

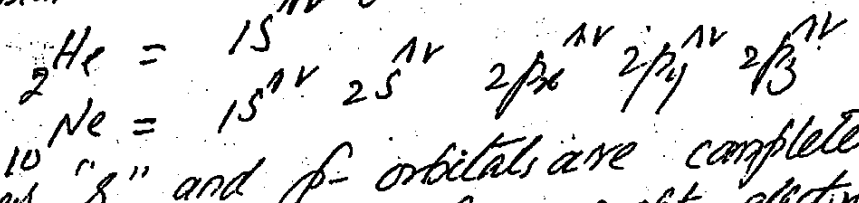
CHAPTER NO. 6

WHAT IS A CHEMICAL BOND? WHAT IS THE CAUSE OF CHEMICAL COMBINATION.

ANS.: BOND:- A chemical bond is the force which holds two or more atoms together to form a large variety of chemical compounds. It is called A BOND. The shape of a molecule also depends upon number and nature of bonds.

CAUSE OF CHEMICAL COMBINATION:- The chemical reactivity of an element depends upon its electronic configuration.

NOBLE GASES Noble gases (He, Ne, Ar, Kr, Xe, Rn) are quite inert and stable. They do not react with one another or with other elements. There are very few stable compounds of noble gases. Like XeF<sub>2</sub>, XeOF<sub>2</sub>, KrF<sub>2</sub>, XeO<sub>3</sub> etc. Their low chemical reactivity and high stability could be explained in terms of their electronic configuration.



Except "s" and p-orbitals are completely filled. Except "He" all noble gases have eight electrons in outer-most shell.

All other elements try to acquire noble gas configuration. For this purpose they gain lose or share electrons. The number of electrons gained lost or shared by an element to acquire noble gas configuration is called its VALENCY.

Some elements can acquire noble gas configuration by both gaining and losing electrons depending upon conditions.

For example "H" when combines with Sodium gains one electron to acquire noble gas configuration of "He".  
 $\text{Na} + \frac{1}{2}\text{H}_2 \longrightarrow \text{Na}^+\text{H}^-$   
However in HF it loses "e<sup>-</sup>" and form H<sup>+</sup> ion.

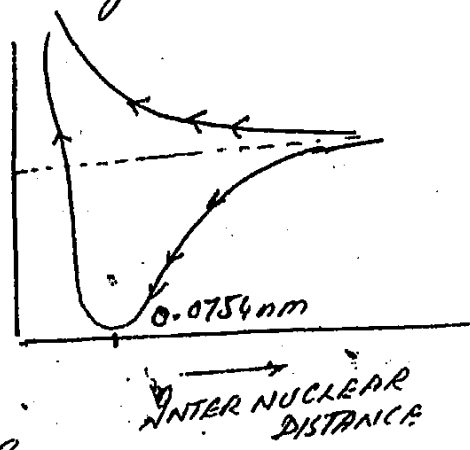
However some elements do not acquire noble gas configuration even after formation of bond. For example  $\text{BF}_3$ ,  $\text{PF}_5$ ,  $\text{SF}_6$ ,  $\text{BeCl}_2$  etc.

### ENERGETICS OF BOND FORMATION:-

According to Modern concept, energy decreases during bond formation. For example when two hydrogen atoms come close to each other both attractions and repulsions are produced

ATTRACTIVE FORCES tend to bring two atoms together and potential energy decreases.

REPULSIVE FORCES tend to push atoms apart and potential energy increases. It has been observed that effect of attractive forces is more pronounced and energy is released during bond formation.



At distance of 0.0754 nm the effect of attractive forces is much more pronounced. The energy is minimum at this distance. It is called bond length. If atoms are brought further close, they begin to repel each other and energy increases. Thus bond is broken. If repulsive forces dominate attractive forces, energy of system increases and no bond is formed.

### ATOMIC SIZE AND ITS PERIODICITY.

Many physical and chemical properties are related with sizes of atoms. Atoms are considered to be spherical. The size of atom is generally expressed in terms of its radius.

Atomic Radius. The average distance between nucleus and outermost electronic shell is called ATOMIC RADIUS. It is generally expressed in Angstrom units.

due to two reasons.

"1" There is no sharp boundary of an atom. The probability of finding electron is never zero even at large distance from nucleus.

"2" The distance of electron from nucleus is affected by neighbouring atoms. Thus size of atom may change from one compound to another.

Thus sizes of atoms are expressed in terms of Atomic Radii, Ionic Radii or Covalent Radii depending upon type of compound used for its measurement.

**DETERMINATION:** - These are measured by measuring distance between adjacent atoms by using X-Rays or by spectroscopic measurements.

**PERIODICITY:** Atomic radii increase down the group in periodic table and decrease as we proceed from left to right in a period.

The increase in size down the group is due to the fact that number of shells go on increasing down the group. Further shielding effect increases down the group. Thus attraction on outermost electron decreases and Atomic radius increases.

In a period number of shells remain the same but nuclear charge increases as we proceed from left to right in a period. Thus atomic size decreases.

**IONIC RADII** The species formed by gain or loss of electron from ~~an~~ an atom is called Ion. These are considered to be spherical. The distance between nucleus and outermost shell of an ion is called Ionic Radius. The radius of positive ion is always smaller than corresponding atom and radius of negative ion is always larger than corresponding atom.

For example radius of "Na" Atom = (186 pm)

Radius of Na<sup>+</sup> ion = (95 pm)

Radius of chlorine Atom = 99 pm

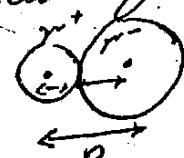
" " " Cl<sup>-</sup> ion = 181 pm

The radius of dipositive ion is smaller than unipositive ion due to increase in effective nuclear charge. The no. of e<sup>-</sup> are decreased during positive ion formation and nucleus attracts remaining electrons more powerfully

due to increase in electron-electron repulsions, due to increase in number of electrons in valence shell.

Let us a positive and negative ion which are held together due to electrostatic forces of attraction in a crystal lattice.

R = r<sup>+</sup> + r<sup>-ve</sup>

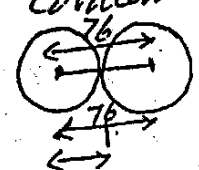


Pauling determined distance "R" between K<sup>+</sup> ions and Cl<sup>-</sup> ions and found that this distance is equal to radius of Cl<sup>-</sup> ion plus radius of K<sup>+</sup>

R = r<sup>+</sup> + r<sup>-ve</sup>  
R = 133 + 181 pm = 314 pm

This ionic radius is an additive property. If we have radius of positive ion say K<sup>+</sup> we can determine radius of negative ion R - r<sup>+</sup> = r<sup>-ve</sup>

COVALENT RADIUS: One half of the distance between centres of two atoms bonded by a single covalent bond is called covalent radius. For example when two hydrogen atoms are bonded by a single covalent bond distance between their centres is 78 pm. Thus covalent radius of hydrogen is = 78 / 2 = 36 pm.



78 pm / 2 = Covalent Radius of H.

Covalent radius of one atom can be used to determine the covalent radius of other atom. For example experimentally determined bond length of C-Cl is 176.7 pm in  $\text{CH}_3\text{-Cl}$ . The covalent radius of Cl is known to be 99.4 pm. Thus covalent radius of carbon could be calculated as:-

$$\text{Bond length} = r_{\text{carbon}} + r_{\text{chlorine}}$$

$$176.7 = r_{\text{carbon}} + 99.4$$

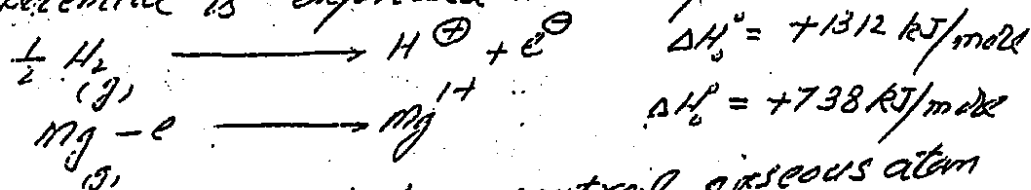
$$176.7 - 99.4 = r_{\text{carbon}}$$

$$77.3 \text{ pm} = r_{\text{carbon}}$$

## WHAT IS IONIZATION POTENTIAL? DISCUSS ITS PERIODICITY.

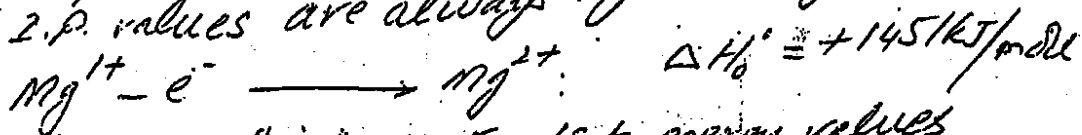
Ans. The minimum amount of energy required to remove most loosely bound electron from an atom <sup>in gaseous form</sup> to produce a unipositive ion is called ionization potential or ionization energy.

Ionization potential is expressed in kJ/mole units



If one electron is removed from neutral gaseous atom to produce unipositive ion it is called First I.P.

If second electron is removed from unipositive ion to produce dipositive ion it is called 2nd I.P. Second and third I.P. values are always higher than first I.P.



NOTE: Subscript zero " $H_0$ " indicates that energy values has been expressed in kJ/mole at  $0^{\circ}C$ .

FACTORS AFFECTING I.P. // The ionization potential depends upon following factors.

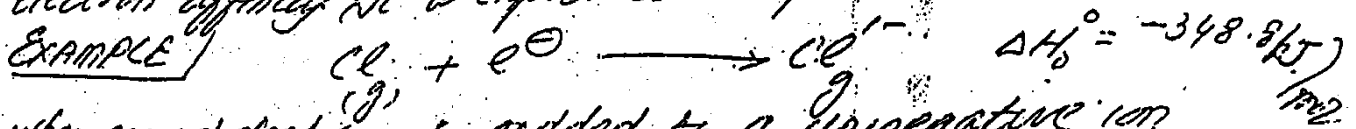
- (1) The magnitude of nuclear charge.
- (2) The distance of outermost electron from nucleus (atomic radius)
- (3) The shielding effect of underlying shells of electrons.
- (4) The degree of penetration

## PERIODICITY OF IONIZATION POTENTIAL

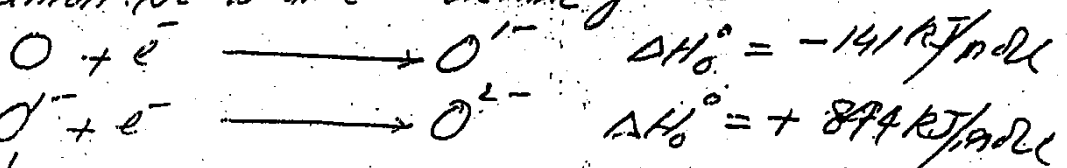
Ionization potential decreases down the group and increases left to right in a period. The decrease in ionization potential down the group is due to the fact that atomic size increases down the group. Each step downwards in a group, number of shells are increased (thus atomic size and shielding effect increases & I.P. decreases). In a PERIOD, number of shells remain constant but nuclear charge increases left to right. Due to increase in nuclear charge, atomic size decreases and ionization increases left to right in a period. The element with max. I.P. is present top right side (Helium) and with minimum I.P. is present at left side at bottom of group Fr.

# ELECTRON AFFINITY & ITS PERIODICITY

DEFINITION The minimum energy released when an electron is absorbed in lowest energy state of an isolated atom in gaseous state to form an anion is called electron affinity. It is expressed in kJ/mole units.



When second electron is added to a uninegative ion to form a dinegative ion, energy is absorbed because electron is repelled by -ve charge already present on anion. It is an endothermic process.



PERIODICITY Electron affinity decreases down the group (lighter to heavier elements in group) while it increases as we proceed from left to right in a period. Down the group number of shells increase and nuclear charge increases but number of shells remain the same.

Representative elements of each group, i.e. Li, Be, B, C, N, O, F have lower electron affinities than next members of group. This is due to the fact that incoming electron is repelled by electrons already present in outermost shell. This effect is especially high for smaller atoms of second period.

Second and third electron affinities always (negative in sign) endothermic because incoming electron is repelled by negative charge already present on atom. It is difficult to calculate electron affinities directly by experiments. These are mostly determined by indirect method. However in some cases these have been determined experimentally.

WRITE A NOTE ON ELECTRONEGATIVITY? (E.N.)

DEFINITION: The power of an atom to attract shared electron pair to itself is called electronegativity. When a covalent bond is formed between two dissimilar atoms one atom attracts the shared electron pair more forcefully than other. Thus one atom acquires partial negative charge and other acquires partial positive charge. Such a bond is called POLAR BOND. For example in  $H-\overset{\ominus}{C}l$  bond chlorine being more electronegative than hydrogen, acquires partial negative charge.

Millican defined electronegativity as average of I.P and E.A. values Pauling assigned each element an arbitrary value of E.N. Fluorine has E.N=4 and Cesium and Francium = 0.7.

Electronegativity values are derived from bond energy data. The bond between two dissimilar atoms is always stronger than a bond between two similar atoms.

FACTORS AFFECTING E.N | Electronegativity depends upon following factors:

- (i) ATOMIC SIZE
  - (ii) NATURE OF COMPARING ATOMS
  - (iii) ATOMIC NO.
  - (iv) I.P.
  - (v) ELECTRON AFFINITIES
  - (vi) PERIODICITY
- Electronegativity decreases down the group and increases left to right in a period. The most E.N. elements are non-metals or left at upper right side of periodic table (F = 4, Cl = 3.0, Br = 2.5). The alkali metals I.A group are least E.N. with Fr = 0.7 has minimum E.N.

USEFULNESS OF E.N | The electronegativity data help to determine nature of bond in a molecule. If  $\Delta E.N$  is greater than 1.7 the bond is ionic. If  $\Delta E.N$  is less than 1.7 the bond is covalent but it may have some ionic character of covalent bond. If  $\Delta E.N = 0.0$  the bond is pure covalent bond. For example NaCl ( $\Delta E.N = 2.1$ ) is ionic compound while H-Cl ( $\Delta E.N = 0.9$ ) is a covalent compound with some ionic character.



**WHAT ARE DIFFERENT TYPES OF CHEMICAL BONDS? EXPLAIN EACH ONE OF THEM.**

Chemical bond can be classified as (i) Ionic bond (ii) Covalent bond (iii) Co-ordinate Covalent Bond.

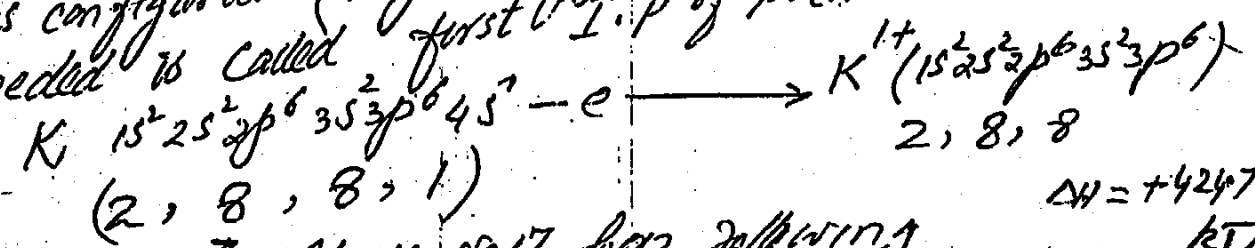
Let us explain these bonds on the basis of different theories.

**LEWIS THEORY:** Lewis theory can explain formation of ionic covalent and co-ordinate covalent bond formation.

**IONIC BOND:** According to Lewis Theory, "Ionic bond is formed by COMPLETE TRANSFER OF ELECTRON FROM ONE ATOM TO ANOTHER." The atom which loses electron has low I.P. and atom which gains electron has high E.A. The element which loses electron and acquires +ve charge and element which gains electron acquires negative charge.

It is considered that electropositive elements are at high energy state than electronegative elements. The difference of energies is responsible for flow of  $e^-$  from higher energy state to low energy state.

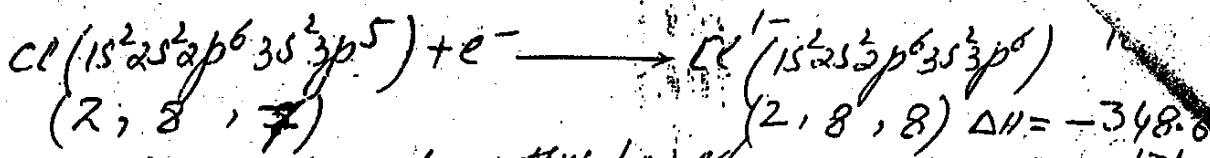
**FORMATION OF KCl:** Potassium has atomic number 19. It has following electronic configuration. It loses one electron from outermost shell to acquire noble gas configuration (Argon Configuration). The energy needed is called first I.P. of potassium.



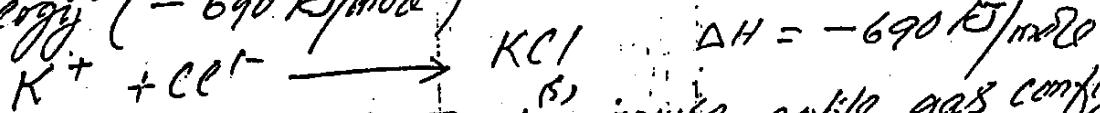
Chlorine with Atomic no 17 has following electronic configuration. It gains one electron to acquire noble gas configuration. The energy released in this process is called E.A. of chlorine. Chlorine also acquire configuration of Argon.

$\Delta H = +4247$

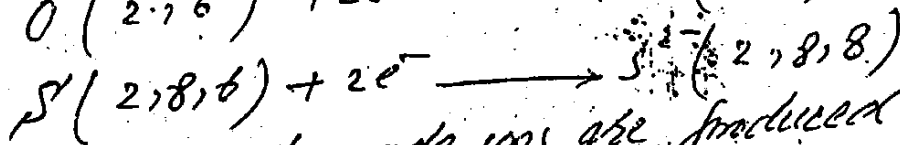
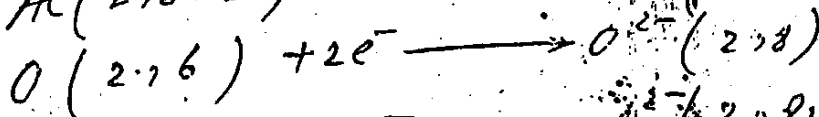
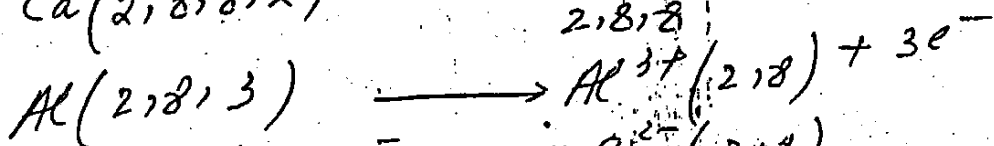
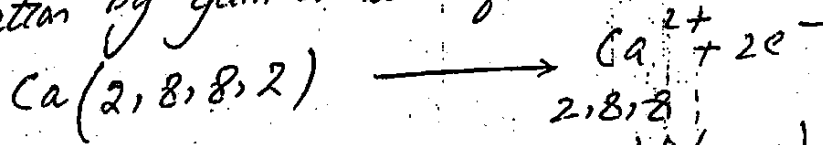
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3:- The oppositely charged ions thus formed attract each other and form crystal lattice. The energy released in this process is called lattice energy (-690 kJ/mole)



Some other elements which acquire noble gas configuration by gain or loss of electron are given below:



Since  $\text{Ca}^{2+}$  and oxide ions are produced in 1:1 ratio thus calcium oxide has formula  $\text{CaO}$ . While Aluminium oxide has formula  $\text{Al}_2\text{O}_3$ .

Such compounds formed by electrostatic forces of attraction between oppositely charged ions are called ionic compounds.

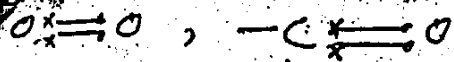
### COVALENT BOND (ELECTRON PAIR BOND)

According to Kossel and Lewis, the bond formed by mutual sharing of electrons between two atoms is called covalent bond. Each atom tries to acquire noble gas configuration after sharing electrons.

A covalent bond may be single double or triple bond

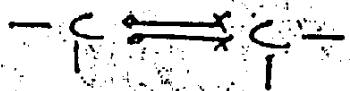
SINGLE COVALENT BOND (The covalent bond formed by sharing of one electron pair is called single covalent bond. For example  $\text{H}-\text{H}$ ,  $\text{Cl}-\text{Cl}$  etc.)

DOUBLE COVALENT BOND If there are ~~two~~ <sup>two</sup> shared electron pairs between two atoms it is called double covalent bond. Some examples are given below

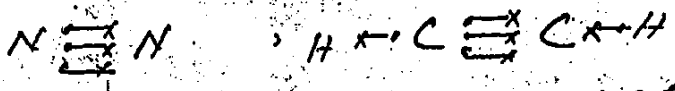


(11)

TRIPLE COVALENT BOND



Three shared electron pairs are called triple covalent bond

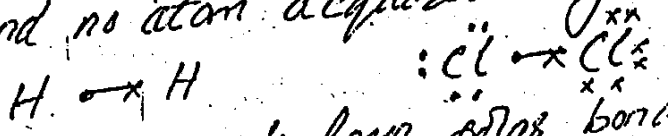


POLAR AND NON POLAR COVALENT BOND.

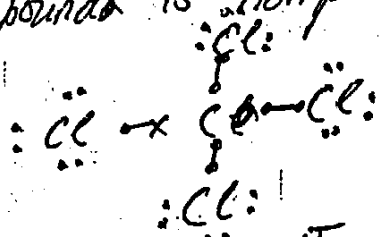
A covalent bond may be non polar or polar

NON POLAR COVALENT BOND

The covalent bond formed between two identical atoms is non polar. The electron pair is equally attracted by two atoms and no atom acquires any charge.

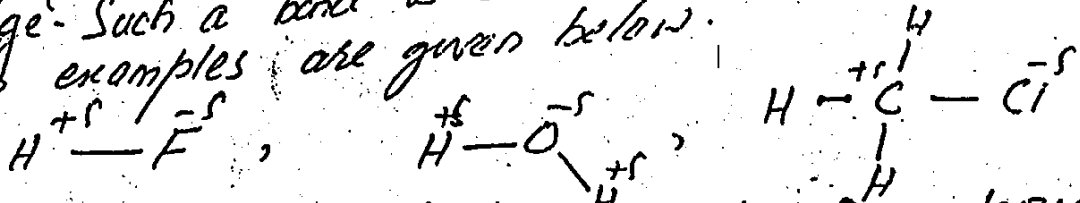


Some compounds have polar bonds but as a whole compound is non polar as a whole.



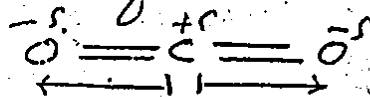
POLAR COVALENT BOND

When a covalent bond is formed between two dissimilar atoms shared electron pair is attracted more towards one atom than the other. The atom which attracts shared electron pair more powerfully is called more E.N. atom. It acquires partial negative charge. The less E.N. atom acquires partial positive charge. Such a bond is called POLAR BOND. Some examples are given below.



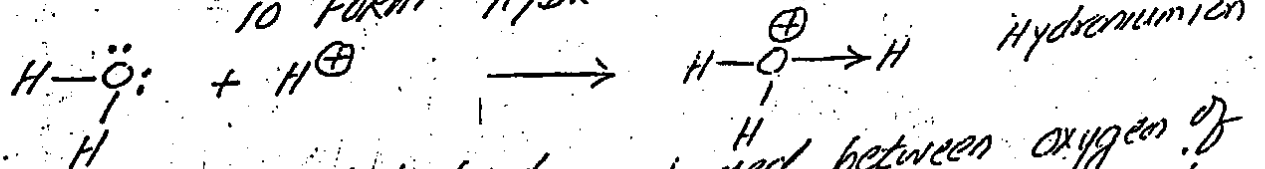
However term ionic bond is used for compounds which are predominantly ionic. Term covalent is used for non polar bonds. The bonds having some degree of polarity are said to possess ionic character of covalent bond. CO<sub>2</sub> has polar bonds but

as a whole molecule is non polar because the polar character on both sides of carbon atom cancel out each other.



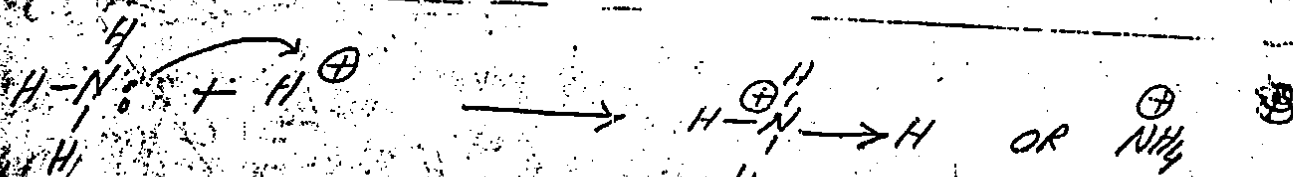
CO-ORDINATE COVALENT BOND:- A covalent bond in which both electrons of a bond pair are donated by one atom is called CO-ORDINATE COVALENT BOND. The atom which donates the electron pair is called DONOR ATOM. The atom which accepts the electron pair for bond formation is called ACCEPTOR ATOM. This bond is represented by an arrow which runs from donor to acceptor atom.

EXAMPLES:- REACTION OF WATER WITH AN ACID TO FORM HYDRONIUM ION " $\text{H}_3\text{O}^+$ "

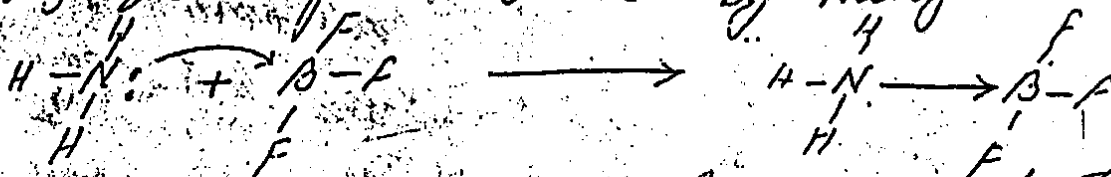


A coordinate covalent bond is formed between oxygen of water and  $\text{H}^+$  ion. Oxygen is donor atom and  $\text{H}^+$  is acceptor atom.

2) REACTION OF  $\text{NH}_3$  WITH  $\text{H}^+$  ION TO FORM  $\text{NH}_4^+$  ION  
A coordinate covalent bond is formed between  $\text{NH}_3$  and  $\text{H}^+$  ion. Nitrogen donates the electron pair for the bond.



3) REACTION BETWEEN  $\text{NH}_3$  AND  $\text{BF}_3$  A coordinate covalent bond is formed between nitrogen of  $\text{NH}_3$  and Boron of  $\text{BF}_3$ . Electron pair is donated by Nitrogen atom.

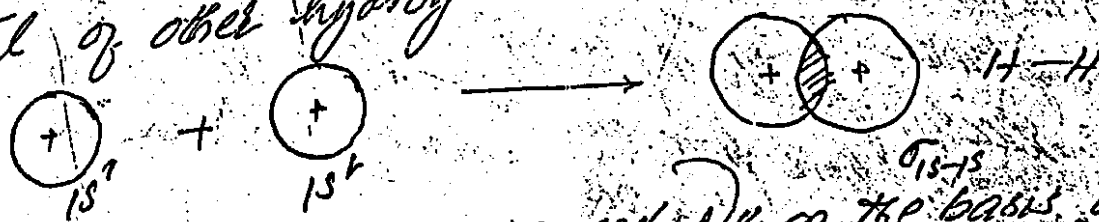


The properties of compounds having co-ordinate covalent bond are intermediate between properties of covalent and

EXPLAIN V.B.T. DISCUSS FORMATION OF  $H_2O$  AND  $NH_3$  ON THE BASIS OF THIS THEORY. P-12, B

1. According to V.B.T. covalent bond is formed by overlap of Atomic orbitals.
2. The overlapping orbitals must have unpaired electrons with opposite spin.
3. Larger the overlap of Atomic orbitals, the stronger is the bond.
4. The direction of bond depends upon direction of overlapping orbitals.
5. The bond formed by linear overlap of Atomic orbitals is called Sigma bond. In sigma bond electron density is concentrated between two nuclei. The electron density is maximum around the line joining the two nuclei.
6. If two A.O. overlap in such a way that their axis are parallel to each other, a  $\pi$ -bond is formed. In  $\pi$ -bond electron density is maximum above & below the two nuclei.

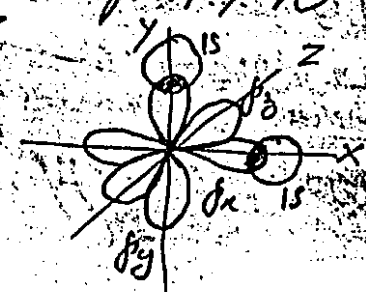
For example spherical and symmetrical  $1s^1$  orbital of one hydrogen atom overlaps with  $1s^1$  orbital of other hydrogen atom to form  $\sigma_{1s-1s}$  bond.



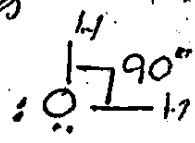
Let us explain formation of  $H_2O$  and  $NH_3$  on the basis of this theory.

**WATER MOLECULE:** Central atom in water is oxygen. It has atomic no = 8 =  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^2$

The two p orbitals with unpaired electrons ( $2p_x^1$  and  $2p_y^1$ ) overlaps



with  $1s$  orbitals of two hydrogen atoms. Thus water has planar angular structure.

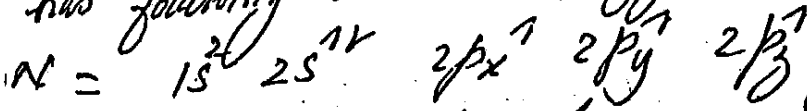


The bond angle is expected to be  $90^\circ$ .

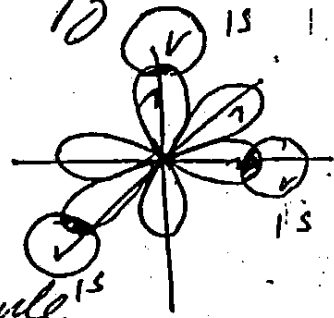
The experimentally determined angle is  $104.5^\circ$ . This may be explained on the basis of coulombic forces of repulsion between partially positively charged hydrogen. Further two lone pairs of electrons may also play a role in widening of bond angle from  $90^\circ$  to  $104.5^\circ$ .

### AMMONIA MOLECULE FORMATION:

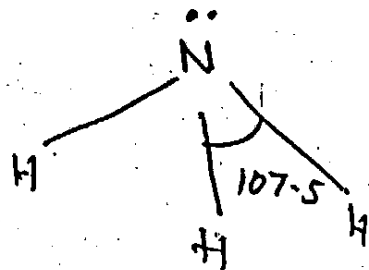
Nitrogen has following electronic configuration.



Three "p" orbitals with unpaired electrons overlap with  $1s$  orbitals of three hydrogen atoms to form three sigma bonds. Thus  $NH_3$  molecule



should have pyramidal shape. The  $H-N-H$  bond angle is expected to be  $90^\circ$ . The experimentally determined bond angle is  $107.5^\circ$ . This can be explained on the basis of repulsions between partially positively charged hydrogens. The repulsion between lone pair and bond pair may also be responsible for this widening of angle.



# ORBITAL HYBRIDIZATION

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WHAT IS ORBITAL HYBRIDIZATION? DISCUSS HYBRIDIZATION IN METHANE, ETHYLENE & ACETYLENE?

ANSWER:-

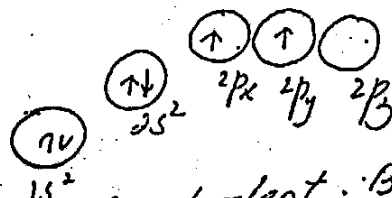
**DEFINITION:-** The process in which atomic orbitals of different energies and shapes are mixed together to form a new set of equivalent orbitals of same energy and shape is called HYBRIDIZATION. The new orbitals thus formed are called HYBRID ORBITALS.

There are many different types of orbital hybridization. The three types have been discussed over here.

**$sp^3$  HYBRIDIZATION** The mixing of one "s" and three p-orbitals to form four equivalent  $sp^3$  hybrid orbitals is called  $sp^3$  hybridization. Each hybrid orbital has 25% s-character and 75% p-character. The four hybrid orbitals are arranged at an angle of  $109.5^\circ$  from each other. This is called Tetrahedral arrangement. It is non-planar. Let us consider formation of METHANE MOLECULE.

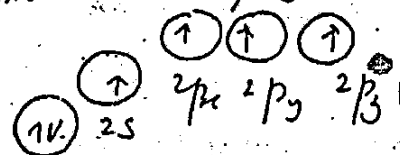
Carbon has atomic no = 6. Its electronic configuration in ground state is  $C = 1s^2 2s^2 2p^2$

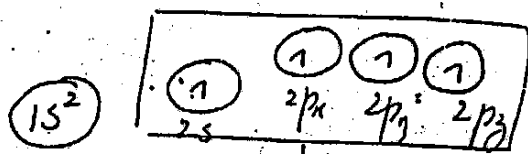
It can be represented as  
It has two unpaired electrons in ground state



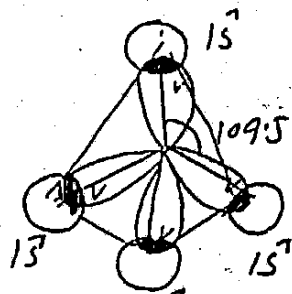
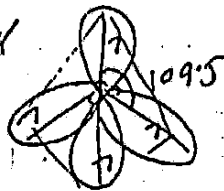
According to V.B.T. It should be divalent. But carbon is tetravalent in most of its compounds. In order to explain tetravalency let us consider carbon in excited state. One electron from  $2s$  is promoted to empty  $2p_z$ .

The mixing of  $2s$  and three p-orbitals produces four hybrid orbitals called  $sp^3$ -hybrid which are tetrahedrally arranged as shown below



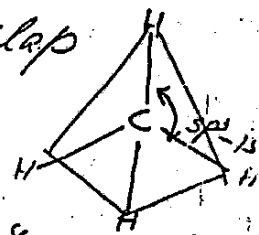


4  $sp^3$  Hybrid

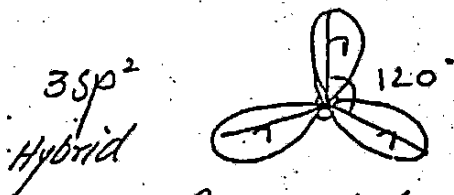
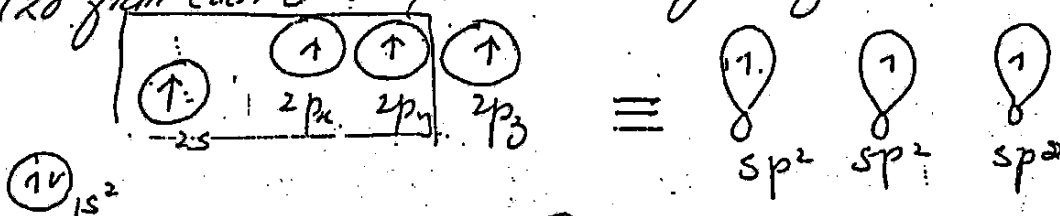


The four hybrid orbitals of carbon atom overlap with the  $1s$  orbitals of four hydrogen atoms thus four sigma bonds are produced each due to  $sp^3-1s$  overlap.

The bond angle is  $109.5^\circ$ . Thus a nonplanar tetrahedral structure of methane is produced.



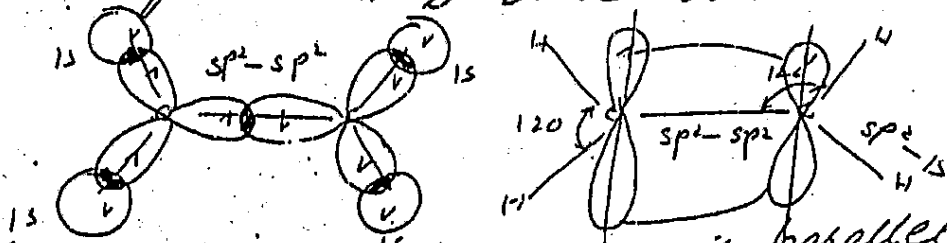
$sp^2$  HYBRIDIZATION The mixing of one  $s$  and two  $p$  orbitals to produce three equivalent orbitals is called  $sp^2$ -hybridization. Each hybrid orbital is called  $sp^2$ -hybrid.  $s$  and  $p$ -orbitals have mixed in 1:2 ratio. The three hybrid orbitals are situated at an angle of  $120^\circ$  from each other. These are trigonal planar.



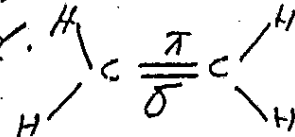
One unhybridized  $p$ -orbital remains present on these three hybrid orbitals. It is utilized in  $\pi$ -bond formation. An example of  $sp^2$ -hybridization is ethylene molecule. Each carbon in ethylene is  $sp^2$  hybridized. This producing three  $sp^2$  on each carbon. One  $sp^2$  of each carbon overlaps linearly with  $sp^2$  of other carbon.



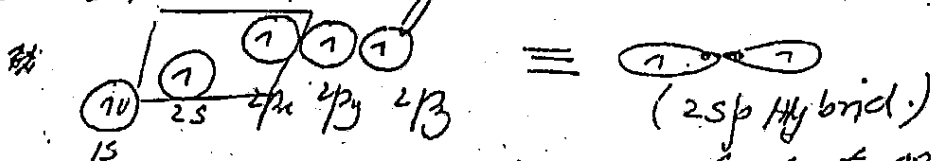
16  
 Thus, C-C  $\sigma$ -bond is formed. The remaining two  $sp^2$  of each carbon overlap with  $1s$  orbitals of two hydrogens to form C-H  $\sigma$  bonds as shown below



The unhybridized  $p$ -orbitals have their axis parallel to each other. They form a  $\pi$ -bond. Thus in a double bond there is a sigma and a  $\pi$ -bond.



SP-HYBRIDIZATION In this type of hybridization one  $s$  and one  $p$ -orbital mix to form two equivalent  $sp$  hybrid orbitals. These two hybrid orbitals are located at an angle of  $180^\circ$  from each other. Thus a linear structure is produced. They are co-axial.

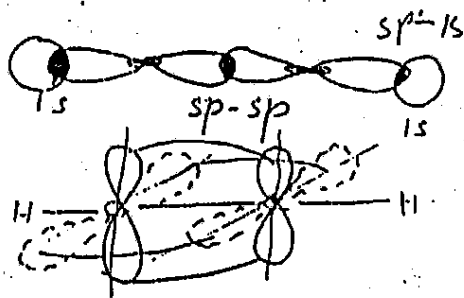


Two unhybridized  $p$ -orbitals remain present on each carbon atom. These are utilized in  $\pi$ -bond formation.

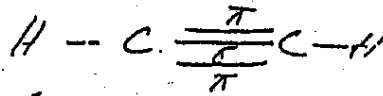
In ACETYLENE each carbon is  $sp$ -hybridized. The C-C  $\sigma$ -bond is formed due to  $sp$ - $sp$  linear overlap. C-H sigma bonds are formed due to  $sp$ - $1s$  overlap.



The two unhybridized  $p$ -orbitals are perpendicular to each other and also perpendicular to C-C long axis.



The  $p_y$ - $p_y$  and  $p_z$ - $p_z$  overlap to form two  $\pi$ -bonds between two carbon atoms. Thus there is a triple bond present between two carbons. In a triple bond there is one sigma and two  $\pi$ -bonds.



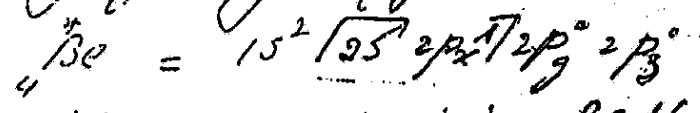
Thus Acetylene has linear structure.  
 (CONSULT PAGE NO. 7 OF EXERCISE)

### HYBRIDIZATION IN BERYLIUM.

Beryllium has atomic number "2" with electronic configuration  ${}^4\text{Be} = 1s^2 2s^2 2p_x^0 2p_y^0 2p_z^0$

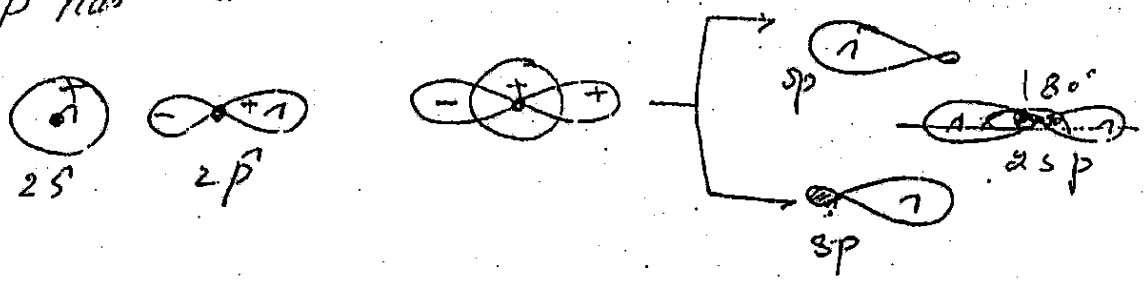
According to V.B.T. valency of an element depends upon number of unpaired electrons. The above electronic configuration of "Be" shows that "Be" should be INERT OR ZEROVALENT.

But "Be" is divalent in its compounds like  $\text{BeCl}_2$ ,  $\text{BeH}_2$  etc. Its divalency can be explained considering that in excited state an electron from  $2s$  is promoted to an empty "p" orbital giving following configuration.

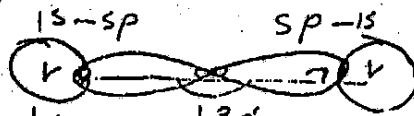


If it is considered that in  $\text{BeH}_2$  each one Be-H bond is formed due to  $2s^1 - 1s^1$  overlap and other due to  $2p_x^1 - 1s^1$  overlap then two Be-H bonds should not be equivalent (they should have different stabilities and different bond lengths) But in fact the two Be-H bonds are exactly equivalent in their stabilities and bond lengths etc.

Thus it is considered that  $2s^1$  and  $2p_x^1$  combine to produce two hybrid orbitals each one of them called sp-hybrid. The  $2sp$  are situated at an angle of  $180^\circ$  from each other. Each hybrid has 50% 's' and 50% 'p' character. "sp" indicates that 's' and 'p' has combined in 1:1 ratio



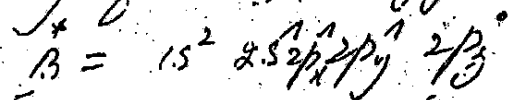
The "s" orbital of hydrogen overlaps with  $sp^2$  hybrid orbital to form a sigma bond. Thus two sigma bonds are equivalent (each due to  $sp-s$  overlap)



Thus  $BH_3$  has linear structure (bond angle  $180^\circ$ ) which is in accordance with V.S.E.P.R. THEORY. The hybrid orbitals have slightly higher energy than combining orbitals and energy is absorbed during hybridization process. Thus hybrid orbitals are slightly unstable than atomic orbitals. However this decreased stability is compensated due to greater stability of bonds formed due to  $sp-s$  overlap. (more energy is released due to two  $sp-s$  overlap than released due to  $sp-s$ ,  $s-s$ ,  $s-p$  overlap) This is also called DIAGONAL HYBRIDIZATION.

### $3sp^2$ HYBRIDIZATION IN BORON.

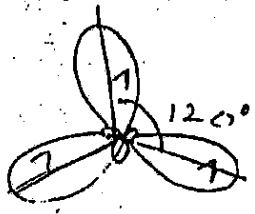
Boron with atomic number "5" has following electronic configuration =  $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$ . According to this configuration Boron should be monovalent but Boron is trivalent in most of its compounds. Let us consider that in excited state one electron from  $2s^2$  is promoted to an empty  $2p_z^0$  giving following configuration



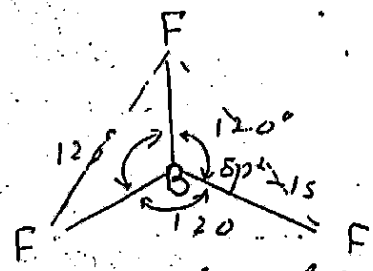
One "2s" and two "2p" orbitals ( $2p_x^1 2p_y^1$ ) combine to produce three hybrid orbitals. Each hybrid is called  $sp^2$  hybrid.  $sp^2$  indicates that "s" and p- have combined in 1:2 ratio. Each hybrid has  $\frac{1}{3}$  s and  $\frac{2}{3}$  p-character.

The three  $sp^2$  hybrid orbitals are situated at an angle of  $120^\circ$  from each other.

The three  $sp^2$  are co-planar, directed towards corners of an equilateral triangle. This is called trigonal hybridization.



In  $BF_3$ , each B-F bond is formed due to linear overlap of  $sp^2-2p^1$  overlap. Thus 3 bonds are identical in all respects.



The shapes of ammonia and  $H_2O$  can also be explained on the basis of hybridization.

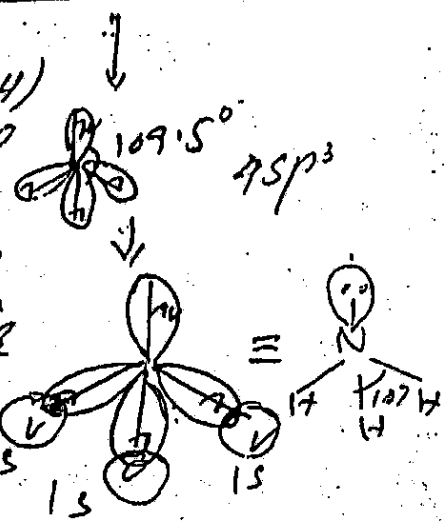
SHAPE OF  $NH_3$  Nitrogen has following electronic configuration

$7N = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ . If it is considered that three hydrogens are attached to three "p" orbitals then bond angle should be  $90^\circ$  each. But in actual it is  $107^\circ$ .

Thus it is considered that in nitrogen  $sp^3$  hybridization occurs. These five electrons to be placed in the four  $sp^3$  hybrid orbitals. One hybrid orbital has paired electron and it remains as lone pair. Three hydrogens each having  $1s$ -orbital overlaps with  $sp^3$  hybrid orbitals having unpaired electron.

Thus three (N-H) sigma bonds are formed due to  $sp^3-1s$  overlap. The bond angle is reduced to  $107.5^\circ$  due to greater repulsion of lone pair.

$NH_3$  has trigonal pyramidal structure.



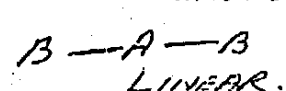
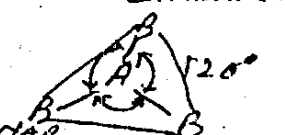
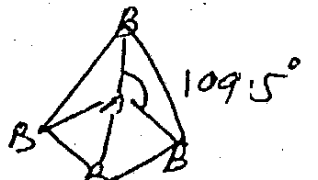
# WRITE IMPORTANT POSTULATES OF V.S.E.P.R. THEORY. EXPLAIN SHAPES OF DIFFERENT MOLECULES ON THE BASIS OF THIS THEORY.

## THEORY. EXPLAIN SHAPES OF DIFFERENT MOLECULES ON THE BASIS OF THIS THEORY.

This theory was proposed by Sidwick and Powell and later on developed by Gillespie and Nyholm in 1957. The important postulates of this theory are given below.

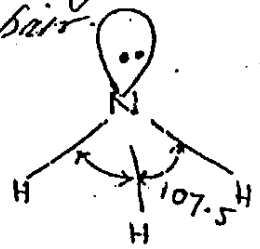
- 1) The shape of molecule depends upon number of electron pairs present in valence shell of central atom.
- 2) The electron pairs present in valence shell of central atom repel each other. They try to be at maximum distance from each other so as to have minimum repulsion among them.
- 3 - A lone pair of electron exerts more repulsion than bond pair. In other words lone pair tries to occupy more space on surface of central atom than bond pair. This is due to the fact that lone pair is attracted by one nucleus. While bond pair is attracted by two nuclei.
- 4 - The repulsion between bonding electron pairs decreases with increase in E.N. of atoms attached to central atom.
- 5 - Two electron pairs of a double bond or three electron pairs of a triple bond take up more space on surface of central atom than one electron pair of a single bond.

These postulates are applicable for non transition elements only. The general shapes and angles of different types of molecules are given below.

GENERAL FORMULA	ELECTRON PAIR	BOND ANGLE	MOLECULAR STRUCTURE
$AB_2$	2	$180^\circ$	 <p>LINEAR.</p>
$AB_3$	3	$120^\circ$	 <p>TRIGONAL PLANAR</p>
$AB_4$	4	$109.5^\circ$	 <p>TETRAHEDRAL.</p>

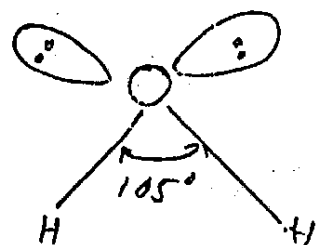
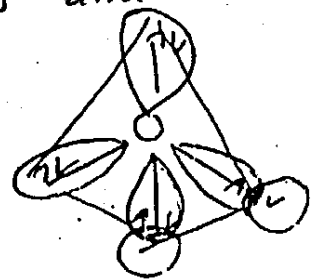
If lone pairs of electrons are present or if central atom is attached with different kind of atoms, some deviations from regular shape are observed. The deviation of bond angle from normal angle expected from hybridization can be explained on the basis of V.S.E.P.R. THEORY.

**SHAPE OF  $NH_3$  MOLECULE** :: In  $NH_3$  central atom is nitrogen. It has four electron pairs in valence shell. Three of them are bond pairs and one is lone pair. Four electron pairs arrange in a tetrahedral manner around central atom. Three corners of tetrahedron are occupied by bond pairs and one corner is occupied by lone pair. Due to greater repulsion of lone pairs, the angle ~~between~~ between bond pairs is reduced to  $107.5^\circ$ . The atomic arrangement is called trigonal pyramidal.



In  $NF_3$ , the nitrogen is attached with more E.N. atoms "F". The bond pairs are closer to fluorine. Thus repulsion between bond pairs is decreased. Due to greater repulsion of lone pair bond angle  $\angle (F-N-F)$  is  $102^\circ$ . However, shape of molecule remains trigonal pyramidal.

**SHAPE OF WATER MOLECULE** :: In water central atom is oxygen. It has four electron pairs in its valence shell. Two of them are bond pairs and two are lone pairs. Oxygen is  $sp^3$  hybridized. Thus four hybrid orbitals have tetrahedral arrangement. Two corners of tetrahedron are occupied by lone pairs and two corners are occupied by bond pairs. Due to greater repulsions of lone pairs the bond angle  $\angle H-O-H$  is reduced to  $105^\circ$ . Thus water molecule has inverted V shaped structure.



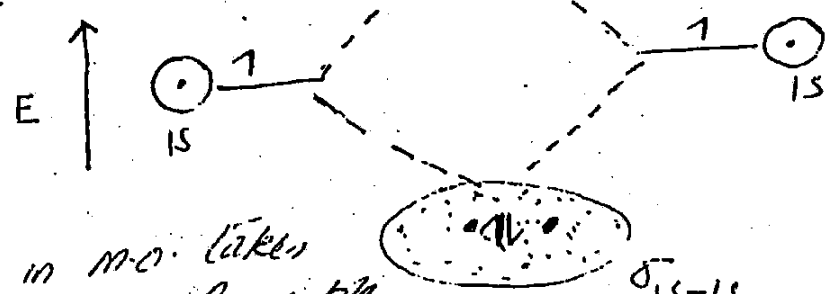
# WHAT IS MOLECULAR ORBITAL THEORY? EXPLAIN

## RELATIVE ENERGIES OF MOLECULAR ORBITALS.

The MOT considers the whole molecule as a single unit. This theory is based upon following postulates.

1. When A.O. of combining atoms overlap, they give rise to new orbitals called MOLECULAR ORBITALS. One molecular orbital has lower energy than combining A.O. It is called BONDING MOLECULAR ORBITAL. It is symmetrical about molecular axis. It is designated as  $\sigma$  bonding molecule's orbital.

Higher energy than A.O. The other M.O. has higher energy than A.O. It is called Antibonding. M.O. designated as  $\sigma^*$ . For example consider BMO formed by overlap of 1s orbitals of two hydrogen atoms.



2) The filling of electrons in M.O. takes place according to Aufbau Principle, Pauli Exclusion Principle, Hund's Rule. Thus two electrons of two hydrogen atoms enter in  $\sigma_{1s-1s}$  and remain paired. The antibonding M.O. remains empty.

3) The molecule orbitals differ in electron density distributed around nuclei. The electron density map of BMO of hydrogen molecule is shown below.

A BMO is associated with buildup of electron density between two nuclei. It is associated with lowering of energy.

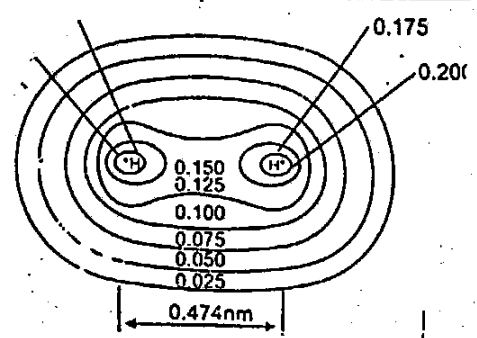
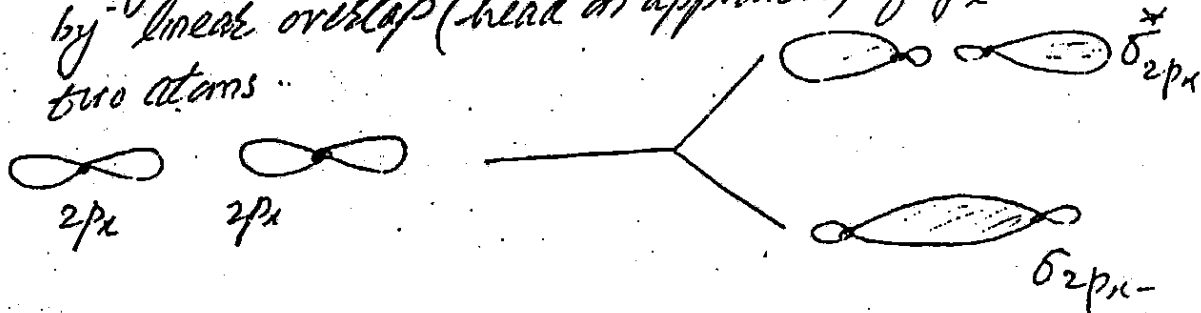


Fig. 6.22 Electron density map of the bonding molecule

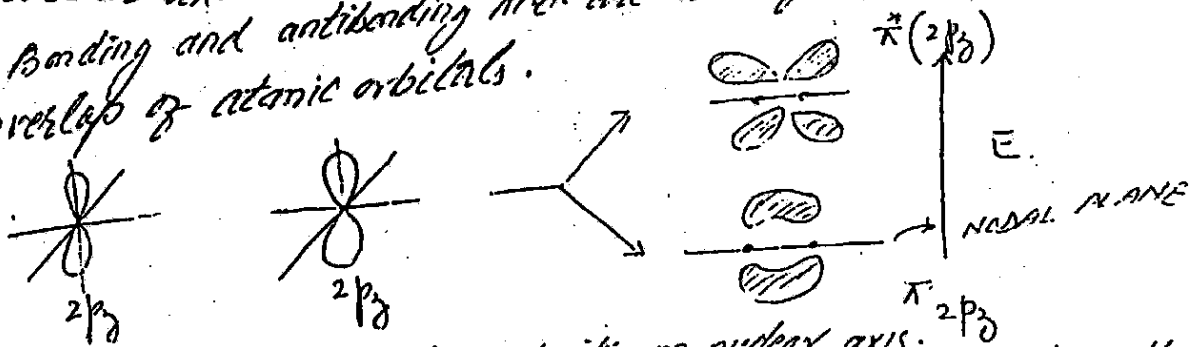
The antibonding m.o is associated with decrease of electron density between two nuclei. The two electrons in  $\sigma$ -m.o. which hold two atomic nuclei are called  $\sigma$ -electrons.

4- A sigma BMO and sigma ABMO ( $\sigma^*$ ) are also formed by linear overlap (head on approach) of  $p_x$  orbitals two atoms.



Both  $\sigma_{2p_x}$  and  $\sigma_{2p_x}^*$  are symmetrical about nuclear axis.

5- Bonding and antibonding m.o. are also formed by parallel overlap of atomic orbitals.



The BMO " $\pi$ " has zero electron density on nuclear axis. This is called nodal plane. The electron density is uniformly distributed above and below nodal plane. It has least electron density in the internuclear axis.

Since  $p_y$  and  $p_z$  are degenerate A.O. thus their corresponding BMO and ABMO are also degenerate.

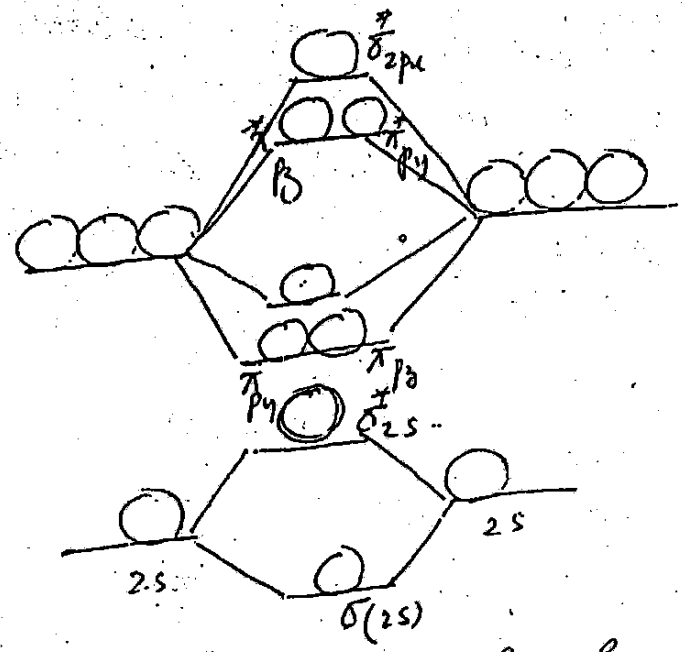
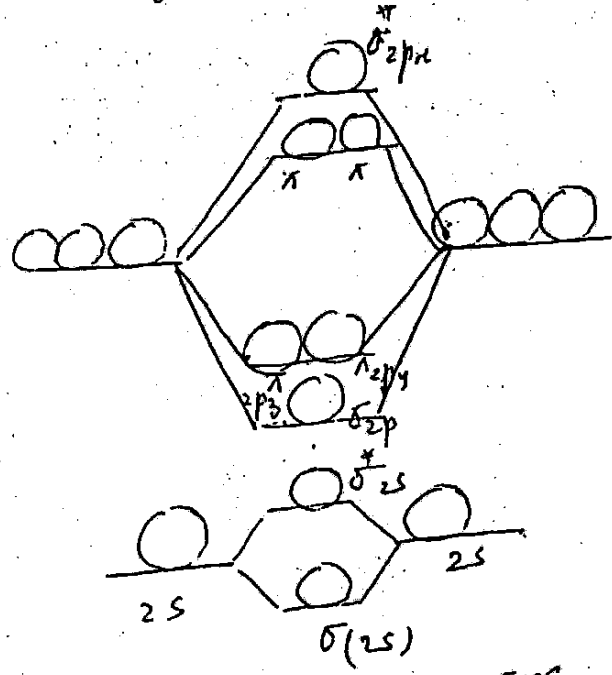
Six m.o. are formed from two sets of "p" orbitals. A " $\sigma$ " and  $\sigma^*$  is formed by linear overlap of  $2p_x$  orbital. Two " $\pi$ " and two " $\pi^*$ " are formed by parallel overlap of  $p_y$  and  $p_z$  and  $p_z$  and  $p_y$ .

Thus overlap of two sets of "p" orbitals lead to formation of triple bond. One is sigma bond and other two are  $\pi$ -Bond.



RELATIVE ENERGIES OF M.O. :-

The relative energies of m.o. are determined from spectroscopic measurements. The m.o. of diatomic molecules O<sub>2</sub>, F<sub>2</sub>, and their positive and negative ions are shown below



M.O. OF N<sub>2</sub>, Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>

M.O. OF (O<sub>2</sub>, F<sub>2</sub>) + POSITIVE OR NEGATIVE IONS.

$$\sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_{2p} = \pi_{2p}^* < \sigma_{2p} < \pi_{2p}^* < \sigma_{2p}^*$$

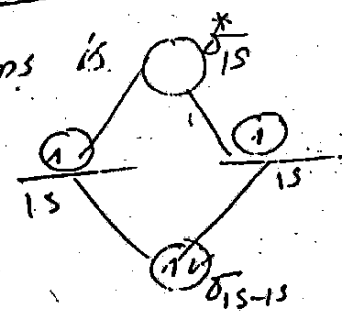
BOND ORDER :-

The number of bonds formed after A.O. overlap is called bond order.

$$\text{Bond order} = \frac{\text{Number of } e^- \text{ bond.} - \text{No. of } e^- \text{ antibond.}}$$

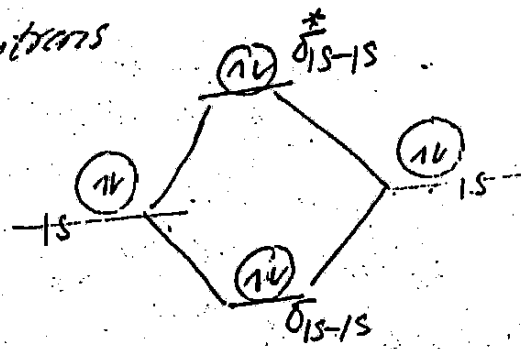
The number of bonds formed between two H-Atoms is

$$\text{Bonds order} = \frac{2 - 0}{2} = 1$$



DRAW M.O. DIAGRAM OF FOLLOWING :-

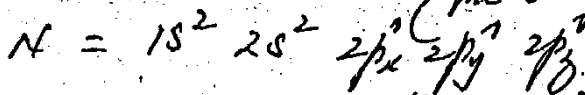
He :- <sup>2</sup>He = 1s<sup>2</sup>  
Each Helium atom has two electrons in 1s. Thus there are four e<sup>-</sup> to be placed in m.o. Two e<sup>-</sup> enter in BMO and two in ABMO.



$$\text{BOND ORDER} = \frac{2 - 2}{2} = \text{ZERO}$$

∴ Thus Helium molecule is not formed.

NITROGEN MOLECULE:



The electronic Config. of "N" is  
 $n = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

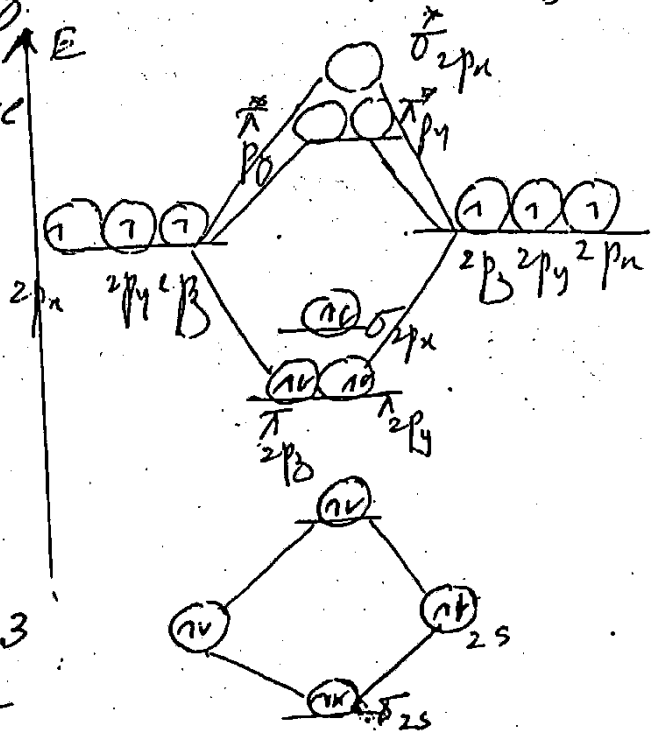
It is clear from m.o. diagram that out of ten e<sup>-</sup> in valence shell of two nitrogen atoms 8-e<sup>-</sup> enter in BMO and two in AB.M.O

Bond order =  $\frac{8-2}{2} = 3$

It can also be written considering all e<sup>-</sup> of two nitrogen atoms.

Bond order =  $\frac{10-4}{2} = 3$

There is a sigma and two pi bonds between two nitrogen atoms.



OXYGEN MOLECULE:-

Oxygen has atomic no - 8  
 Electronic Configuration =  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$

The m.o. diagram of O<sub>2</sub> is given below

$\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2p_y}^2 = \pi_{2p_x}^2 < \sigma_{2p_z}^2 < \sigma_{2p_z}^{*2} < \pi_{2p_y}^{*1} = \pi_{2p_x}^{*1}$

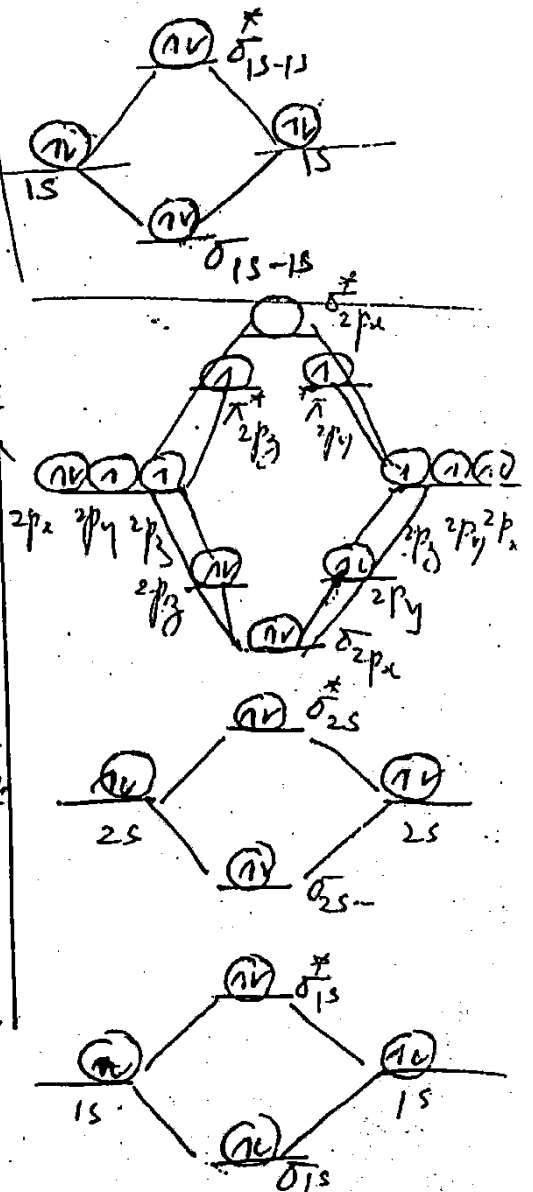
$\pi_{2p_y}^{*1} = \pi_{2p_x}^{*1}$

BOND ORDER =  $\frac{10-6}{2} = \frac{4}{2} = 2$

Thus O<sub>2</sub> has a double bond which corresponds to high B.E 413 kJ/mole

It is clear from m.o. diagram that two unpaired electrons are present in Antibonding MO  $\pi_{2p_y}^{*1}$  and  $\pi_{2p_x}^{*1}$ .

This explains paramagnetic behaviour of oxygen. Its major success of M.O Theory.

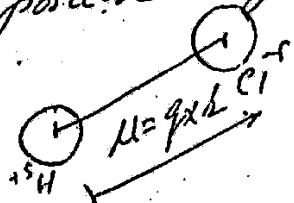


# DIPOLE MOMENT. ROLE OF DIPOLE MOMENT IN 26

The separation of charges on the molecule is called dipole. The polarity of molecule is measured in terms of dipole moment.

For example let us consider HCl molecule. Chlorine being more E.N. attracts shared electron pair more powerfully than Hydrogen. Thus chlorine acquires partial negative charge and hydrogen acquires partial positive charge.

This polarity is expressed in terms of dipole moment  $\mu = q \times r$ .

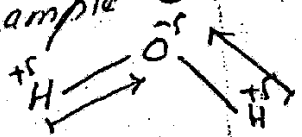


The dipole moment can be defined as product of charge and distance between charges.

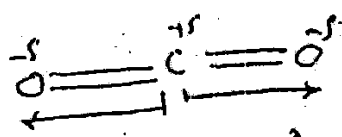
Dipole moment is a vector quantity its direction is from positive end to negative end.

In POLYATOMIC MOLECULES having more than one bonds with dipoles, the resultant dipole moment is vectorial sum of individual bond moments.

For example consider H<sub>2</sub>O and CO<sub>2</sub> molecules.



$\mu = 1.84 \text{ D}$



$\mu = 0.0 \text{ D}$

CO<sub>2</sub> has zero dipole moment because individual dipoles cancel each other out. While H<sub>2</sub>O has dipole moment due to non linear molecule.

UNIT OF DIPOLE MOMENT The unit of dipole moment is Deby unit.

$1 \text{ D} = 3.336 \times 10^{-30} \text{ Coulomb meter}$   
 Example if  $r = 100 \text{ pm}$   $q = 1.6022 \times 10^{-19} \text{ Coulomb}$

$$\mu = 1.6022 \times 10^{-19} \text{ C} \times 100 \times 10^{-12} \text{ m}$$

$$\mu = \frac{1.6022 \times 10^{-29}}{3.336 \times 10^{-30} \text{ cm}} = 4.8 \text{ D}$$

APPLICATIONS OF DIPOLE MOMENT Dipole moment gives two important informations about structure of molecule

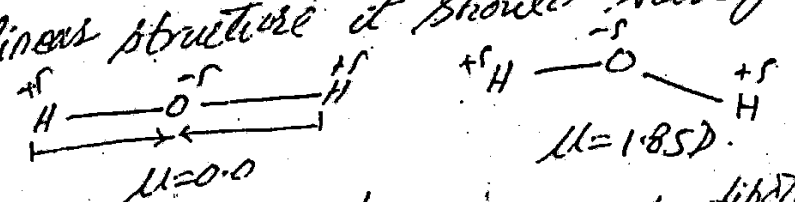
- (1) % of ionic character of a bond.
- (2) Angles between bonds or geometry of molecule.

1) PERCENTAGE OF IONIC CHARACTER  
 From experimentally determined value of  $\mu$  we can calculate % of ionic character

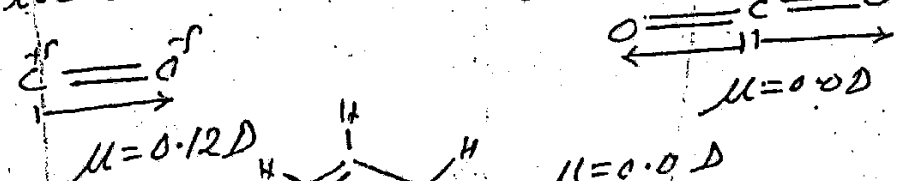
$$\% \text{ of ionic character} = \frac{\mu_{obs.}}{\mu_{calculated}} \times 100$$

% of ionic character in H-F, H-Cl, H-Br and H-I is 43%, 17%, 12%, 5% respectively.  
 (see example no. on page 226)

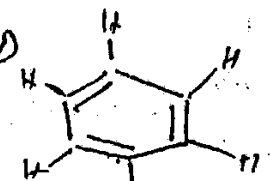
2) GEOMETRY OF MOLECULE | Water has dipole moment 1.85 D which shows that it has bent structure. If it had linear structure it should have zero dipole moment.



3) STRUCTURE OF CO<sub>2</sub> AND CO | CO<sub>2</sub> has zero dipole moment. Because it has linear structure - the individual dipoles cancel each other out. However CO has  $\mu = 0.12$  D it has a single bond with dipole.

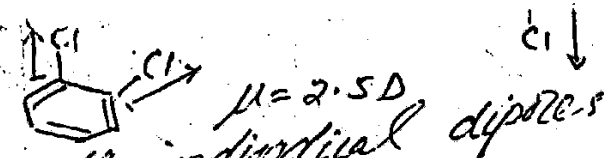


4) BENZENE



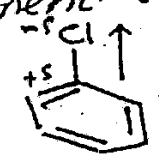
Benzene has  $\mu = 0.0$  D due to symmetrical planar structure.

p-DICHLOROBENZENE



It has dipole moment because individual dipoles don't cancel each other out.

CHLOROBENZENE | It also has dipole moment  $\mu = 1.7$  D



## DISCUSS EFFECT OF BONDING ON PROPERTIES OF COMPOUND. 28

The properties of compound depend upon nature of bond.

Consider some important properties.

SOLUBILITY / Ionic compounds are soluble in polar solvents but insoluble in non polar solvents. When ionic compound is placed in water the polar water molecules detach cations from anions due to electrostatic forces of attraction the ions are freed from crystal lattice by hydration. It is possible if hydration energy is greater than lattice energy the heat of hydration is used to break crystal lattice.

If heat of hydration is not sufficient to break crystal lattice, ionic compound will not dissolve in water. Thus ionic compounds are not soluble in non polar solvents like cyclohexane, benzene etc.

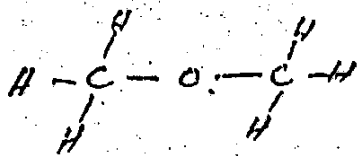
NON RIGID NON DIRECTIONAL / The electrostatic forces of attraction are non directional. Thus ionic compounds do not exhibit phenomenon of isomerism.

FAST REACTIONS / The ionic compounds exist in the form of ions. The chemical reaction of ionic compounds are v. fast. For example reaction of NaCl with AgNO<sub>3</sub> in aqueous sol is very fast. During reaction between ions, no bonds are required to be broken new bonds are formed.

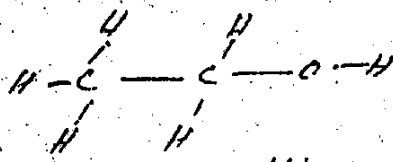
SOLUBILITY OF COVALENT COMPOUNDS / Covalent compounds are soluble in non polar organic solvents. The forces of attraction between solvent molecules and covalent compound are strong enough to break intermolecular forces of attraction. Mostly covalent compounds are insoluble in water. Some covalent compounds are soluble in water due to hydrogen bonding.

ISOMERISM / Covalent bonds are rigid and non directional.

Thus covalent compounds show different types of isomerism. For example C<sub>2</sub>H<sub>6</sub>O has two isomers.



DIMETHYL ETHER



ETHANOL

RATES OF REACTIONS | The reactions of covalent compounds involve breaking and remaking of bonds. Thus these reactions are quite slow. The reactivity of covalent compounds depends upon nature of products and mechanism of chemical reaction.

WHAT IS BOND ENERGY? WRITE FACTORS AFFECTING BOND ENERGY?

DEF: - The amount of energy required to break all bonds in 1 mole of substance is called Bond Energy. The same amount of energy is released when 1 mole of bonds are formed from corresponding atoms. It is called Bond enthalpy.

ENTHALPY OF ATOMIZATION | The enthalpy change in splitting a molecule into its component atoms is called enthalpy of atomization.

UNIT OF BOND ENERGY | It is generally expressed in kJ/mole. It is amount of energy released when Avogadro's No. of bonds are formed from corresponding atoms or Energy required to break Avogadro's No. of bonds are broken.

EFFECT OF POLARITY ON BOND ENERGY

The bond energy of a polar bond is greater than that of a non polar bond. Let us calculate. ~~can~~ increase in bond energy due to ionic character of covalent bond in H-Cl molecule.

Bond energy of  $H_2$  is = 431 kJ/mole.

$$B.E. \text{ OF 1 MOLECULE OF } H_2 = \frac{431}{6.022 \times 10^{23}} = 71.59 \times 10^{-23} \text{ kJ/molecule}$$

$$B.E. \text{ OF 1 HYDROGEN ATOM} = \frac{71.59 \times 10^{-23}}{2} = 35.79 \times 10^{-23} \text{ kJ/ATOM}$$

$$B.E. \text{ OF MOLE OF } Cl_2 = 240 \text{ kJ/mole}$$

$$B.E. \text{ OF MOLECULE OF } Cl_2 = \frac{240}{6.022 \times 10^{23}} = 39.86 \times 10^{-23} \text{ kJ/MOLECULE}$$

$$B.E. \text{ OF 1 ATOM OF } Cl = \frac{39.86 \times 10^{-23}}{2} = 19.93 \times 10^{-23} \text{ kJ/ATOM}$$

$$\text{EXPECTED B.E. OF } H-Cl = 35.79 \times 10^{-23} + 19.93 \times 10^{-23} = 55.72 \times 10^{-23} \text{ kJ/molecule}$$

$$\text{CALCULATED B.E. PER MOLE OF } HCl = 336 \text{ kJ/mole}$$

$$\text{EXPERIMENTAL B.E. OF } HCl = 432 \text{ kJ/mole}$$

$$\text{EXTRA BINDING ENERGY} = 96 \text{ kJ/mole}$$

This extra binding energy is due to ionic character of covalent bond. Thus a covalent bond between two dissimilar atoms is always stronger than that between two identical atoms.

### FACTORS AFFECTING BOND ENERGY | The strength of bond and its B.E. depends upon following factors.

- 1) ELECTRONEGATIVITIES OF ATOMS
- 2) SIZE OF ATOMS
- 3) BOND LENGTHS.

RELATIVE B.E. OF HALOGEN ACIDS | Among halogen acids, H-F has maximum B.E. while H-I has minimum.

This is due to maximum difference in E.N. between "H" and F. and minimum between "H" and "I". The decreasing order of B.E. is  $H-F > H-Cl > H-Br > HI$

Thus HF has maximum enthalpy of formation because it has maximum % of ionic character.

B.E and enthalpy of formation are used to calculate Electronegativities of Atoms.

B.E are useful to calculate heats of gaseous reaction involving covalent compounds.

The bond energy depend upon sizes of atoms. Generally B.E. decreases with increase in size of combining atoms.  $H-F > H-Cl > H-Br > H-I$  is order of B.E. It can be explained on the basis of size of halogen atom.

The bond energy increases with decreasing bond length. The order of B.E. is  $C \equiv C > C = C > C - C$ . While order of bond length is  $C - C > C = C > C \equiv C$ .

The bond energy of double bond is greater than single bond but it is not twice as strong as single bond. Similarly triple bond is not thrice as strong as single bond.

Q WHAT IS BOND LENGTH? WRITE ITS PERIODICITY.

ANS:- The distance between nuclei of two atoms forming a covalent bond is called bond length. Bond lengths are generally determined by physical methods like X-Ray diffraction, electron diffraction, Spectral lines.

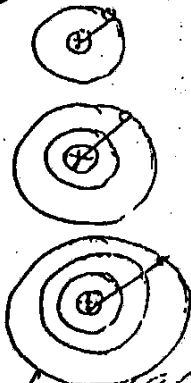
The covalent bond length between two atoms is mostly independent of molecule. For example C-C bond length in diamond and aliphatic hydrocarbons is 154 pm.



PERIODICITY OF BOND LENGTHS | The bond length increases as we proceed from top to the bottom in the group of periodic table. Down the group, number of shells are increased and atomic radius increases.

For example bond length of Si-Si is greater than that of C-C. Similarly P-P bond length is greater than that of N-N bond length.

In periods bond length decreases left to right.



FACTORS AFFECTING BOND LENGTHS

1. In some cases bond length of a bond between two dissimilar atoms is equal to sum of their covalent radii. For example  $\text{C}-\text{H}$  bond length of a bond between C and hydrogen is equal to sum of covalent radii of carbon and hydrogen. ( $0.77 + 0.17 = 0.94 \text{ \AA}$ )

But some times the actual bond length of a bond between two dissimilar atoms is shorter than that expected from sum of covalent radii.

For example Si-F bond length =  $\frac{154 + 159}{2} = 181 \text{ pm}$  (expected) vs  $154 - 159 \text{ pm}$  (Actual)

It is due to ionic character of covalent bond.

2) NATURE OF HYBRIDIZATION | The bond length depends upon nature and % of 's' orbital in hybrid orbital involved in bond formation. The greater the % of 's' orbital in hybrid orbital, the greater lesser is the bond length.

3) MULTIPLE BONDS | The triple bond in  $\text{HC}\equiv\text{CH}$  has least bond length. Double bond has larger bond length than triple bond but lesser than C-C single bond length.  $\text{C}-\text{C} = 154 \text{ pm}$ ,  $\text{C}=\text{C} = 134 \text{ pm}$ ,  $\text{C}\equiv\text{C} = 120 \text{ pm}$

$\pi$  Bond also reduces inter-nuclear distance. In ethane, ethene and ethyne carbon is  $sp^3$ ,  $sp^2$  and  $sp$ .

p-33

hybridized. Thus bond length decreases with increase in % of 's' character in hybrid orbital.  
Bond length decreases as we proceed from left to right in a period. This is increase in nuclear charge as we proceed from left to right in a period. However number of shells remain the same in a period.