GENERAL CHEMISTRY-II

UNIT-I

Chemical bonding

UNIT - 1

CHEMICAL BONDING

Ionic bond:-

* An ionic bond is formed as a Result of the transparents of electrons from one atom from Other

* Element have the tendency to loose one or more eletron are Called electro-positive [Ex:- Alkali metals].

* While those have the tendency to gain electrons are Called electronegative [Ex:- Halogens]

* The formed Cation and anion involued mutual electrostatic attraction between, an ionic (or) electrovalent bond is formed.

Example:

* The anion formed always achieve an innergas Configuration when forming onic bond, while the Cation formed may achieve any of the following configuration:

1. Inert gas configiration [
2. Pseudo Inert gas Configuration [$Ns_2 P_6 B_{10}$]
3. The inert pair configuration (or) 18^{+2} Electron configuration [$N^{-1} S_2 d_{10} Ns^2$]

$Ns^2 P_6 dx$ $2+6+x$

. 9 to 17.

Such type of configuration is very much found in transition metal Cation

5. Irregular configuration

Ex1 Hg_2^{2+} (Hg^+ - Hg^+) etc

Ex2 Ga_2^{4+} (Ga^{2+} - Ga^{2+})

Characteristic of ionic compounds:-

* The Cation and anion the ionic compound are held together by electro-Static line of forces.

* This compound (or) polar. Soluble in polar Solvent Such as: H_2O, NH_3, $CHCl_3$ But insoluble in non-polar Solvent Such as: CCl_4, C_6H_6.

* This are ionizable in Solution are in fused State

* They are good conductors of electricity and high melting and boiling. polar linkages present in ionic bond

Condition for the formation of ionic bond

* Atom gives an electron by absorbing energy equal to its ionization energy and converted into Cation.

* The atom picks up the electron Released by metal and converted into anion.

* In this process, Energy equal to affinity energy [electron affinity] is released.

Example:-

* non-metals

* Halogens

* In this final type, Cation and anion due to electrostatic attraction combain together to give a Stable ionic Crystals.

Ex: C^+a^- Crystals

* In this process energy equal to heat of formation of the ionic compound Is released.

* The formation of Stable ionic compound. to Stable ionic bond the following Condition must be Statisfy

1. The Cation formed atom Should be an electropositive element Such as: Alkali metal (or) Alkali earth metal

2. The anion formed atom Should be an electronegative element Such as: Halogen (or) Element of 6th A group element

3. Since, each ion pair C^+a^-, resulting from transfer of electron and has a Strong Residual electric field. attract other Ion pairs and large no. of ion pair will arrange themself to form most Stable ionic Crystal formed

* In this process further energy released.

Variable ElectroValency :-

* A many transition and non-transition Show variable electrovalency due to the presents of Unstable Configuration.

* Unstable configuration of the Core (or) Kernal.

* If all the Valency electrons from an atom are removed, the residue obtained Is Called **core** (or) Kernal.

* The core Is Stable because it has two or eight electron [Inert gas configuration], while core obtained from a transition metal Unstable.

The following arther the important Unstable configuration of a core of transition metal

(a) configuration varying from $(N-1)S^2p^6d^1$ to $(N-1)S^2p^6d^7$.

For example:

The configuration of ~~$Fe^{2+}(3s^2d^6$~~

$Fe^{2+}(3s^2+d^6) \xrightarrow{-e^-} Fe^{3+}(3s^2p^6d^5$

$Co^{2+}(3s^2p^6d^7 \xrightarrow{-e^-} \overset{3+}{Co}(3s^2p^6d^6)$

Stable

* Fe^{2+} Unstable than Fe^{3+}. Similarly Co^{2+} less Stable than Co^{3+}. But, Co^{3+} ion is less Stable than Fe^{3+} ion due to nuclear Charge in this ion is not Sufficiently strong to keep the electron of the configuration intact in their position.

(b) pseudo inert gas configuration [Eighteen electron configuration]

* This type of configuration found in the Cation formed from the element of I^{st} B and II^{nd} B groups

For example:

$Cu(3s^2p^6d^{10}_4s^1)$, $Cu^+($ $)$: $Cu^{2+}($

$Ag(4s^2p^6d^{10}5s^1)$, $Ag^+($ $)$: $Ag^{2+}($

$Au(5s^2p^6d^{10}6s^1)$; $Au^+($ $)$: $Au^{3+}($

* The monovalent Cation Cu^+ and Au^+ are Unstable due to the presents of Unstable $[N-1\,S^2p^6d^{10}]$ configuration So, these are Readily converted into Cu^{2+} and Au^{2+} ions [More Stable]. It also due to nuclear charge is enof to hold the 18 electrons

* Similary group 2B Zink, Cadmium, Mercury [Zn, Cd, Hg] are formed Zn^{2+} Cd^{2+} Hg^{2+} Here the nuclear charge is higher than Cu^+, Ag^+, Au^+. All the electron in Zn^{2+} Cd^{2+} Hg^{2+}

are more Strongly with hald with the nucleus. which are not involved further Oxidation form higher Oxidation State

INERT PAIR EFFECT:

* The elements of groups IIIA, IVA, VA, VIA are have Variable electro Valency [P-Block element]. In this elements group number Oxidation State [G] is Obtained when all the ns and np electrons are lost is known as group oxidation State In addition to this many heaver p-Block elements like Sn, Pb, Sb, Bi, Te, and po exibute lower oxidation State equal up (G-2). Due to the removal of electron takes places from np and ns electron pair not involved Oxidation, Bonding and Remains inert are Obtain Extra Stability.

* Such a pair of ns electron is Called Inert pair and effect Caused by it known as inert pair effect.

III A	IV A	V A	VI A
(ns^2p^1)	(ns^2p^2)	(ns^2p^3)	(ns^2p^4)
-	-	-	-
-	-	-	-
Ga(+1, +3)	Ge(+2, +4)	-	-
In(+1, +3)	Sn(+2, +4)	Sb(+3, +5)	Te(+4, +6)
Tl(+1, +3)	Pb(+2, +4)	Bi(+3, +5)	Po(+2, +4)

10 M Latice energy: Born - Haber Cycle

$$M_{(s)} + \frac{1}{2} X_{2(g)} \xrightarrow[-(\Delta H_f)MX]{\text{Dired combination}} MX\,(\text{solid})$$

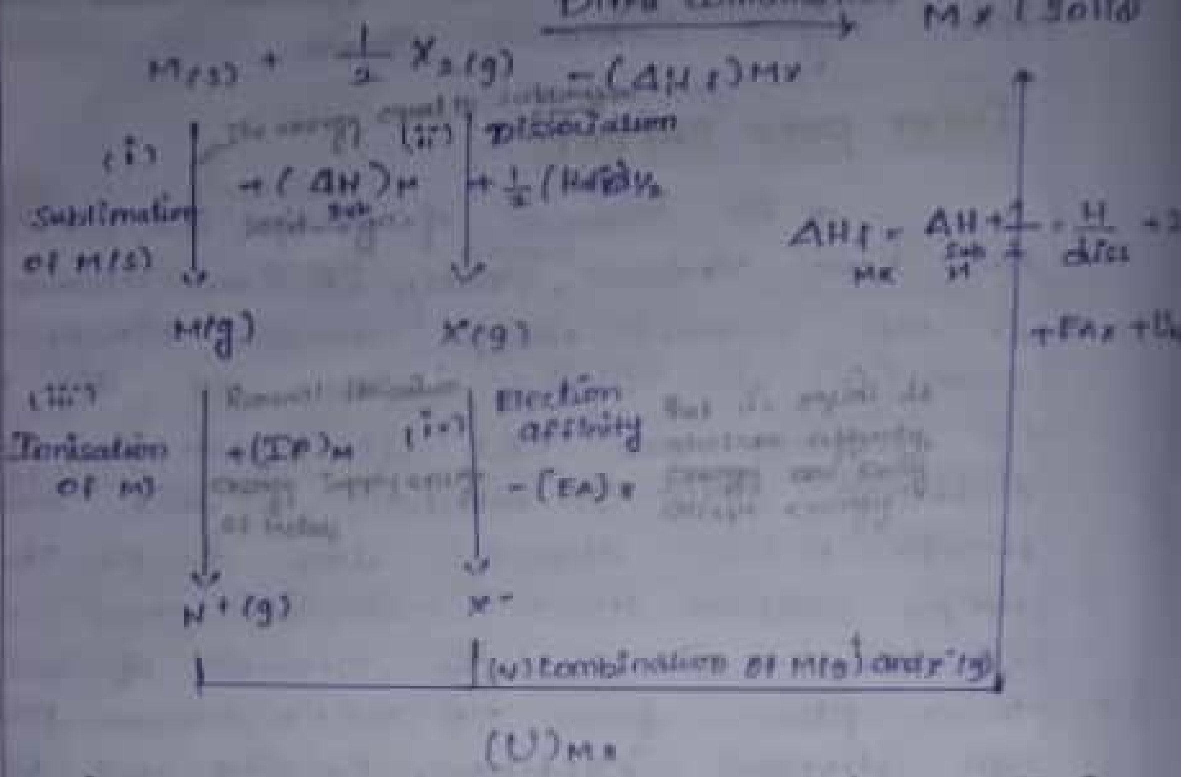


Fig:- Born haber cycle for formation of Ionic Solid Mx.

Lattice energy.

* It is defined as the energy required the remove ions of One gram mole of the Solid ionic Crystals from there equilibrium position in the Crystal to infinity

$M + X^-(s) \longrightarrow M^+(g) + X^-(s)$ (Form the lattice to apply energy)

Ionic lattice Crystal energy required

Experimental determination of LE of an ionic Solid:- To form of a Halogenation

* Lattice energy determined by the process known as born haber cycle devised by born haber in 1919. The Various Step of this process Shown graphically as a cycle.

* This methods is based on the assumption that the formation of 1 mole of Crystalline Mx occurred either by the direct Computation process consist of 5 Steps

(i) Direct Compunation of $M(s)$ and $\frac{1}{2} X_2(g)$

* It is a Single Step reaction and energy equal to the heat of formation of Mx. $\overset{\text{Heat formation}}{(\Delta H\ For)}_{Mx}$. It is Exothermic process the release of energy Shown by negative Sign

(ii) An alternative process:

* This process consist of the following five steps:-

* Sublimation of $M(s)$ to $M(g)$:-

* One mole of Solid absorbs energy equal to Sublimation energy $(\Delta H\ Sub)_m$. It is endothermic process due to absorption of energy Shown by positive Sign.

* Dissociation of $\frac{1}{2}(H_{diss})X_2$:

* In this Step 1/2 mole of $X_2(g)$ absorbs energy equal to 1/2 the dissociation energy of $X_2(g)$. It is Shown by positive Sign.

* Ionisation of $M(g)$ to $M^+(g)$:-

* Each metal gaseous atom absorb energy is equal to its ionisation energy and loses it outermost e⊖ form M^+. It is endothermic process due to absorption of energy Shown by positive sign with $+(IP)_M$ (or) $(IE)_M$.

* Convertion of $X(g)$ to $X^-(g)$:-

* Here $X(g)$ atom accept e⊖ gives on out by metal (M) in step (iii) to form $X^-(g)$ State. In this process energy is released equal to its e⊖ affinity energy $-(EA)_X$ and Shows negative Sign for an exothermic process

* the polarization effect produces covalency in lithium iodide molecule because some electron density in between the nuclei as a sharing of electron in covalent bond. The power of an ion to distort the other ion is known as "polarising power". and the tendency of Ation is known as polari ability.

* The polarising power of Cation is proportional to its charge / radius ration This elluistated

* This results is deformation of electron cloud an anion called the polarisation of anion. Due to small size of Cation, polarization of Cation is not much. Existentive polarization when Cation penitra the anionic electron cloud giving the co-valent bond.

* In a compound consisting of large (-) and small (+), the polarisation leaves to partial covalent character in ionic compound

Example:- of Such ~~Ex~~ ionic compound

$FeCl_3$, $AlCl_3$ etc...

2m **Fajan's Rule:**

* Fajan's Rule's saying that the molecules containing high (+) charge of Cation, high (-) charge of anion. in small Cation (or) large anion (or) covalent in character. Why make containing low positive charge low negative charge of anion, large Cation (or) small anion Show ionic Character.

* The molecules having cation with 18- electron valency shell configuration are more covalent than those having 8- electron [noble gas] valency shell configuration.

Fajan's rule Explanation

* Charge on a cation or anion

The polaring power of a cation to polarize an anion increase with the with increase in its (+) charge due to higher charge can attract electron more efficientively

Example:-

NaCl, $Ngcl_2$, $AlCl_3$

* The polarizing power of the cation increasing in the order $Na^+ > Ng^{2+} > Al_3^+$

* Similarly the polarize ability of anion also increases with the increase in its negative charge Due to anion able to repel its ~~[illegible]~~ outermost electron more effectively

Example

* Fluoris and Oxide of metal cation, O_2^{2-} ion is more polarized F⁻ because it has only one negative charge why O^{2-} has two negative charge. As a result oxide is more covalent than fluoride

Size of the (+) and (-)

* The polarizing power of the cation an anion increases with the decrease of its size

Example :-

* The polarization power of anion is in the order

$$\overset{[\text{High}]}{Be^{2+}} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > \overset{[\text{low}]}{Ra^{2+}}$$

(0.31 Å) (0.99 Å) (1.35 Å) (1.40 Å)

(More Covalent Character)

* The polarize ability of anion increases with increasing in its size

$$F^- < Cl^- < Br^- < I^-$$

(Low polarization) (high polarization ability)

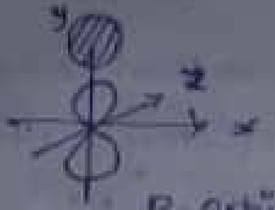
* The large anion is more easyly polarized by cation the outermost cation are farthere from the (+) charge and more loosely attracked by the anion.

* The Cation which 18- electron in its Outermost Shell has greater polarize power to polarize an anion than a Cation with 8- electron Configuration Even if both the Cation Same Size and Charge this is because that d- electrons of ns^2 Sooled the nuclear charge of the Cation less effectively than s and p electrons are ns^2p^6 shell

Example:-

* Cu^+ Cation has greater polarizing power to polarize Cl^- anion then Na^+ Cation Seen NaCl

S-P Overlap:-



P-Orbital

Strength of bond
$s \times p$
$= 1 \times \sqrt{3}$
$= 1 \times 1.732$
$= 1.732.$

* To explain the concept of covalent bond, the two important theorys used to explain covalent bonds are formed between atom, how the electron are arranged in a space in molecule, how that sharing of electron would explain the of moleculesetc...

* Developments in wave mechanic have lead to 2 theorys of chemical bonding

1. Valence Bond Theory [VBT]
2. Molecular Orbital Theory [MOT]

5 M

Valence Bond Theory [VBT]

* This theory was propased by heitler and london, was modified by pauli and Slater In 1931 to account for the formation and directional properties of covalent bond.

* Since, according pauli's Slater theory, covalent bond is obtain, when the atomic atomic valence shell containing to only of the overlap together, these theory is also called orbital overlap theory

Postulates:-

* This theory explain the formation and directional characterist of covalent bond.

* A covalent bond is formed by a overlap of pure atomic orbital atom between a bond is present

* A overlap is takeplace only between atomic orbital of valence shell

each atom contain unpaired electron opposite space.

* If the spins of electron are parallel due to repulsion tendency the [++] the energy of the system and become unstable [no covalent bond formed]

* The atomic orbitals involved in the valency shell of the atoms have paired electron [completely filled orbital] do not praticipate in overlapping and its not contribute to the bond formation.

* The electron pairs in the orbital are called non-bonding orbital electrons (or) loan pair electrons.

* The orbitals overlapping together together the same symmetry [orientation]

* Greater is the extend of overlapping between the atomic orbital greater is the strength of the resulten in the covalent bond

Eg: * s-s overlap is relative weak due to the s-orbital have spherical distribution of

* Covalent bond d-p orbitals are relatively stronger due to p-orbital concentrated in a prabicular direction and there lobe on larger than radius of s-orbital.

* The relative strength of Covalen bond

* Overlapping between atomic orbital increases the electron density in the reagent between the nuclei of the ombining atoms, which holds the two tom together and a bond is formed.

* Covalent bonds have directional roperties because overlapping orbitals have the greatest electron density by their overlapping are also directed towards the z axis that is p- orbital

* Energy is released when a covalent ond is formed. This energy used to unpair the paired electrons by transferin the Vacant orbitals have slighly high energy and present in the Same main energy level

For example :-

* In PCl_5 molecule the 5pcl covalent bond are formed by this process So propose atom for penta (5) covalency

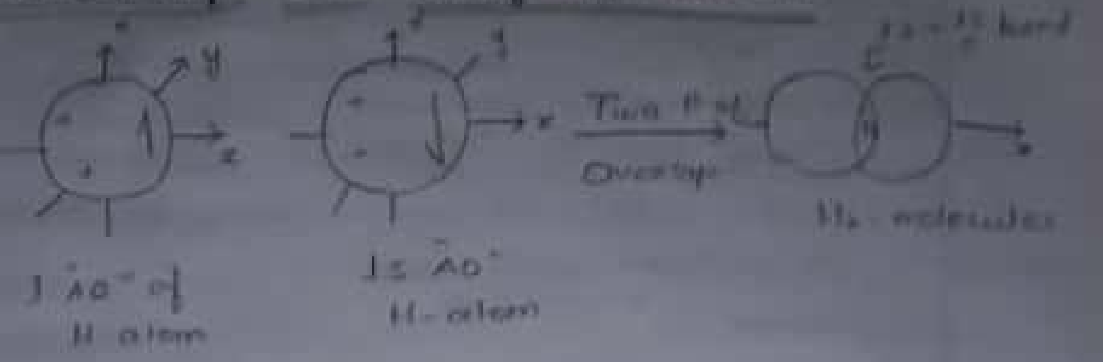
* Depending on the overlap together. two type of covalent bond are formed :-

1. Sigma covalent bond
2. pi covalent bond

* The atom are atomic orbital overlap together to form covalent bond do not lose there individual identity of atom

* According to this theory, an electron moves under the influence of only one nuclear of an atom and resonance also places important role

(i) S-S overlap and Str of H_2 molecule



* 1s atomic orbitals of 2 Hydrogen atoms in a hydrogen molecules overlap with eachother and gave a co-valent bond between them

(ii) P_x-P_x overlap and Str of X_2 molecules:

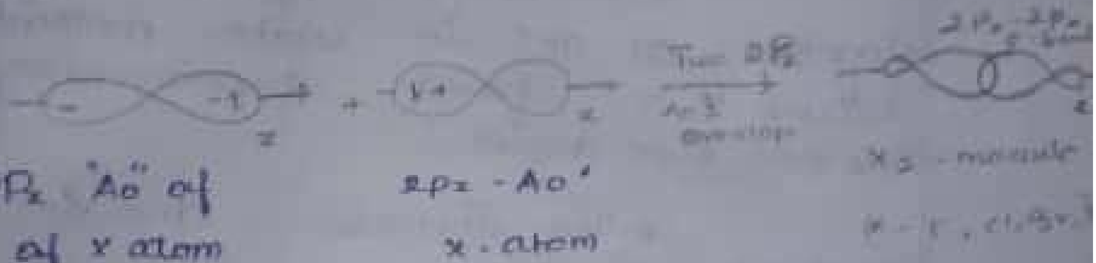
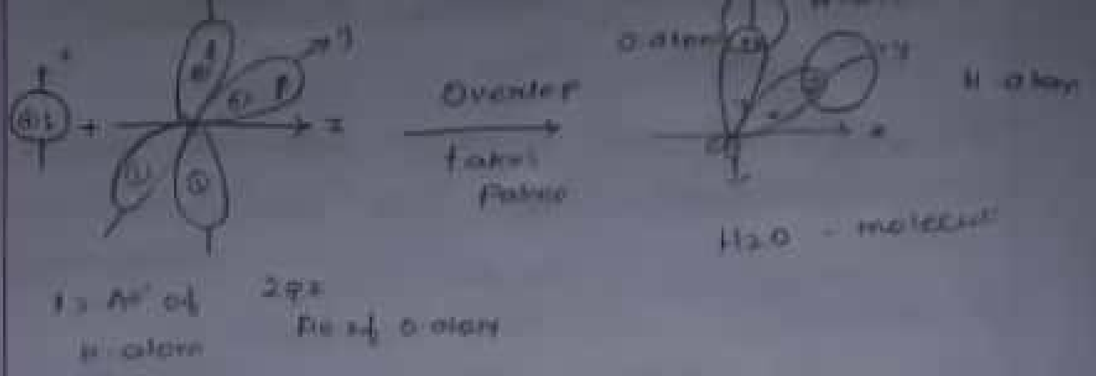


Fig:. Formation of x-molecules.

* The bonding X_2 molecule formed by the overlap of 2px - AO's and is linearly directed along the x-axis.

(iii) S-Px Overlap in hx molecules

This bond also formed by the one 1s AO of hydrogen atom with 2pz AO Overlap of 1s AO of hydrogen atom with 2p z AO of x - atom both AO's Single Oxpide fig:3



* Water molecule a 2 AO's Px-Py have Unpaired Electrons in Oxygen atom Overlap with two 1s Orbital of 2 hydrogen atom and two sp S-P σ bond are formed.

* Since 2Px-2Py are Right angle together at 90° in water molecule, but actual H-O found experimentally One less five degree

* The increase due to mutual Electrostatic repulsion the 2 H's positive atom.

π - bond

* Covalent bond formed by between 2 atom by Overlap of atom along a line molecular axis [Side to Side] is Called π-bond

Ex O_2 molecule, N_2 molecule

Sr σ vs π bond

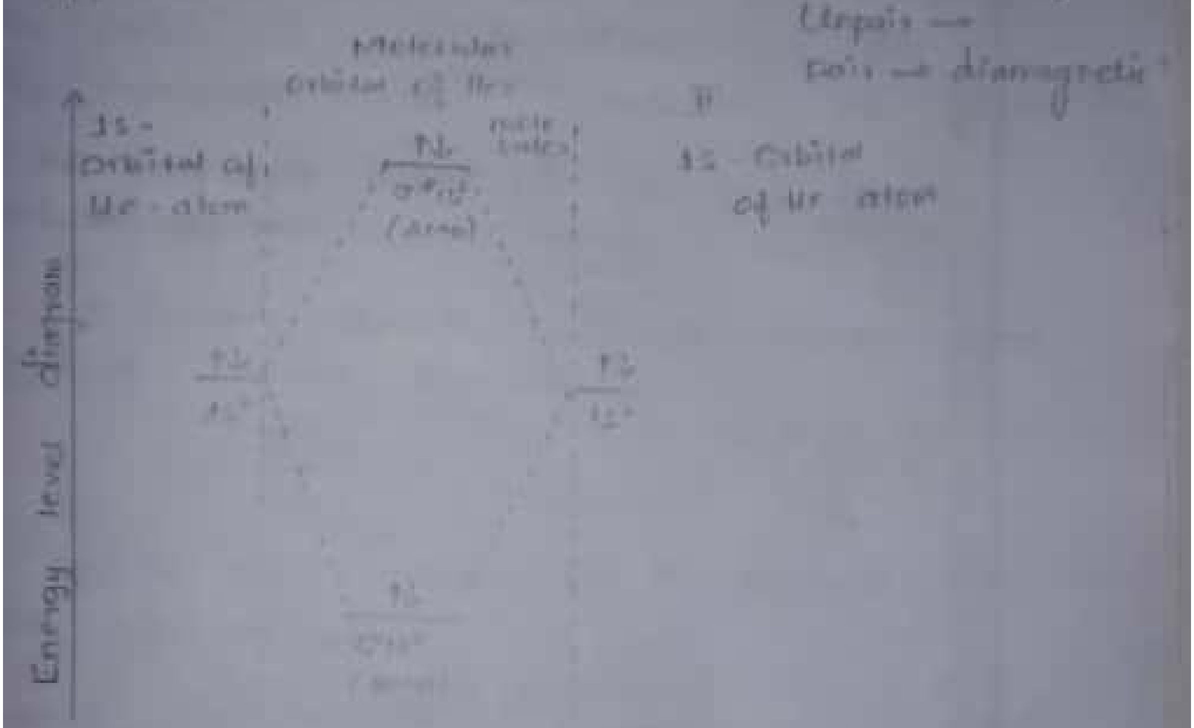
* σ bond is formed by Overlap of Orbital 'along their bond' [head to head] overlap, while π bond result from [Side to Side perpendicular axis]

* Sigma bond is Stronger due to extend of Overlapping along the x-axis

MO diagram for helium Molecule:

* Helium atoms have the configuration $1s^2$ for the formation of He_2 molecule, the MO's required as $\sigma 1s$ and $\sigma^* 1s$ which have to accomodate for $e^\ominus$ ($2e^\ominus$ each contributed by each helium atom). Each one of these MO's would accomodate $2e^\ominus$ has shown below figure.

$He_2 = 1s^2$



MO diagram of Helium molecule:-

* The molecule of He is represented by equation:

$$2\,He\,(1s^2) \rightarrow He_2\,[\sigma(1s^2)\,\sigma^*(1s^2)]$$

Sequence of energy of MO's = $\sigma 1s^2 < \sigma^* 1s^2$

Bond Order

* The B.O of He_2 molecule is = $\frac{1}{2}(nb - na)$

$$= \frac{1}{2}(2-2)$$

$$= \frac{1}{2}(0)$$

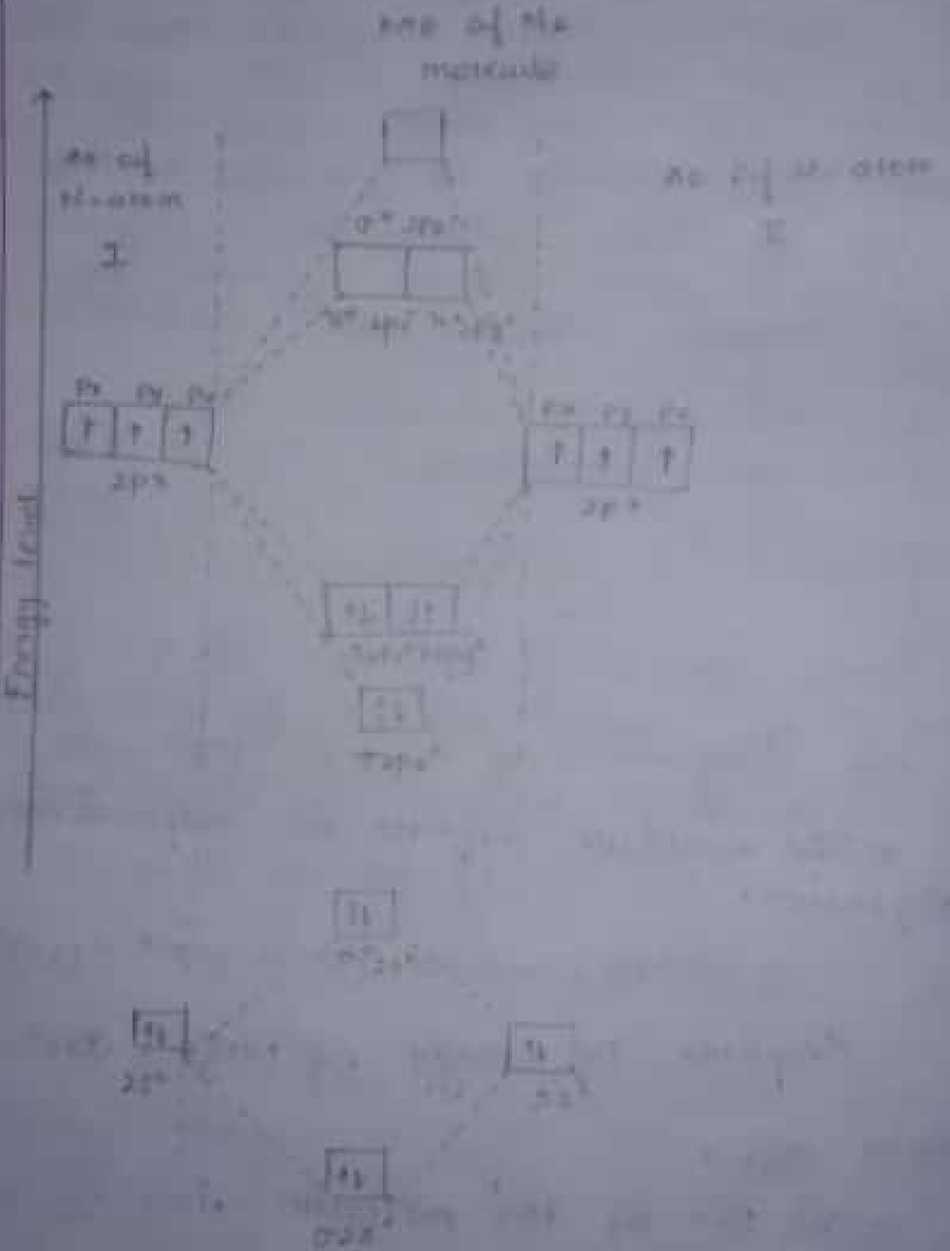
$$= 0$$

* The BO of He₂ molecule is zero. So, the No. of bonds b/w 2He atoms is zero. So this He molecule doesn't exist from the molecular orbital diagram.

MO of N² molecule:-

(N=7)

* Electronic configuration of N= $1S^2\ 2S^2\ 2p$



Bond Order = $\frac{1}{2}(N_b - N_a)$

= $\frac{1}{2}(8-2)$

= $\frac{1}{2}(6)$

= 3

* Each of the two N-atom contributes 5 valence $e^{\ominus}$ and 4 atomic orbitals towards the molecule. The molecule would have 8 MO's and 10 $e^{\ominus}$ to be accomulated. The electronic configuration of the N_2 molecule, is represent in figure (5)

* There are 8 $e^{\ominus}$ in the BMO and antibonding MO

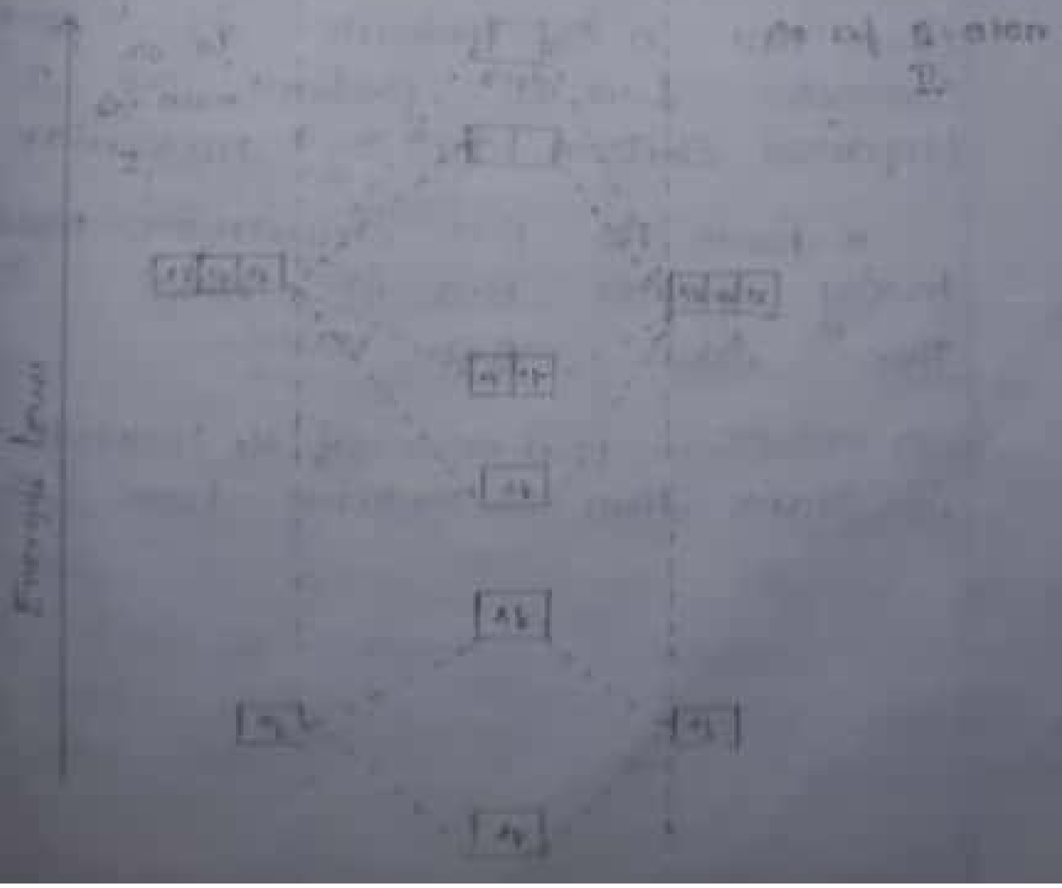
* From the B.O the 3-covalent bond present in the N_2 molecule

$N \equiv N$ → 1 σ bond (middle)

2 π bond

* The N_2 molecule is diamagnetic due to no unpaired $e^{\ominus}$.

MO of O_2 molecule



* The Oxygen molecules electronic configuration $1s^2\ 2s^2\ 2p_x, 2p_y, 2p_z$ with 8 electrons thus in O_2 molecule have 16 electrons to be accumulated among this the valency electrons occupied (MO) of O_2 molecules are 12 electrons.

* The molecular orbital configuration of O_2 is: $\sigma 2s(2)\ \sigma_{2s}^{*(2)}, (\pi_x{}^{b})^2 = (\pi_y{}^{b})^2, (\sigma_{zp})^2$

Bond order:-

* Bond order $= \frac{1}{2}(n_b - n_a)$

$$= 1/2(8-4)$$
$$= 1/2(4)$$
$$= 2$$

* Thus O_2 molecules consist of double bond which is consist of 1 and 2 bond. It has bond desociation 1.1.8

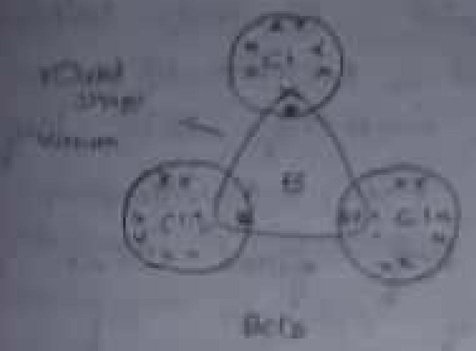
The MOB diagram show that a O_2 molecule is paramagneti character. Due du present of 2-unpaired electron πx^* πy^* molecular Orbital

* From the B.O calculation, Molecules having greater B.O is more stable than less B.O value.

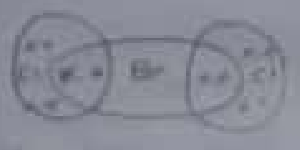
For example:- Bond order of N_2 molecule = 3 is Stable than O_2 molecule have B.O = 2

Hybridization of Atomic Orbital

1) B → $1s^2 2s^2 2p^1$ Valence electron = 3



2) $BeCl_2$ → $1s^2 2s^2$ Valence electron = 2



(3) NH_3

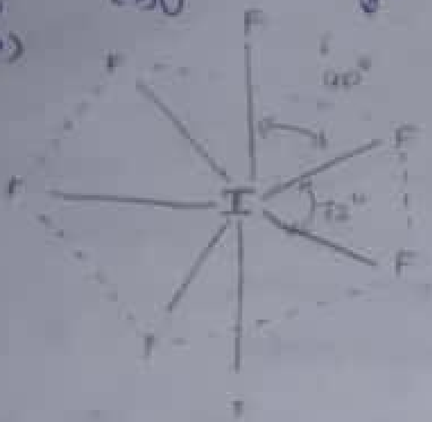
4) PCl_5

Hybridisation : (rules)

* Hybridisation → In Order to account for the equivalents of covalent bond in particular molecular the unequalent energy of the orbitals are mixed (or) hybridised together to form equivalent hybrid orbitals of same in energy. This type of mixing of pure A.O to give equal amount of hybrid orbital is called hybridisation

* The lewis Structure of this molecule has central Sulphur centre atom Surrounded by 6σ-BPs and no lps. The SF_6 molecules have any of the 3 structure ["planar hexagonal geomentry, trigonal prismatic geomentry, Octa hedral geomentry. Out of this Structions Octa hydral Structure is most Stable due to minimum Bp-Bp repultion at 90°. Each of F-S-F bond angle - 90°. So, SF_6 molecules have Octa hedral geomentry

IF_7 [Pentagonal bipyramidal molecule]
[5]
(AB_7)
(Sp^3d^3)



Sp^3d^3 hybridisation

* IF_7 molecule is the example of AB_7 type. The lewis Structure of this molecule has I- central atom, which is Surrounded by 7σ-BPs and no lp. According to VSEPR theory, this molecule has pentagonal bipermidal geomentry figure (IF_7)

* In this figure the axial IF distances are not Same as equivatorial IF - distanceses The bond angle b/w central atom and fluorine have 72° and 90° due to minimum bond pair-bond pair repultion.

H_2O [AB_2 (lp_2)] σBPs = 2 , lps = 2

Other Example }

SCl_2 , $SeCl_2$, NH_2^- , ICl_2^+

Other Samples

SCl_2 , $SeCl_2$,

NH_2 , ICl_2

* The Lewis Structure of water molecule Shows that the central Oxygen atom is Surrounded by 4 electron pair [σBPS = 2] [σ lps = 2]. The Spacial Orientation of 4 electron pairs around Oxygen atom is tetrahedral according to VSEPR Theory.

* Due to the presence of two lps located at the 2 - tetrahedral position. the space of H_2O molecule gets distrated from tetrahedral Shape and becomes angular Shape [V-shape (or) bend shape] Becomes as Shown in figure.

* H-O-H bond angle is not equal to expected tetrahedral angle [equal to 109.5°] rather this angle = 105.5°.

* According to VSEPRT the magnitude of the repulsion between lp-lp is maximum. The 2 lps on an Oxygen atom repel each other but also repel the 2 BPs and this result the H-O-H bond decreases.

XeF_6 (AB_6 (lp)) (or) pentagonal bi-piram

($\sigma Bp = 6$), $lp = 1$

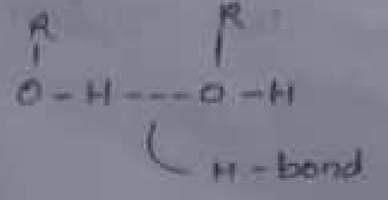
* The Central ~~gent~~ Xe atom have 7 sp^3d^3 hybrid orbitals, among these One loan pair occupy One of the sp^3d^3 hybrid orbitals.

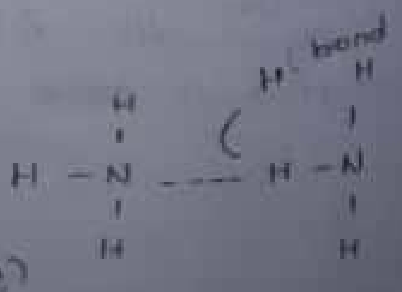
* The Singly filled hybrid orbital overlap with $2p_z$ atomic orbital of 6-fluorine atoms to form 6σ bond.

* According to VSEPR Theory the XeF_6 has pentagonal-bipyramidal (or) distracted octahedral structure with 1 loan pair retaining One of the hybrid orbital at axial position.

* The bond angle due to repulsion between lp-Bp the ~~ax~~ axial bond angle ~~XeF_6~~ F-Xe-F the equatorial bond angle 72°

Hydrogen bonding:





KMnO4

Ca(II)

copper(II)

Mg(II)

Types of Hydrogen bonds

There are two different types of Hydrogen bonds as:

(i) Intermolecular hydrogen bonding:

* This type of bond is formed between the two molecules of the Same or different compounds. Some examples of the compounds exhibiting intermolecules hydrogen bonds are:

1. Hydrogen fluoride, $\overset{\delta+}{H}-\overset{\delta-}{F}$.

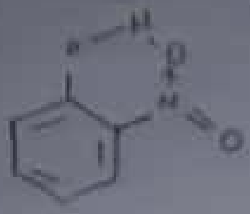
* In the Solid State, hydrogen floride consists of long zig-zag chains of molecules associated by hydrogen bond as shown below.

Therefore, hydrogen fluride is Represent as $(HF)_n$

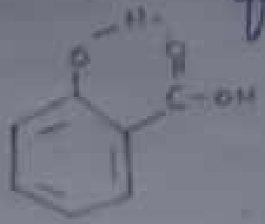
(ii) Intramolecular hydrogen bonding.

* This type of bond is formed between hydrogen atom and and N, O or F atom of the Same molecules. This types of hydrogen bonding is commonly called Chelation and is more frequently found in Organic Compound.

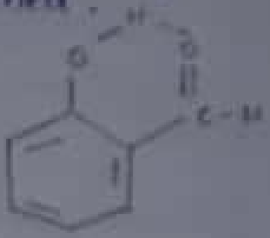
Intramolecular hydrogen bonding is possible when a Six or five membered Can be formed.



O-Nitrophenol



Salicylic Acid



Salicylaldehyde