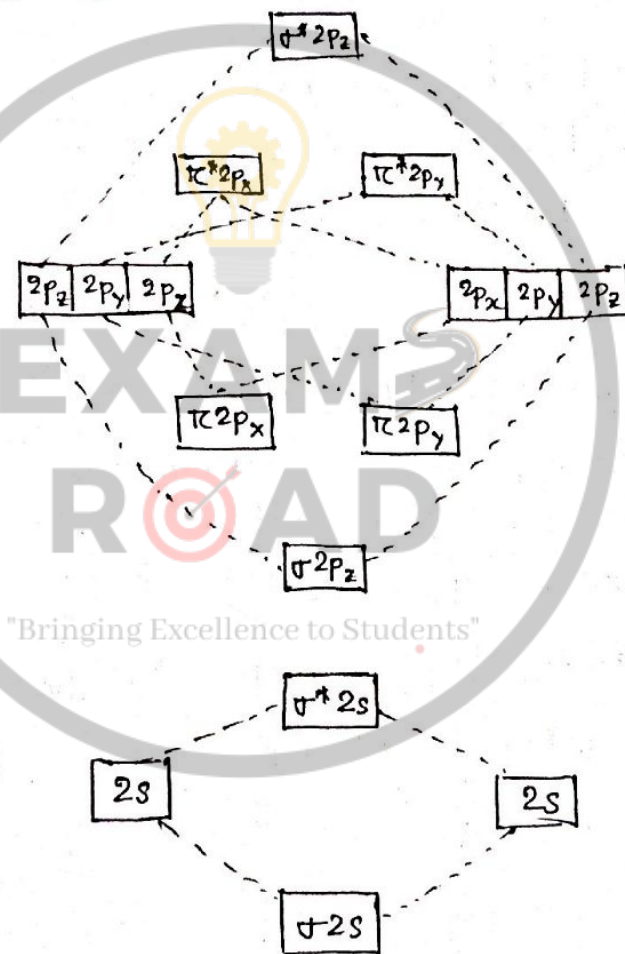
■ p_x orbital will combine with a p_x & the p_y with a p_y . In these cases, MOs are not symmetric around the bond axis.

These MOs are called π -mos.



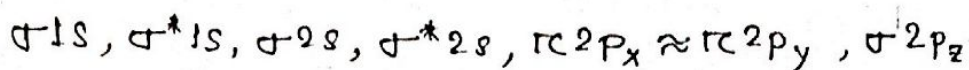
• O_2 & F_2 molecule:

• For diatomic molecules of lighter elements (B, C, N) the energy level diagram is modified as the $2p$ & $2s$ energies are nearly same. So, s & p orbitals get mixed up, eg. $2s$ of first atom can have overlap with $2p_z$.

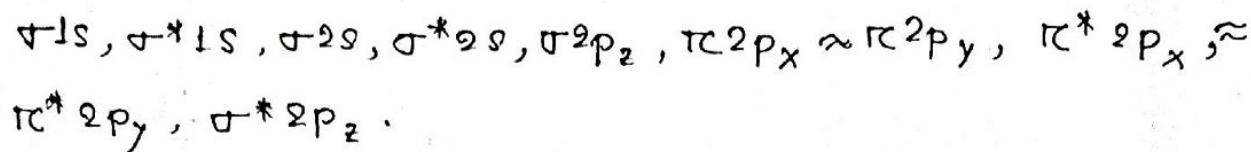


- MO electronic config & properties of molecules:
- a) $BO = \frac{1}{2}(N_b - N_a)$ b) Magnetic nature - If all MOs are doubly occupied the substance is diamagnetic, if MOs are singly occupied (one or more MOs) then paramagnetic.

• MO config of $14 e^-$ (N_2):



• MO config of O_2 molecules ($14 e^-$ or more than $14 e^-$).



• $\sigma 1s$ is the lowest energy Molecular level & $\sigma^* 2p_z$ is the highest.

• BO \propto Bond dissociation energy
 \propto Bond angle
 $\propto 1/\text{Bond length}$.

• All molecules with fractional BO are paramagnetic. Molecules with whole number bond order are diamagnetic (except O_2, B_2, N_2^{2-}).

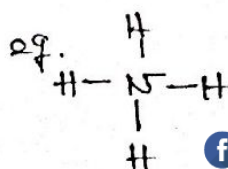
• $\sigma 1s, \sigma 2s, \sigma 2p_z$ do not have any nodal plane; $\sigma^* 1s, \sigma^* 2s, \sigma^* 2p_z, \pi 2p_x, \pi 2p_y$ have one nodal plane; $\pi^* 2p_x, \pi^* 2p_y$ have two nodal planes.

* Formal Charge = $V - N - \frac{1}{2} B$.

$V \rightarrow$ Total no. of valence electrons in free atom

$N \rightarrow$ Total number of lone pair of electrons

$B \rightarrow$ Total no. of shared electrons, i.e. bonded electrons.



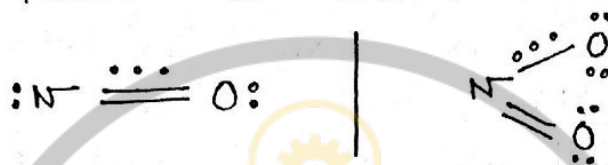
FC on N atom = $5 - 0 - \frac{1}{2} \times 8 = +1$



* Some typical Bonds:

i) Odd electron bond: These include one electron bond & three electron bond. Example of one electron bond is H_2^+ . The bond is half as strong as a shared electron pair bond.

NO & NO_2 are examples of odd molecules having three e bonds.



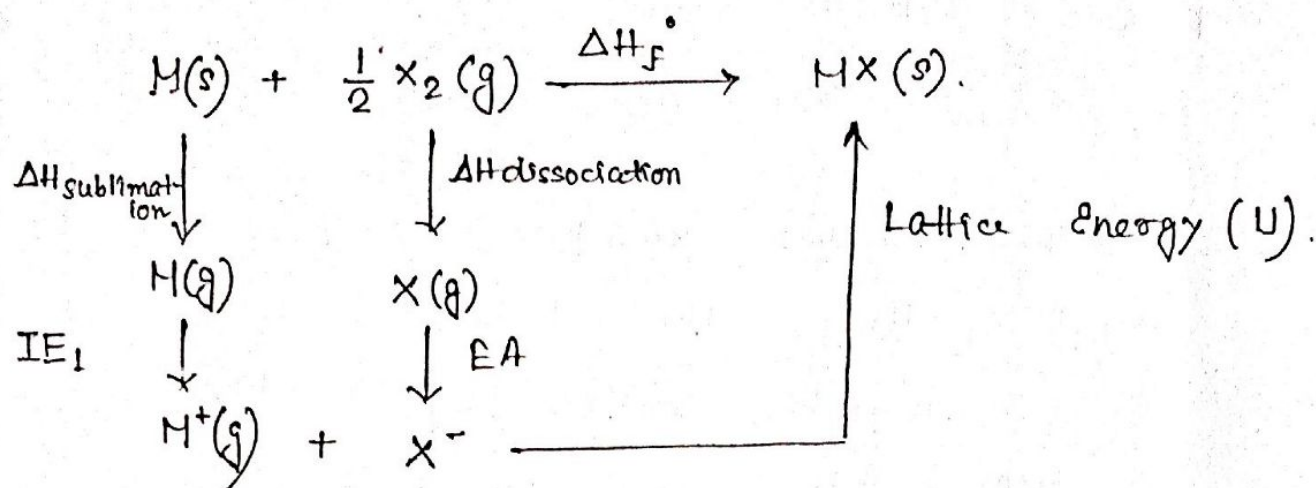
Three electron bond is formed when two atoms have nearly same electronegativity. Fe bonds are also half as strong as a normal bond.

ii) Back bonding: If among the bonded atoms one atom has a vacant orbital & another has excess of e, then a sort of π bonding takes place between the two. If this is between p orbitals of the two, this is p π -p π back bonding.

These bonds are most efficient when the atoms are very small & the orbitals involved of the two are of same energy level.

iii) Banana bond: This structure shows that there are two types of hydrogen atom - terminals & bridging.

* Determination of lattice energy for ionic compounds:



by Hess's Law, $\Delta H_f^\circ = \Delta H_{\text{sub}} + IE_1 + \Delta H_{\text{dis}} + EA + U$

* Rule for determination of total number of hybrid orbitals:

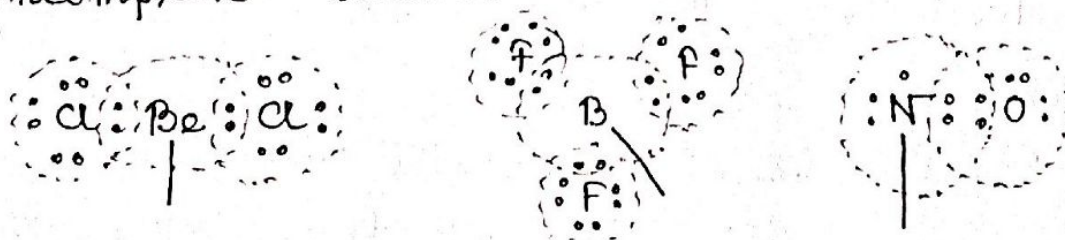
i) Count the number of central atom & peripheral atom's valence electrons. ii) Divide the number by 8. iii) If N is the number, then let $N/8 = 8a + b$. iv) Here, a is the number of σ bonds, b is the number of non-bonding ~~orb~~ electrons.

* Born-Landé Equation:

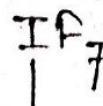
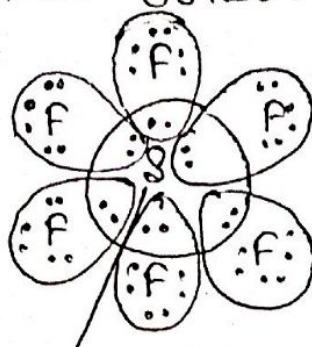
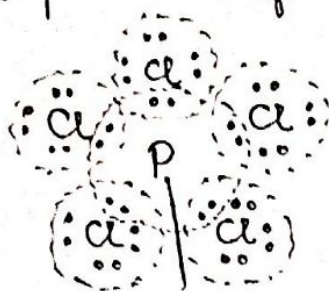
$$\text{Lattice Energy, } U = - \frac{Ae^2 Z_+ Z_- N}{r} \left(1 - \frac{1}{n}\right)$$

$A \rightarrow$ constant, $e \rightarrow$ charge of e , $Z_+, Z_- \rightarrow$ charge of cation, anion, $n \rightarrow$ Born Exponent (generally 9), $r \rightarrow$ distance between cation & anion, $N \rightarrow$ Avogadro no.

* Incomplete Electron Octet:



* Expansion of electron Octet:



Happy Learning :)