

www.gulosta.pk

CHEMISTRY

11

CH#6

Chemical Bonding



These Notes Have been Prepared
and Developed By

ADNAN SHAFIQUE

www.guldasta.pk

Chapter 6

CHEMICAL BONDING

The force of attraction which holds the atoms or ions together is called

chemical bond. e.g. $H-H$, $NaCl$, H_2O

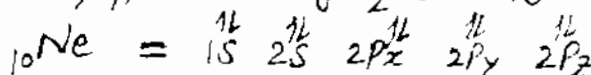
Cause of Chemical Combination: -

The noble gases (He, Ne, Ar, Kr, Xe, Rn)

are the most stable elements. They have a little tendency to show chemical reaction

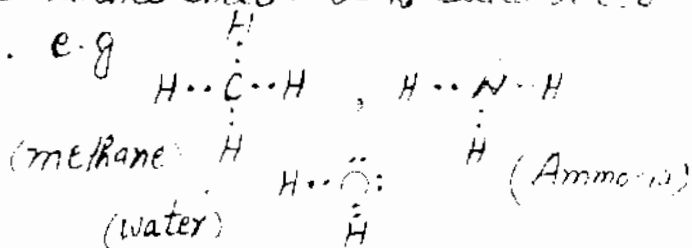
It is due to their special electronic configuration.

Their s and p orbitals are completely filled. e.g. ${}^2_2He = 1s^2$



All other elements try to get stability like noble gases. They attain noble gas configuration by losing, gaining or sharing electrons. Thus a chemical reaction or chemical combination takes place.

Octet Rule: - The atoms have tendency to attain a maximum of eight electrons in the valence shell. It is called octet rule. e.g.



Many elements do not obey octet rule

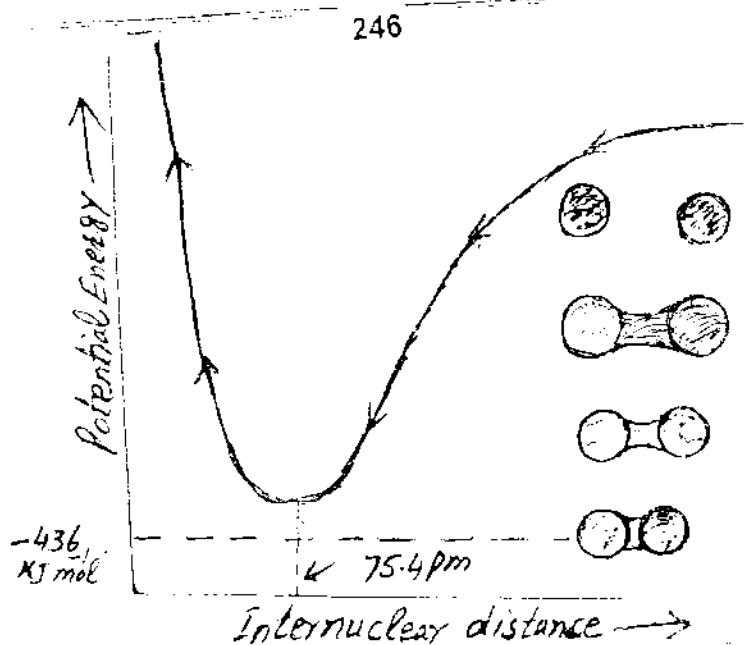
- (i) Some elements have incomplete octet or less than eight electrons. e.g. BeCl_2 , BF_3
- (ii) Some other elements have expansion of octet or more than eight electrons e.g. BCl_3 , PCl_5 , SF_6 etc.

Dual tendency of Hydrogen:- The hydrogen has dual tendency. It has tendency to lose or gain electron. For example in the formation of HF , hydrogen atom loses an electron. But in the formation of NaH , hydrogen atom gains an electron.

Energetics of bond formation:-

When two hydrogen atoms come close to each other, then both the forces of attraction and repulsion act at the same time.

When two atoms attract each other, then P.E of system decreases. When two atoms repel and push each other, then P.E of system increases. At a distance of 75.4 pm the H-atoms have maximum attraction and minimum P.E. Here bond formation takes place and stable molecule (H_2) is formed. It is shown in graph. If the distance between two atoms is further



decreased, then repulsion takes place between two nuclei. Now there is sharp increase in P.E and system becomes unstable. Thus bond is not formed

Atomic Size or

(Atomic radii, Ionic radii, Covalent radii)

Atomic radius:- The average distance between nucleus of an atom and its outermost shell is called atomic radius.

e.g Atomic radius of Na = 154 pm,

Cl = 99 pm, H = 37.7 pm, C = 77 pm

The atomic radii are measured by ~~V.g.~~ X-ray diffraction or by spectroscopic techniques. However accurate and precise

Reasons

measurement of atomic radius is not possible. It is due to following reasons

- (i) There is no sharp boundary of an atom
- (ii) The probability of an electron is affected by neighbouring atoms
- (iii) Atomic radius changes from compound to compound.

Atomic Radii in a group: - The atomic radii increase from top to bottom in a group

It is due to increase in number of shells and screening effect of electrons.

The screening effect is also called shielding effect of electrons. Due to this effect force of attraction between nucleus and outermost electron decreases. Hence atomic radii increase in a group.

Atomic radii in a Period: - The atomic radii decrease from left to right in a period. The reason is that in a period nuclear charge increases but no new shell is introduced. This decrease in atomic radii is more in second period but less in higher periods. For example decrease in atomic radii is small when we go from left to right in transition elements.

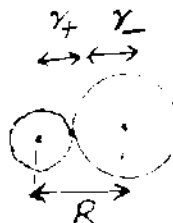
Sc(21) - - Zn(30) and Y(39) - - Cd(48). It is due to intervening (interrupting) electrons.

Ionic Radii:- The radius of ion while considering it to be a spherical in shape is called ionic radius. Some examples are given below.

$$Na^+ = 95 \text{ pm}, \quad Cl^- = 181 \text{ pm}$$

$$Mg^{++} = 61 \text{ pm}, \quad O^{2-} = 132 \text{ pm}$$

Consider a positive and negative ion held together by electrostatic attraction.



Let r_+ is Cationic radius

and r_- is anionic radius. The inter-ionic radius (R) is sum of r_+ and r_-

$$R = r_+ + r_-$$

For example R for K^+ and Cl^- is given

$$\begin{aligned} \text{as } R &= 133 \text{ pm} + 181 \text{ pm} \\ &= 314 \text{ pm} \end{aligned}$$

The above equation can be used to calculate radius of anyone ion

$$r_- = R - r_+$$

$$r_+ = R - r_-$$

Cationic Radius:- The Cationic radius is smaller than atomic radius. The reason is that cation (+ve ion) is formed by loss of electrons. So attraction between nucleus and remaining electrons increases. Thus electronic cloud reduces. Hence Cationic radius is.

Smaller than atomic radius.

e.g. $\rightarrow Na = 154 \text{ pm}$, $Na^+ = 95 \text{ pm}$

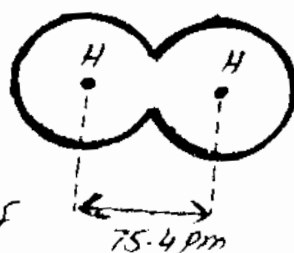
The divalent (Mg^{++}) and trivalent (Al^{+++}) ions are still smaller than atoms.

In this case due to loss of more electrons, the nucleus attracts the remaining electrons very strongly.

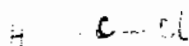
Anionic Radius:- The radius of an anion is greater than atomic radius. The reason is that an anion is formed by gain (addition) of electron. So attraction between nucleus and electrons decreases. Thus electron cloud expands. Hence anionic radius is greater than atomic radius. e.g. $Cl = 99 \text{ pm}$, $\bar{Cl} = 181 \text{ pm}$, $F = 66 \text{ pm}$, $\bar{F} = 136 \text{ pm}$

Covalent Radii:- The half of the single bond length between two similar atoms, covalently bonded in a molecule is called covalent radius of an element.

For example covalent radius of Hydrogen is 37.7 pm . It is half of the single bond length (75.4 pm) of H_2 molecule. It is shown in figure. We can find radius of one atom from radius of other atom.

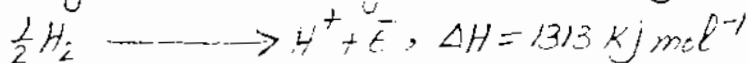
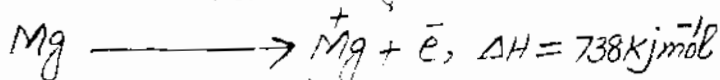


e.g. The bond length of $C-Cl$ in methyl chloride (CH_3Cl) is 176.7 pm and radius of Cl -atom is 99.4 pm . So radius of C -atom $= 176.7 - 99.4 = 77.3 \text{ pm}$



Ionization Energy

The minimum energy required to remove an electron from gaseous atom to form positive ion is called ionization energy. The process is called ionization. e.g.



The ionization energy indicates the stability of an isolated atom. Moreover ionization energy is an index to the metallic character.

- (i) The elements with low I.E are metals
- (ii) The elements with high I.E are non-metals
- (iii) The elements with intermediate I.E values are metalloids

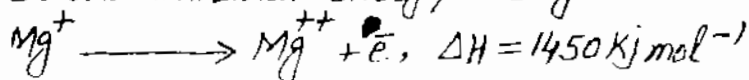
Factors influencing ionization energies

The I.E depends upon following factors

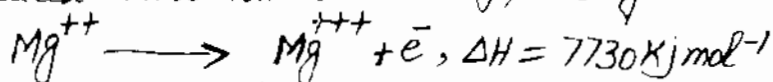
- (i) Atomic radius or atomic size
- (ii) Nuclear charge (Proton number) of atom
- (iii) Shielding effect of inner electrons
- (iv) nature of orbitals

Higher Ionization energies

The energy required to remove an electron after the removal of first electron is called second ionization energy. e.g.



The energy required to remove an electron after the removal of second electron is called third ionization energy. e.g



It is fact that

$$3\text{rd I.E} > 2\text{nd I.E} > 1\text{st I.E}$$

The reason is that after the removal of one or more electrons, the remaining electrons are held tightly by nuclear positive charge. Thus further removal of electrons requires more energy.

Ionization energy and Valency

We can guess the valency of an element from gap between first, second, third and Higher I.E values. If there is big gap between first and second I.E, then valency of element is one. Similarly if there is big gap between second and third I.E, then valency of element is two. e.g Valency of K is one

Variation of I.E in Periodic Table

(a) I.E in a group:- The ionization energy decreases from top to bottom of a group.

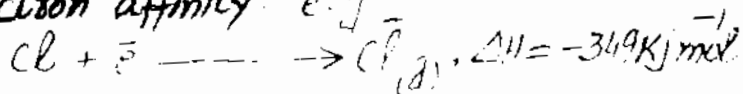
The reason is that new shells are added from top to bottom of group. Thus valence electrons are at larger distance from the nucleus. So force of attraction between nucleus

and outer electron decreases. Therefore I.E decreases down the group.

I.E in a Period:— The I.E increases from left to right of a Period. The reason is that in a Period nuclear charge increases one by one but no new shell is added. So atomic size decreases. Thus force of attraction between nucleus and outer electron increases. Therefore I.E increases in a Period.

Electron Affinity

The energy released when an electron is added to the partially filled orbital of an isolated gaseous atom in its valence energy level to form a negative ion electron affinity. e.g.



Electron affinity is the measure of attraction between nucleus of an atom and extra incoming electron.

Factors Influencing Electron Affinity

Electron affinity depend upon following factors

- Atomic radius
- Nuclear charge
- Shielding effect of inner electrons
- Nature of orbital

— In general electron affinity decreases with

increase of atomic radius. The reason is that by increasing distance between nucleus and valence electrons, the force of attraction decreases. Hence $E.A$ decreases with increase of atomic radius.

Variation of $E.A$ in Periodic Table

(i) **$E.A$ in a group:** - When we go from top to bottom in a group the Proton number increases and new electronic shells are introduced. So atomic radius increases. Thus force of attraction between nucleus and valence electrons decreases. Hence $E.A$ decreases from top to bottom in a group.

(ii) **$E.A$ in a Period:** - When we go from left to right in a Period, the Proton number increases one by one but no new electronic shell is added. So atomic radius decreases. Therefore force of attraction between nucleus and valence electrons increases. Hence $E.A$ increases from left to right in a Period.

Exceptional Cases: - The electron affinity of fluorine is less than that of chlorine. The reason is that seven valence electrons of fluorine are present in $2s$ and $2p$ subshells. These subshells have thick electronic cloud. This

- Thick electronic cloud repels the incoming electron.
- Hence E.A of Fluorine is less than that of Chlorine.

Electronegativity (برق منبیت)

- The tendency of an atom to attract a shared electron pair to itself is called electronegativity.
- For example E.N of Hydrogen = 2.1, Oxygen = 3.5, Chlorine = 3.0, Fluorine = 4.0 (The most E.N)
- The E.N of an atom is related to its I.E and E.A
- From E.N difference of two atoms we can determine the nature of bond. If E.N difference of two atoms is zero, then bond between them will be non-polar.
- If E.N difference of two atoms is more than 1.7, the bond will be ionic. If E.N difference of two atoms is 1.7, the bond will be equally ionic and covalent. Pauling calculated E.N of elements from difference between their expected (متوقع) and experimental bond energies. He devised (gave) an E.N scale. In this scale Fluorine is taken as an arbitrary standard. ^{value 4.0} The E.N has no units.
- E.N in a group:- The E.N decreases down a group. It is due to increase in atomic size. A big sized atom can not hold the electrons firmly.
- E.N in a Period:- The E.N of elements increases from left to right in a period. It is due to decrease in atomic size. A small sized atom holds the incoming electron more firmly (مقبوض).

Types of Bonds

There are three types of chemical bonds

- (i) Ionic bond
- (ii) Covalent bond
- (iii) Coordinate covalent bond.

We can explain these bonds with help of different theories. First of all we discuss the concept of bond formation

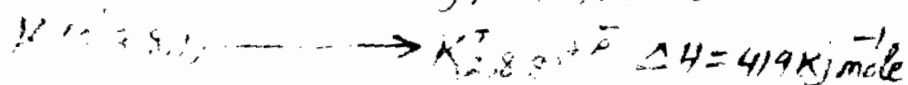
(i) **Ionic Bond**:- The bond formed by the complete transfer of electrons from an atom with low ionization energy to another atom with high electron affinity is called ionic bond OR

A strong electrostatic force of attraction between cations and anions is called ionic Bond. It is also electrovalent bond.

e.g. NaCl, KCl, CaO etc.

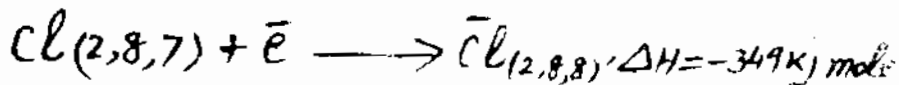
Formation of KCl:- Potassium atom loses the outermost electron and forms K^+ ion.

After the loss of an electron Potassium attains the nearest inert gas configuration. In this step energy is required which is called ionization energy of Potassium.

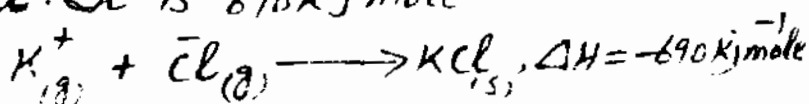


The chlorine atom gains an electron which was lost from Potassium and attains the nearest inert gas configuration of Argon. In this step, energy is

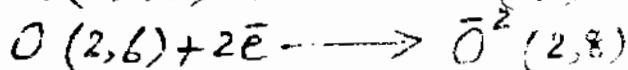
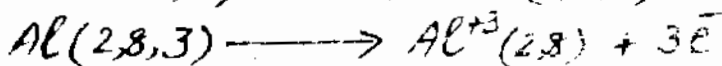
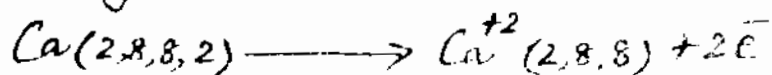
released. It is called electron affinity of chlorine.



The oppositely charged ions K^+ and $\bar{\text{Cl}}$ are held together by strong electrostatic force of attraction. In this step energy is released. It is called lattice energy of KCl. It is 690 kJ mole^{-1}



The elements of group I-A (Li, Na, K, Rb, Cs) are good losers of electron. The elements of group VII-A (F, Cl, Br, I) are good gainers of electron. So these atoms form ionic bonds. The formation of some positive and negative ions is given below.



CaO contains Ca^{+2} and $\bar{\text{O}}^2$ in ratio 1 : 1

Al_2O_3 contains Al^{+3} and $\bar{\text{O}}^2$ ions in ratio 2 : 3

A bond is said to be ionic if electronegativity difference of two atoms is more than 1.7

There is no bond with 100% ionic character

e.g. NaCl has 72% ionic character and

CsF has 92% ionic character

Covalent Bond (electron pair bond)

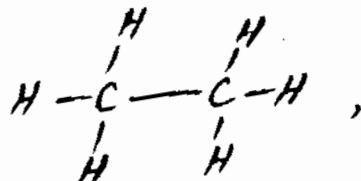
According to Lewis and Kossel, a bond formed by the mutual sharing of electrons between two atoms is called Covalent bond.

e.g. $H-H$, $Cl-Cl$, $H-Cl$, $O=O$

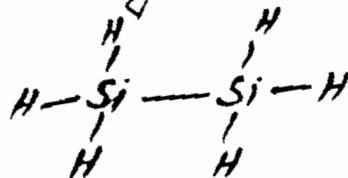
A bond formed by sharing one electron pair between two atoms is called Single Covalent bond.

A bond formed by sharing two electron pairs between two atoms is called double Covalent bond. A bond formed by sharing three electron pairs between two atoms is called triple Covalent bond. They are represented by single line ($-$), double line ($=$) and triple line (\equiv) respectively. Examples are given below. The molecule of H_2 makes a single bond, the molecule of O_2 makes a double bond and the molecule of N_2 makes a triple bond. $H-H$, $\ddot{O}=\ddot{O}$ and $\ddot{N}\equiv\ddot{N}$

Ethane and disilane have single bonds

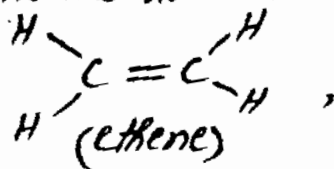


(ethane, C_2H_6)

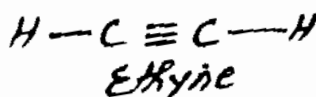


(disilane, Si_2H_6)

Ethene has double bond and Ethyne has triple bond



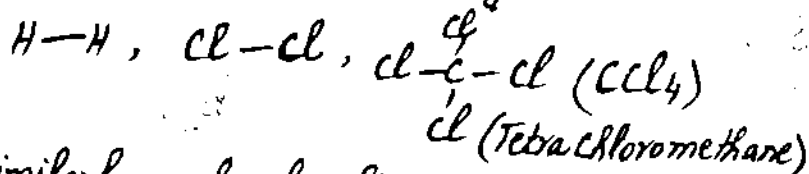
(ethene)



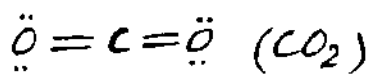
Ethyne

A covalent bond may be non-polar or Polar in character.

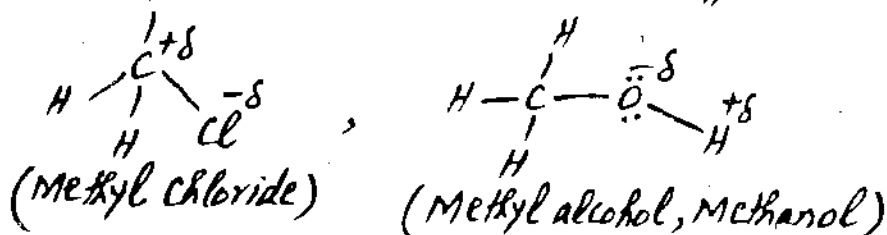
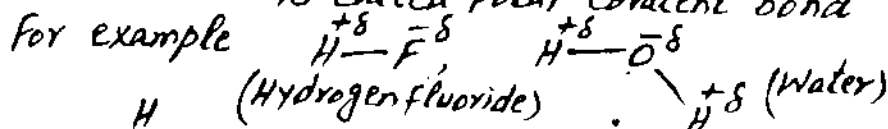
(i) **Non-Polar Covalent bond:-** A covalent bond between two alike atoms is called non-polar covalent bond. OR A covalent bond in which bonding pair of electrons is equally shared between bonded atoms is called non-polar bond. Examples are given below.



Similarly molecules like CH_4 , SiH_4 , SiCl_4 and CO_2 are non-polar due to symmetry of structure. In these molecules each bond is polar but all dipoles cancel due to molecular symmetry. Hence molecules are non-polar overall.



(ii) **Polar Covalent bond:-** A covalent bond between two unlike atoms is called polar covalent bond. OR A covalent bond in which bonding pair of electrons is not equally shared between bonded atoms is called polar covalent bond. For example

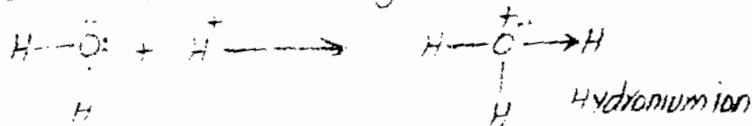


Coordinate Covalent Bond

A Covalent bond in which shared pair of electrons is donated by one atom is called Coordinate Covalent bond. An atom which donates electron pair is called donor and atom which accepts an electron pair is called acceptor.

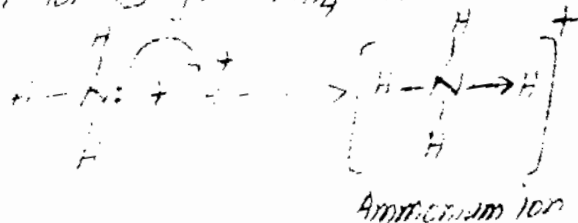
A coordinate bond is represented by an arrow \rightarrow from donor to acceptor

Examples:- in which water donates electron pair to H^+ ion, then H_3O^+ ion is produced.



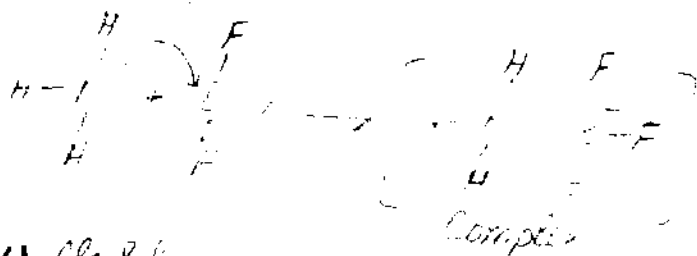
In H_3O^+ ion, every bond is 33% Coordinate and 66% Covalent in character.

(ii) Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion.

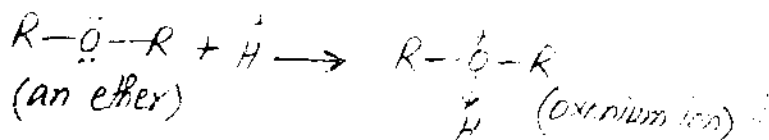
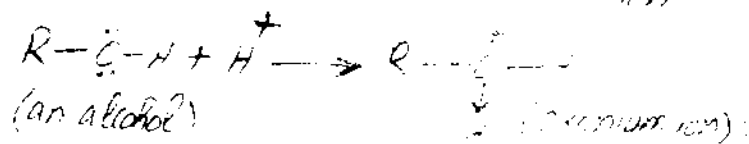


(iii) NH_3 has a lone pair of electrons.

BF_3 is electron deficient molecule due to incomplete octet of Boron. Therefore, NH_3 donates electron pair to BF_3 with the formation of coordinate covalent bond complex.



(iv) Alcohols and ether can also form coordinate covalent bonds with H^+ ion



Modern theories of Covalent bond (Limitations of Lewis model)

Lewis model explains about the formation of bonds by transfer and sharing of electrons.

It has following limitations

- (i) It cannot explain shape of molecules
- (ii) It cannot explain bond polarity
- (iii) It cannot explain bond length and bond energy. Since it does not explain the above facts clearly.

- (1) Valence shell electron pair repulsion theory
- (2) Valence bond theory (3) Molecular orbital theory. The 3rd theory can explain the above facts clearly. It is based on quantum mechanics and quantum field theory.

Valence Shell Electron Pair Repulsion Theory (VSEPR THEORY)

Sidgwick and Powell (1940) pointed out that shape of molecules can be explained by the number of electron pairs in the outer orbit of central atom. Recently Nyholm and Gillespie gave VSEPR theory. It explains the shapes of molecules for non-transition elements.

Basic Assumption

The valence electron pairs (lone pairs, bond pairs) are arranged around the central atom to remain at maximum distance apart to keep minimum repulsions.

Postulates of VSEPR theory:-

- (i) Both the bond pairs and lone pairs of electrons determine geometry of molecules.
- (ii) The electron pairs around the central atom remain at a maximum distance to keep a minimum
- (iii) The lone pairs of electrons occupy more space than the bond pairs.
- (iv) The repulsions between electron pairs

decreases in the following order

$\text{Lone pair-Lone pair} > \text{Lone pair-bond pair} > \text{bond pair-bond pair}$

The repulsions between electron pairs are

Called Vander Waal's repulsions or exchange repulsions

(v) A multiple bond (double or triple bond) occupies more space than a single bond. However it is counted as one electron pair.

(vi) If all the electron pairs are bonding, then shape of molecule will be a regular.

(vii) If a molecule contains some lone pairs of electrons, then its structure will be not regular i.e. distorted structure.

Now we explain shapes of molecules of types AB_2 , AB_3 , AB_4 , AB_5 and AB_6 .

1 :- Molecules of type AB_2

In these molecules central atom contains two electron pairs. These electron pairs are at an angle of 180° . Thus molecules give linear geometry. ($B-A-B$)

e.g. $BeCl_2$, $MgCl_2$, $SrCl_2$, $CdCl_2$, $HgCl_2$



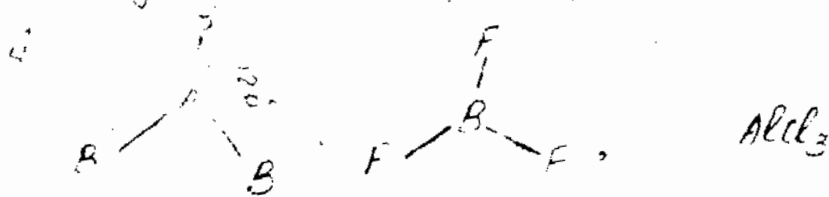
2:- Molecules of Type AB_3 :-

In these molecules central atom contains three electron pairs. Such molecules have

Further the types

(a) AB_3 -type with no lone pair :-

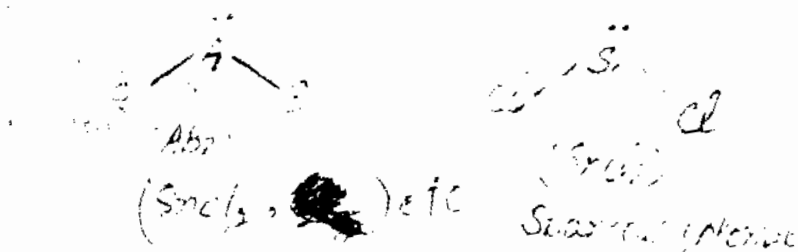
In these molecules central atom contains three bond pairs of electrons. These electron pairs are at an angle of 120° from each other. Thus molecules give planar triangular geometry.



and hydrides of group IIIA (BH_3 , BF_3 , $AlCl_3$) etc.

(b) AB_3 -Type with one lone pair :-

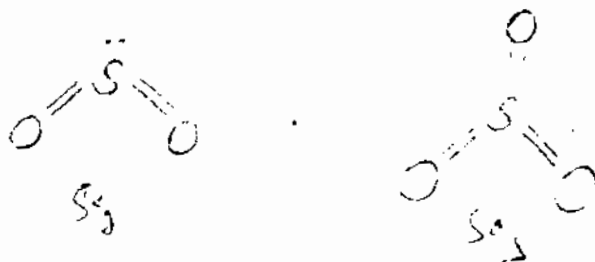
In these molecules the central atom contains one lone pair and two bond pairs of electrons. The lone pair occupies one corner of triangle. Thus molecules give bent or angular geometry. It is called distorted triangular structure.



(c) AB_3 -type with multiple bond :-

In these molecules the central atom is bonded by multiple bonds. For example in CO_2 , there

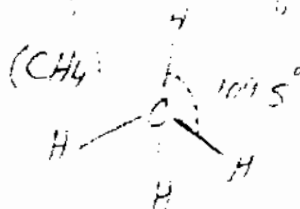
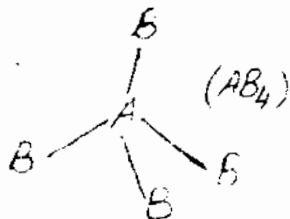
is one lone pair and two double bonds
Thus SO_2 has angular geometry. In case
of SO_3 there are three double bonds
So it has plane triangular geometry.



(3) Molecules Containing four electron pairs (AB_4 - type molecules)

(a) AB_4 -type with no lone pair :-

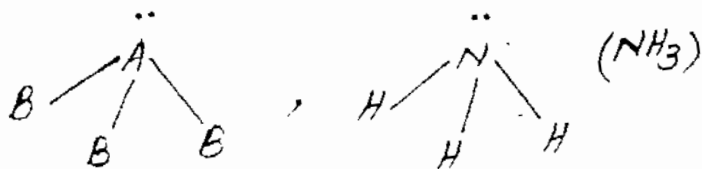
In these molecules the central atom contains four bonding pairs of electrons. These four bond pairs are directed towards the corners of tetrahedron. Each BAB angle is of 109.5° . Thus molecule gives regular tetrahedral geometry. For example methane has four bond pairs of electrons. They are directed towards the corners of tetrahedron. Each HCH angle is of 109.5° . Each tetrahedron has four corners, four faces, six edges and six angles.



In the same way molecules CCl_4 , SiCl_4 , BF_4^- , NH_4^+ , SO_4^{2-} and PF_6^- all have tetrahedral shapes.

(b) AB_3 type with one lone pair and three bond pairs

In these molecules central atom contains one lone pair and three bond pairs. Here shape becomes trigonal pyramidal (bipy) instead of regular tetrahedron. For example NH_3 , PH_3 , AsH_3 , SbH_3 and BiH_3 . In NH_3 , the lone pair of electron occupies more space than bond pairs of electrons and it exerts more repulsion on bond pairs of electron. Thus each H-N-H bond angle decreases from 109.5° to 107.5° .



In NF_3 , fluorine is the most electronegative. So N-F bond has strong polarity. Therefore lone pair exerts more repulsion on bonding pairs. Hence bond angle further shrinks to 102° .

(c) AB_2 type with two lone pairs and two bond pairs

In these molecules central atom contains two lone pairs and two bond pairs.

The lone pairs occupy more space than the bond pairs. Moreover lone pair-lone pair repulsion is greater than lone pair-bond pair and bond pair-bond pair repulsions.

Therefore molecules have bent or angular geometry. Here each bond angle decreases to 104.5° instead of 109.5°

For example, H_2O , H_2S , H_2Se , H_2Te



Valence Bond theory (VBT)

The valence bond theory explains the formation of bonds and shapes of molecules

The main points of VBT are given below.

(i) A covalent bond is formed by overlapping of partially filled atomic orbitals of two bonded atoms.

(ii) By overlap we mean a common region of two orbitals with high electron density.

(iii) During overlapping of two orbitals, their electrons become paired to get stability.

(iv) Larger the overlap, the stronger is the bond.

(v) The direction of a bond depends upon

the direction of overlapping orbitals

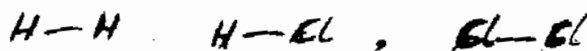
(vi) The electron density is maximum between two nuclei and bond axis.

half filled orbitals \longleftrightarrow Partially filled orbitals

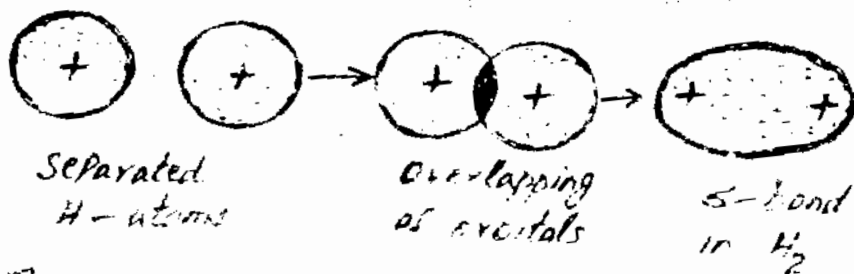
According to valence bond theory, the overlap of orbitals gives two types of bonds. They are sigma bond and pi-bond.

Sigma Bond

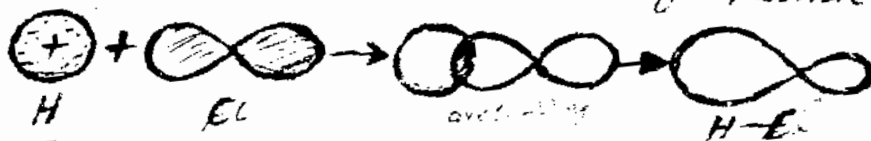
A bond formed by linear overlap of two half filled orbitals such that the probability of finding the electron is maximum around the line joining the two nuclei is called sigma-bond. A single bond between two atoms is always sigma bond. Examples of sigma bond are



The s-s overlap of two hydrogen atoms gives σ -bond in hydrogen molecule



The s-p overlap of hydrogen and fluorine atoms gives σ -bond in hydrogen fluoride



The σ bond in Cl_2 molecule is shown below



H_2S molecule:- ${}_1H = 1s$

${}_16S = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$

In Sulphur two orbitals

$3p_y^1$ and $3p_z^1$ are partially

filled. They overlap with

1s orbitals of two H-

atoms. So angle b/w

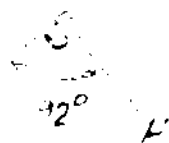
H-S bonds should be 90° . But

due to repulsion between

lone pair and bond pairs, angle

increases from 90° to 92° .

H_2S is a non-linear molecule,



π -Bond:- A bond formed by the sideways

overlap of two half filled p -orbitals

such that the probability of finding the electron

is maximum perpendicular to the line

joining the two nuclei is called π -bond.

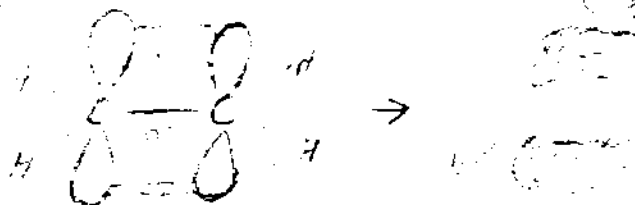
The two atoms form a T -bond only when they

are already bonded by a σ -bond. e.g. C_2H_4 .

The formation of π -bond in ethene (C_2H_4) is

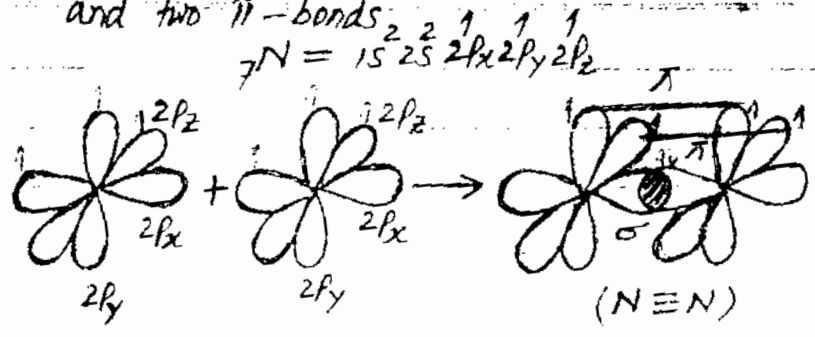
given below

Example (C_2H_4) π -bonding.



Single bond - 1 pair of electrons
Double bond - 2 pairs of electrons
Triple bond - 3 pairs of electrons
N₂ ← 289

Example The formation of σ and π -bonds in Nitrogen molecule is shown below. It has one σ -bond and two π -bonds.



Orbital Hybridization

The process in which different atomic orbitals intermix and form a new set of hybrid orbitals (دو گونہ)

→ orbitals (with same shape and energy) is called Orbital hybridization. e.g. sp^3 , sp^2 , sp etc.

The hybridization explains followings

- (i). Valency of elements.
- (ii). Shape and geometry of molecules.
- (iii). The orientation of the valency orbitals of atom.

The electrons in ground state are promoted.

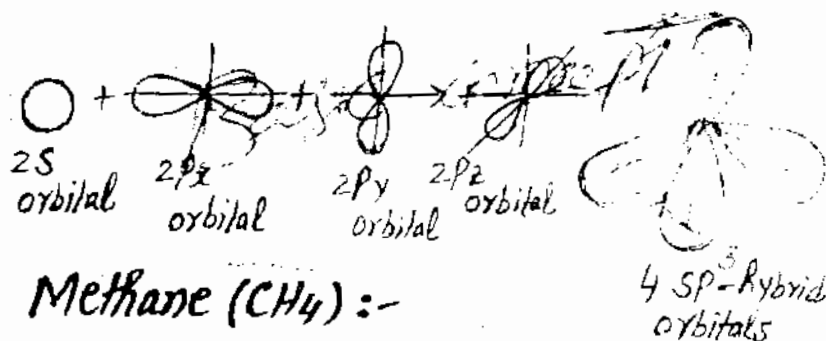
It is called excitation of orbitals. This excitation

and hybridization take place simultaneously (ایک وقت).

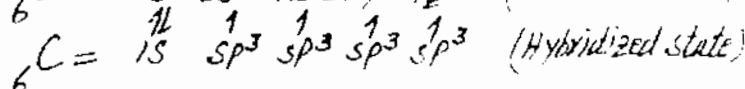
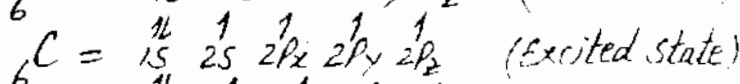
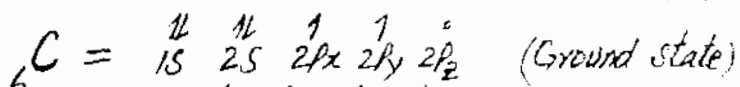
The overall energy of system decreases to get stability.

sp^3 -hybridization:- The process in which one 's' and three 'p' orbitals intermix to form four equivalent orbitals.

is called sp^3 -hybridization. The four hybrid orbitals are directed towards the corners of tetrahedron. They are at an angle of 109.5° from one another and do not lie in one plane.

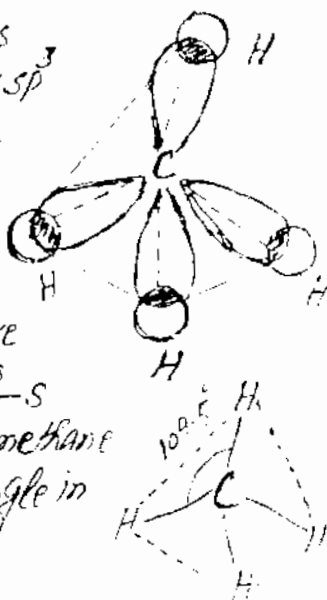


Methane (CH_4):-

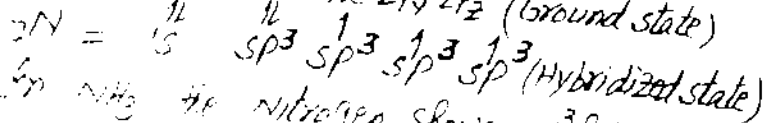
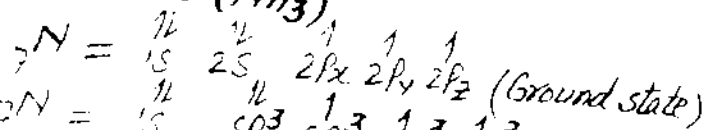


In methane Carbon shows sp^3 -hybridization. The four sp^3 hybrid orbitals are formed. They overlap with 1s orbitals of four H-atoms.

The four C-H bonds are σ bonds formed by sp^3-s overlaps. The shape of methane is tetrahedral. Each angle in methane is 109.5° .



Ammonia (NH_3)



In NH_3 the Nitrogen shows sp^3 hybridization. One s and three p orbitals intermix and form four sp^3 hybrid orbitals.

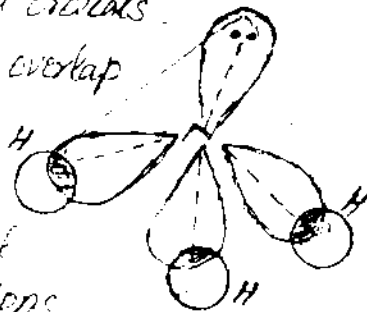
Three sp^3 orbitals overlap with 1s orbitals

of three H-atoms

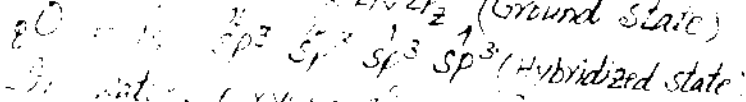
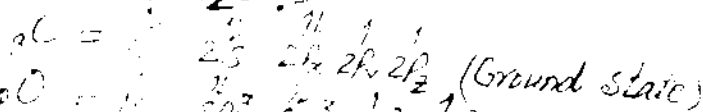
In fourth sp^3 orbital

lone pair of electrons

is present. Due to repulsion between lone pair and bond pair angle H-N-H decreases to 107.5° instead of 109.5° . The shape of molecule is pyramidal.



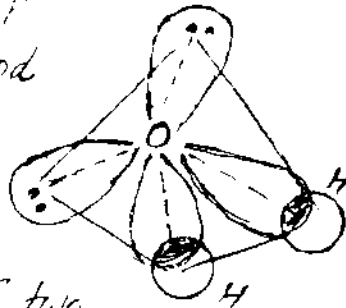
Water, H_2O :



In water, Oxygen shows sp^3 hybridization. One s and three p orbitals intermix and form four sp^3 hybrid orbitals.

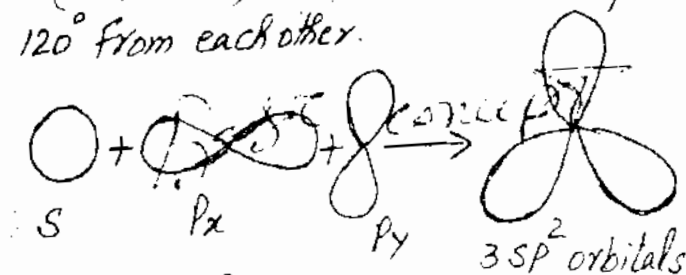
Two sp^3 orbitals overlap

with 1s orbitals of two



The bond angle $\text{H}\hat{\text{O}}\text{H}$

The process in which one 's' orbital and two 'p' orbitals intermix and form three sp^2 hybrid orbitals is called sp^2 -hybridization. The three sp^2 hybrid orbitals lie in same plane (Co-planar). They are at an angle of 120° from each other.

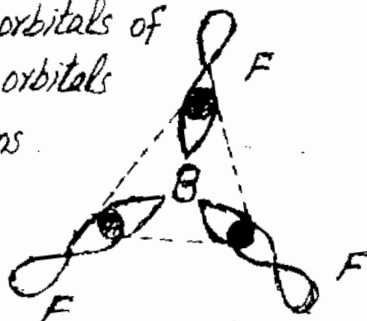

$$5B = \begin{matrix} 11 & 11 & 1 \\ 15 & 25 & 2f_x \end{matrix} \begin{matrix} 2f_y & 2f_z \end{matrix} \text{ (Ground state)}$$
$$5B = \begin{matrix} & 1s & 2s & 2p_x & 2p_y & 2p_z \end{matrix} \text{ (Excited state)}$$
$$5B = 1s^2 \quad sp^2 \quad sp^2 \quad sp^2 \quad (\text{Hybridized state})$$

<http://www.guldasta.pk/b.sc>

One 's' orbital and two 'p' orbitals intermix and form three sp^2 -hybrid orbitals...

The three sp^2 -hybrid orbitals of Boron overlap with p-orbitals of three fluorine atoms.

Each angle in BF_3 is 120° .



(b) Ethene ($CH_2=CH_2$)

${}_6C = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$ (ground state)

${}_6C = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ (Excited state)

${}_6C = 1s^2 sp^2 sp^2 sp^2 2p_z^1$ (hybridized state)

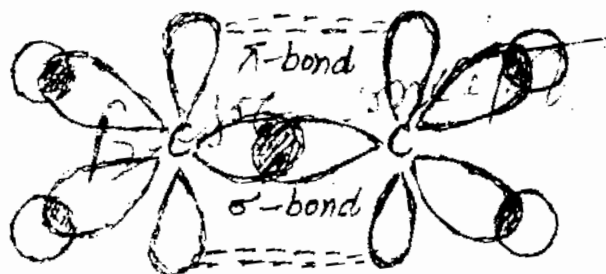
In ethene each carbon shows sp^2 -hybridization.

Three sp^2 hybrid orbitals are produced on each carbon.

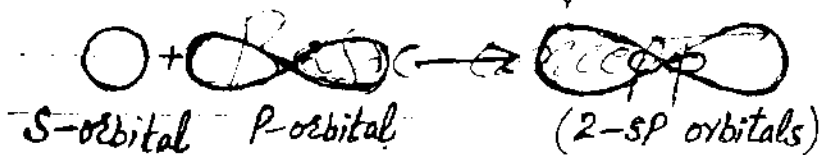
Two sp^2 orbitals of each carbon overlap with s orbitals of two H-atoms.

There is one σ -bond between two C-atoms due to sp^2-sp^2 overlap.

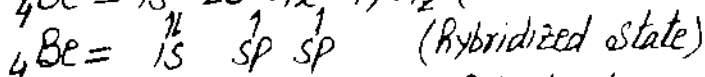
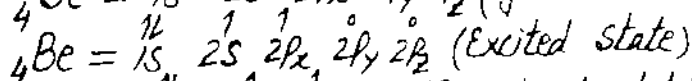
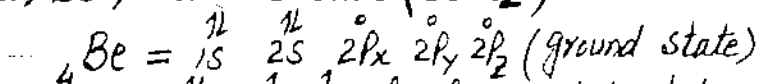
Each Carbon atom has one unhybrid "p" orbital. Their parallel overlap gives a π -bond between two carbon atoms.



SP-Hybridization:- The Process in which one 's' orbital and one 'p' orbital intermix and form two sp-hybrid orbitals is called sp-hybridization. The two sp-hybrid orbitals are on same line at an angle of 180° .

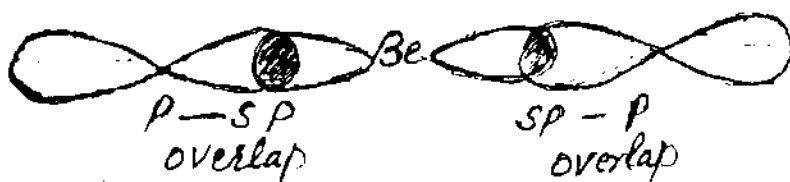


(a) Beryllium Dichloride (BeCl_2)

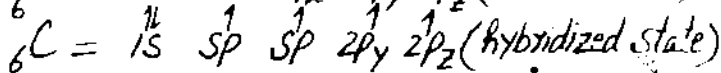
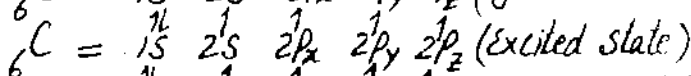
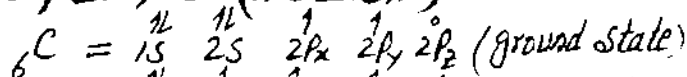


In BeCl_2 , Be shows sp hybridization.

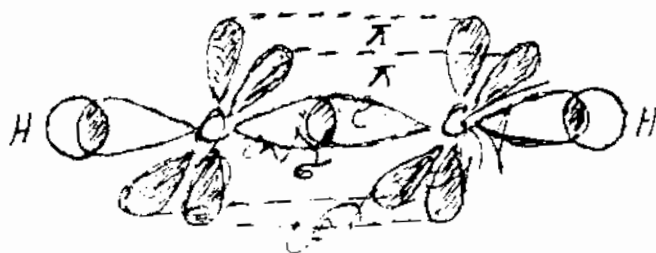
Two sp-hybrid orbitals are produced on Be. These two hybrid orbitals overlap with p-orbitals of two Chlorine atoms. Thus BeCl_2 is a linear molecule. $\text{Cl}-\text{Be}-\text{Cl}$



(b) Ethyne ($\text{HC}\equiv\text{CH}$)



In ethyne each carbon shows sp -hybridization. Two sp hybrid orbitals are resulted on each carbon. The $C-C$ sigma bond is due to $sp-sp$ overlap. The two $C-H$ bonds are due to $sp-s$ overlap. There are two unhybrid p -orbitals on each carbon atom. Two π -bonds are formed due to parallel overlaps of unhybrid p -orbitals. Ethyne is linear molecule.



Two
~~the~~ Atomic orbitals $H - C \equiv C - H$ (Ethyne)

combine to

give molecular orbitals. When one is low energy orbital and other is high energy orbital. MOT tells us the paramagnetic behaviour of orbitals.

- Molecular Orbital theory**
- (i) A molecule is a set of molecular orbitals formed by overlap of atomic orbitals.
 - (ii) An orbital which surrounds a single nucleus is called atomic orbital.
 - (iii) An orbital which surrounds two or more nuclei is called molecular orbital.

(iv) The combination of " n " atomic orbitals gives " n " molecular orbitals. Half of them are bonding and half are antibonding molecular orbitals.

(v) The molecular orbital which has lower energy than its parent atomic orbitals is called bonding molecular orbital.
 e.g. σ , π -orbitals

(vi) The molecular orbital which has higher energy than its parent atomic orbitals is called anti-bonding molecular orbitals. e.g. σ^* , π^* etc.

(vii) The molecular orbitals are filled by electrons according to Aufbau principle, Pauli exclusion principle and Hund's rule which are also applied to the filling of atomic orbitals.

Formation of Molecular Orbitals:

Molecular orbitals are formed due to

(i) S-S overlap (ii) P-P overlap

(i) S-S overlap:- When two S-orbitals overlap, then two molecular orbitals are produced.

σ is called bonding MO and σ^* is called antibonding MO.

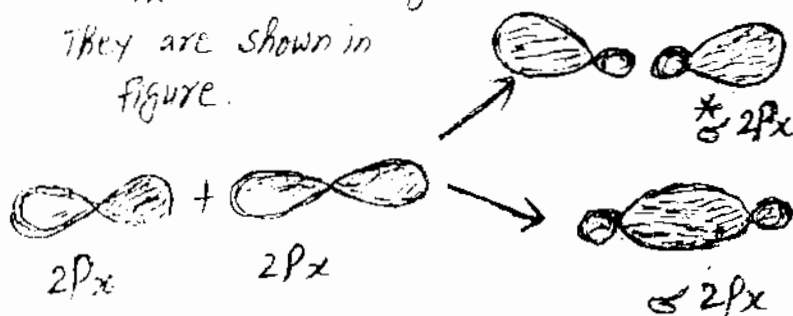


(ii) **P-P overlap**:- There are two types of P-P overlap.

(a) Head on approach (b) Sideways approach.

(a) **Head on approach**:- The overlap of two P-orbitals along the same axis is called head on approach. They give two molecular orbitals. The $\sigma 2p_x$ is bonding M.O and $\sigma^* 2p_x$ is antibonding M.O.

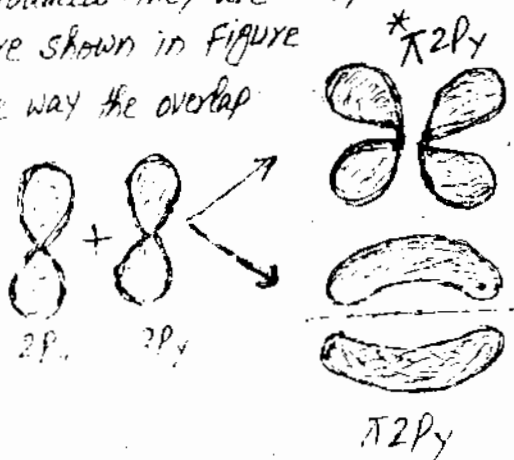
They are shown in figure.



(b) **Sideways approach**:- The overlap of two P-orbitals (p_y, p_z) along the parallel direction

is called sideways approach. The two molecular orbitals are produced. They are $\pi 2p_y$ and $\pi^* 2p_y$. They are shown in figure.

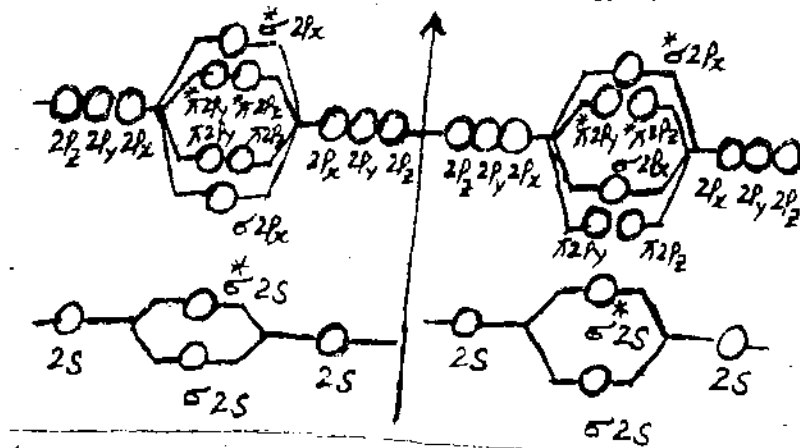
In the same way the overlap of two $2p_z$ orbitals produces $\pi 2p_z$ and $\pi^* 2p_z$ M.O.s



Relative Energies of Molecular Orbitals

The relative energies of molecular orbitals are determined by spectroscopic measurements. There are two types of orders of energy. The order of energy for O_2 , F_2 and their ions is $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi_{2p_y}^* = \pi_{2p_z}^* < \sigma_{2p_x}^*$.

The order of energy for Li_2 , Be_2 , B_2 , C_2 and N_2 is $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi_{2p_y}^* = \pi_{2p_z}^* < \sigma_{2p_x}^*$. These two types of order are shown below.



(M.O. Energy diagram for)
 F_2 , O_2 and their ions

(M.O. Energy diagram for)
 Li_2 , Be_2 , B_2 , C_2 and N_2)

Reason:- In case of Li_2 , B_2 , C_2 and N_2 , the energy of σ_{2p_x} is higher than $\pi_{2p_y} = \pi_{2p_z}$ MOs. It is explained as follows. The difference of energy between atomic orbitals $2s$ and $2p_x$ is small. So they mix up and show hybridization. Thus the molecular orbitals σ_{2s} and σ_{2s}^* do not have pure s -character. Similarly σ_{2p_x} and $\sigma_{2p_x}^*$ do not have pure p -character. All these four MOs show sp -character. Due to this mixing the MOs σ_{2s} and σ_{2s}^* get lower energy and more stability. The MOs σ_{2p_x} and $\sigma_{2p_x}^*$ get higher energy and less stability. The energy of $\pi_{2p_y} = \pi_{2p_z}$ remain

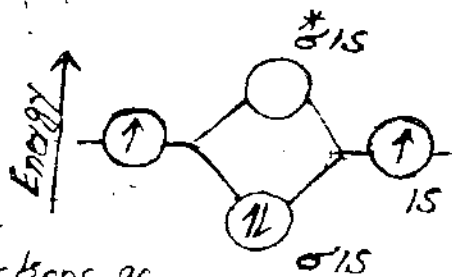
unchanged because they do not involve in mixing the molecules O_2 and F_2 do not do so. The reason is that difference of energy in their orbitals $2s$ and $2p$ is high. These differences of energy are 2078 kJ mol^{-1} for O_2 , 1595 kJ mol^{-1} for F_2 , 554 kJ mol^{-1} for Boron, 846 kJ mol^{-1} for Carbon and 1195 kJ mol^{-1} for Nitrogen.

Bond Order: - The number of bonds formed between two atoms after the overlapping of their atomic orbitals is called Bond order. It is half of the difference between the number of bonding electrons and anti-bonding electrons e.g. the bond order of Hydrogen is one.

Molecular Orbital Structures of Molecules

(i) Hydrogen, H_2 :-

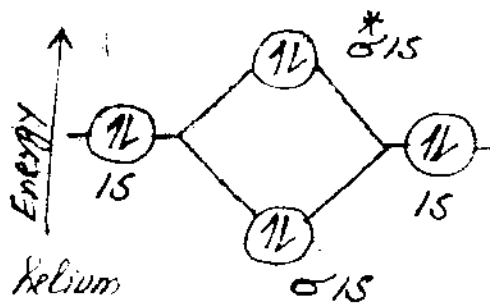
The $1s$ orbitals of two Hydrogen atoms combine and give two molecular orbitals (σ_{1s} and σ^*_{1s}). Each H-atom provides one electron. Two electrons go to B.M.O σ_{1s} and A.B.M.O σ^*_{1s} remain empty.



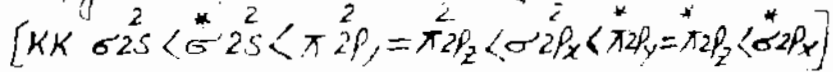
$$\text{Bond order} = \frac{2 - 0}{2} = 1$$

(ii) Helium, He_2 :-

The $1s^2$ orbitals of two Helium atoms combine and give two molecular orbitals (σ_{1s} and σ^*_{1s}). Each Helium atom provides two electrons. Two electrons go to B.M.O σ_{1s} and two electrons go to A.B.M.O σ^*_{1s} . Bond order = $\frac{2 - 2}{2} = 0$. Because bond order of He_2 is Zero. So He_2 molecule is not formed.



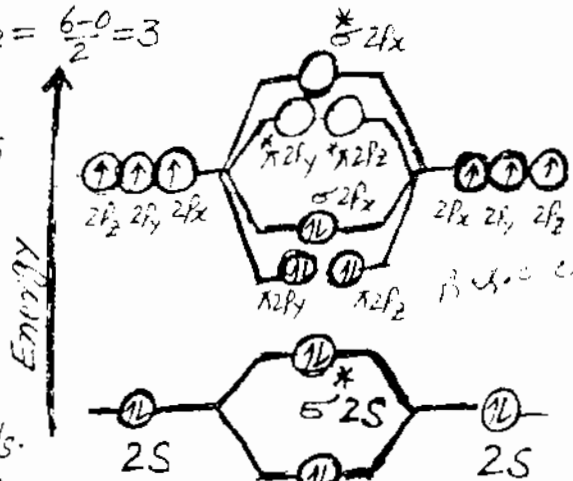
(iii) Nitrogen, N_2 :- The molecular orbital diagram of N_2 molecule is shown in figure. The electronic configuration of N_2 molecule is given as



$$\text{Bond order in } N_2 = \frac{6-0}{2} = 3$$

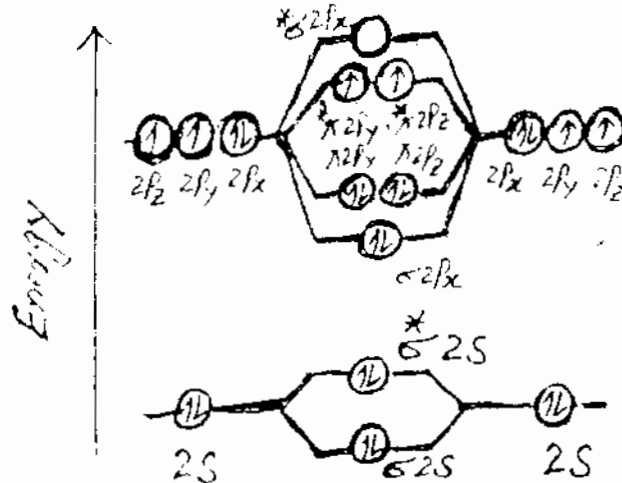
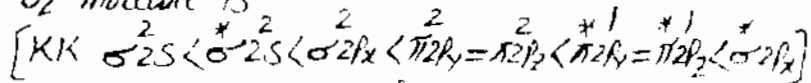
It means that N_2 molecule has a triple bond.

This triple bond consists of one σ bond and two π bonds.



(iv) Oxygen, O_2 :-

The M.O. diagram of O_2 molecule is shown in figure. The electronic configuration of O_2 molecule is



The bond order of O_2 is two

$$\text{Bond order of Oxygen} = \frac{6-2}{2} = 2$$

It means that O_2 molecule has a double bond. The last two electrons in the $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals remain un-paired. Due to two un-paired electrons liquid oxygen is attracted towards the magnet. Thus O_2 shows Paramagnetic Properties.

The V.B and VSEPR theories can not explain the Paramagnetic nature of oxygen. Hence MO theory is superior than V.B and VSEPR theories. When O_2 takes two electrons, then O_2^{2-} is formed. It has no un-paired electrons. So it has no Paramagnetic Property. When O_2 loses two electrons, then O_2^{+2} is formed. It has no Paramagnetic Property. The bond order of O_2^{2-} is one and that of O_2^{+2} is three.

Bond Energy

The average amount of energy required to break all bonds of Particular type in one mole of a substance is called bond energy or bond enthalpy. e.g Bond energy of H_2 is 436 KJ/mol

The enthalpy change in splitting a molecule into its component atoms is called enthalpy of atomization. The bond energy is given in KJ/mol . It is the energy required to break an Avogadro's number (6.02×10^{23}) of bonds.

The bond energy of a multiple bond is greater than that of a single bond. A double bond is not twice as strong as a single bond. A triple bond is not thrice as strong as a single bond. It means that σ -bond is stronger than π -bond. Similarly a Polar Covalent is stronger than a non-polar Covalent bond.

→ The bond energy of a multiple bond is greater than that of a single bond. Avogadro's number of bonds are formed.

Bond Energy and Bond Strength

Bond energy depends upon strength of a bond. The stronger a bond, greater will be its bond energy ~~and vice versa~~. The strength of a bond depends upon following factors.

- (i) Electronegativity difference of bonded atoms
- (ii) Sizes of atoms
- (iii) Bond lengths.

Ionic Character and Bond Energy:-

The bond energy depends upon electronegativity difference of two bonded atoms. When a covalent bond is between two unlike atoms, then bonding electrons are not equally shared between two bonded atoms. A more electronegative atom shows more attraction for the bonding pair of electrons. So partial negative charge is produced on more E.N atom and partial positive charge is produced on less E.N atom. It is called Polarity or Ionic Character of Covalent bond. It gives extra stability to the molecule. Thus observed bond energy of a polar molecule is greater than calculated one. For example, we calculate increase in strength of H-Cl bond due to ionic character.

$$\text{Bond energy of } H_2 = 436 \text{ kJ mol}^{-1}$$

$$\text{Bond energy of } H_2 \text{ per molecule} = \frac{436}{6.02 \times 10^{23}} = 72.42 \times 10^{-23} \text{ kJ}$$

$$\text{Bond energy of one H-atom} = \frac{72.42 \times 10^{-23}}{2} = 36.21 \times 10^{-23} \text{ kJ}$$

$$\text{Bond energy of } Cl_2 = 240 \text{ kJ mol}^{-1}$$

$$\text{Bond energy of } Cl_2 \text{ per molecule} = \frac{240}{6.02 \times 10^{23}} = 39.86 \times 10^{-23} \text{ kJ}$$

$$\text{Bond energy of one Cl-atom} = \frac{39.86 \times 10^{-23}}{2} = 19.93 \times 10^{-23} \text{ kJ}$$

$$\text{Expected Bond energy of H-Cl} = 39.86 \times 10^{-23} + 19.93 \times 10^{-23} = 59.79 \times 10^{-23} \text{ kJ}$$

$$\text{Expected bond energy of HCl per mole} = 59.79 \times 10^{-23} \times 6.02 \times 10^{23} = 359.95 \text{ kJ}$$

$$\text{But experimental (observed) bond energy of HCl} = 431 \text{ kJ mol}^{-1}$$

$$C \equiv C > C = C > C - C$$

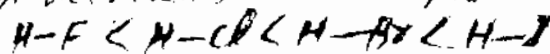
Key bond lengths are in the sp^2sp^2 order:
 Bond length: 124 pm, 133 pm, 120 pm
 $\text{C}=\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C}$

The $C=C$ bond length is 133pm . The bond length is determined by following physical techniques.

Factors affecting band length:- Following factors affect the band length of a molecule.

i) Size of atom:- When size of bonded atoms increase, then bond length of the molecule increases and vice versa.

The bond length of a molecule decreases with increase of E.N difference of bonded atoms. The reason is that ionic character (Polarity) of a bond increases with increase of E.N difference of bonded atoms. Thus atoms having more partial charges are strongly attracted. Hence bond length decreases. For example



(iii) **Type of Hybridization:** - The bond length is affected by the type of hybridization. e.g. the C-C bond length in ethane, ethene and ethyne are 154, 133 and 120 pm respectively. The reason is that ethane, ethene and ethyne have sp^3 , sp^2 and sp hybridization respectively. Moreover ethene and ethyne have π -bond which reduces the bond length. ^{size} ^{simultaneously} ^{change as} ^{bond} ^{length} ^{increases} as we go from top to bottom of a group. For example in group IVA Si-Si bond length is greater than C-C length. In group VA P-P bond length is more than N-N bond length. The reason is that from top to bottom of a group atomic radii increase due to addition of new electronic shells.

Bond length in a Period:-

The bond length decreases from left to right of a period. For example in the 2nd period N-N bond length is shorter than C-C bond length. The reason is that from left to right of a period atomic radii decrease due to strong pull of nuclear charge and non-addition of new electronic shells.

Dipole Moment

- A vector quantity which expresses the polarity and measures the charge separation in a molecule is called dipole moment. OR The product of electric charge and distance between positive and negative centres in a molecule is called dipole moment. e.g. Dipole moment of water is 1.85 Debye, and that of HCl is 1.03 Debye

Dipole moment = Charge \times distance

$$\mu = q \times r$$

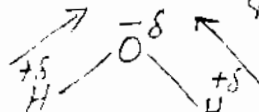
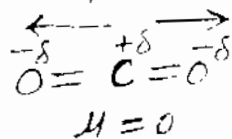
There are two units of dipole moment. They are

(i) Debye (ii) Coulomb meter

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

$$1 \text{ Debye} = 3.336 \times 10^{-30} \text{ Coulomb meter.}$$

A Polyatomic molecule contains two or more dipoles. So net dipole moment is the Vector sum of all bond moments. e.g. CO_2 and H_2O



Consider a hypothetical molecule ($\text{A}^+ \text{---} \text{B}^-$) in which unit negative and unit Positive charges are at a distance of 100 pm.

Here charge $q = 1.60 \times 10^{-19} \text{ Coulomb}$

$$\text{distance } r = 100 \text{ pm} = 100 \times 10^{-12} \text{ m}$$

$$\begin{aligned}\text{Dipole moment } \mu &= q \times r \\ &= 1.60 \times 10^{-19} \times 100 \times 10^{-12} \\ &= 1.60 \times 10^{-29} \text{ C.m} \\ &= \frac{1.60 \times 10^{-29}}{3.36 \times 10^{-30}} = 4.8 \text{ D}\end{aligned}$$

Applications of dipole moment

There are two applications of dipole moment

- (i) %age ionic character of a bond
- (ii) Geometry of molecules or ~~Angles~~ how the bonds.

(i) Percentage Ionic Character:-

We can find %age ionic character of a bond by comparing its observed dipole moment and ionic dipole moment.

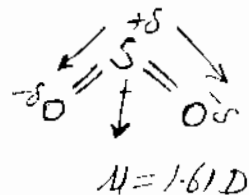
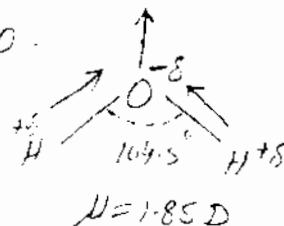
$$\% \text{age ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{ionic}}} \times 100$$

(ii) Geometry of molecules:-

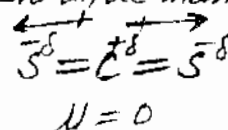
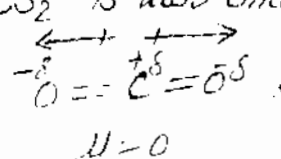
From dipole moment we can find geometry or shape of molecules.

(a) H_2O molecule:- The dipole moment of H_2O is 1.85 D. So its structure can not be linear. There are two dipoles in H_2O . They are equal but not opposite. So they do not cancel each other. Hence structure of H_2O is angular or bent.

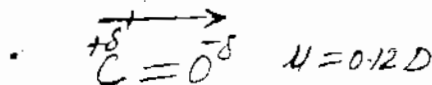
Similarly molecules H_2S and SO_2 are bent like H_2O .



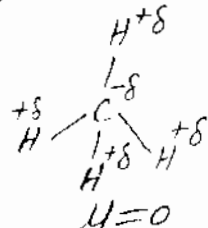
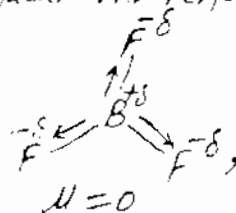
(b) CO_2 molecule :- Dipole moment of CO_2 is zero. There are two dipoles in CO_2 . They are equal and opposite. So they cancel each other. Thus CO_2 is linear molecule. Similarly CS_2 is also linear with zero dipole moment.



(c) Carbon monoxide :- Carbon monoxide has dipole moment of $0.12 D$.



(d) Symmetrical molecules :- The symmetrical molecules have zero dipole moments. The reason is that in symmetrical molecules all bond moments cancel one another. For example plane triangular and perfectly tetrahedral molecules.



The Effect of bonding on the Properties of Compounds

The Properties of Compounds depend upon the type of bonding present in them. We explain them

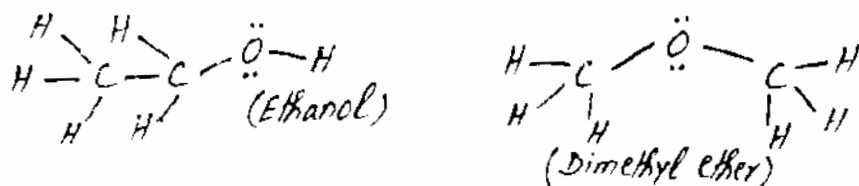
(1) Solubility:- (a) Ionic Compounds are soluble in Polar solvents (Water). When ionic crystal is placed in water, then water molecules break up the crystal lattice. So ions become free and then surrounded by water molecules. It is called hydration. The energy evolved during hydration is called hydration energy. Some ionic compounds (e.g. AgCl) do not dissolve in water because in this case hydration energy is less than the lattice energy.

(b) Covalent Compounds are soluble in non-polar solvents. e.g. benzene, ether. Some covalent compounds are soluble in water due to H-bonding e.g. Ethyl alcohol, acetic acid are soluble in water.

(2) Isomerism:- (a) Ionic compounds have electrostatic forces of forces between opposite ions. So ionic bonds are non-rigid and non-directional. It is the reason that ionic compounds do not show isomerism.

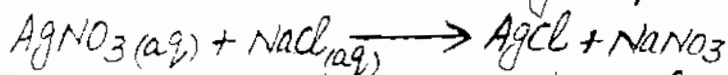
(b) The covalent bonds are rigid and directional. It is called directional nature of covalent bonds. Due to the directional nature of covalent bonds, the covalent

Compounds show structural isomerism. For example,



(3) Reaction Kinetics (speed of reaction).

(a):- The ionic reactions are very fast because they do not involve bond breaking. e.g.



This reaction takes place instantaneously because ions are already separated and new bond is formed only.

(b):- Covalent reactions are slow. The reason is that they involve breaking and formation of bonds.

EXAMPLE: The observed dipole moment of HF is 1.90 D. Find the percentage ionic character in H-F bond. The distance between the charges is 0.917×10^{-10} m. (unit positive charge = 1.6022×10^{-19} C)

Solution:- $\mu_{\text{obs}} = 1.9 \text{ D}$, $q = 1.6022 \times 10^{-19} \text{ C}$

distance, $r = 0.917 \times 10^{-10} \text{ m}$

$$\begin{aligned}
 \mu_{\text{ionic}} &= q \times r \\
 &= 1.6022 \times 10^{-19} \times 0.917 \times 10^{-10} \\
 &= 1.469 \times 10^{-29} \text{ C.m} \\
 &= \frac{1.469 \times 10^{-29}}{3.336 \times 10^{-30}} = 4.4 \text{ D}
 \end{aligned}$$

$$\begin{aligned}
 \% \text{ age ionic character} &= \frac{\mu_{\text{obs}}}{\mu_{\text{ionic}}} \times 100 \\
 &= \frac{1.90}{4.4} \times 100 = 43.2\%
 \end{aligned}$$

EXERCISE

Q.1 Select the correct statement.

- (i) An ionic compound A^+B^- is most likely to be formed when
 - (a) the ionization energy of A is high and electron affinity of B is low.
 - (b) the ionization energy of A is low and electron affinity of B is high.
 - (c) both the ionization energy of A and electron affinity of B is high.
 - (d) both the ionization energy of A and electron affinity of B is low.
- (ii) The number of bonds in nitrogen molecule is
 - (a) one σ and one π
 - (b) one σ and two π
 - (c) three sigma only
 - (d) two σ and one π
- (iii) Which of the following statements is not correct regarding bonding molecular orbitals?
 - (a) Bonding molecular orbitals possess less energy than atomic orbitals from which they are formed.
 - (b) Bonding molecular orbitals have low electron density between the two nuclei
 - (c) Every electron in the bonding molecular orbitals contributes to the attraction between atoms.
 - (d) Bonding molecular orbitals are formed when the electron waves undergo constructive interference.
- (iv) Which of the following molecules has zero dipole moment?
 - (a) NH_3 (b) $CHCl_3$ (c) H_2O (d) BF_3
- (v) Which of the hydrogen halides has the highest percentage of ionic character?
 - (a) HCl (b) HBr (c) HF (d) HI
- (vi) Which of the following species has unpaired electrons antibonding molecular orbitals?
 - (a) O_2^{+2} (b) N_2^{-2} (c) B_2 (d) F_2

Ans: (i) b (ii) b (iii) b (iv) d (v) c (vi) b

Q. 2. Fill in the blanks.

- (i) The tendency of atoms to attain maximum of _____ electrons in the valence shell is called completion of octet
- (ii) The geometrical shape of $SiCl_4$ and PCl_5 can be explained on the basis of _____ and _____ hybridizations.
- (iii) The VSEPR theory stands for _____.
- (iv) For N_2 molecule the energy of $\sigma(2p_x)$ orbital is _____ than $\pi(2p_y)$ orbital.

(vi) The paramagnetic property of \hat{O}_2 is well explained on the basis of M.O theory in terms of the presence of _____ electrons in two M.O orbitals.

(vii) The bond order of N_2 is _____ while that of Ne_2 is _____.

(viii) The values of dipole moment for CS_2 is _____ while for SO_2 is _____.

Ans: (i) eight (ii) sp^3 , sp^2 (iii) valence shell electron pair repulsion (iv) greater (v) un-pairs electron (vi) three, zero (vii) zero, 1.61D

Q 3. Give each one statements as true or false. Explain with reasons.

- (i) The core of an atom is the atom minus its valence shell.
- (ii) The molecules of nitrogen ($N \equiv N$) and acetylene ($HC \equiv CH$) are not iso-electronic.
- (iii) There are four coordinate covalent bonds in NH_4^+ ion.
- (iv) π bond is stronger than σ bond and the electrons of π bond are more diffused than σ bond.
- (v) The bond energy of heteroatomic diatomic molecules increases with increase in the electronegativities of the bonded atoms.
- (vi) With increase in bond order, bond length decreases and bond strength increases.
- (vii) The first ionization energies of the elements rise steadily with increasing atomic number from top to bottom in a group.
- (viii) A double bond is stronger than a single bond and a triple bond is weaker than a double bond.
- (ix) The bonds formed between the elements having electronegativity difference more than 1.7 are said to be covalent in nature.
- (x) The repulsive force between the two bonding pairs is less than that between the two lone pairs.
- (xi) The number of covalent bonds an atom can form is related to the number of unpaired electrons it has.
- (xii) The rules which govern the filling of electrons into the atomic orbitals also govern filling of electrons into the molecular orbitals.

Ans: (i) true (ii) false (iii) false (iv) false (v) false (vi) true (vii) false (viii) true (ix) false (x) false (xi) true (xii) true

Q 4. What is bond? A bond? Discuss the formation of ionic and covalent bonds. Give the ΔH values for H_2 and Cl_2 and compare them with the ΔH of equivalent ionic bond.

Ans: See previous page.

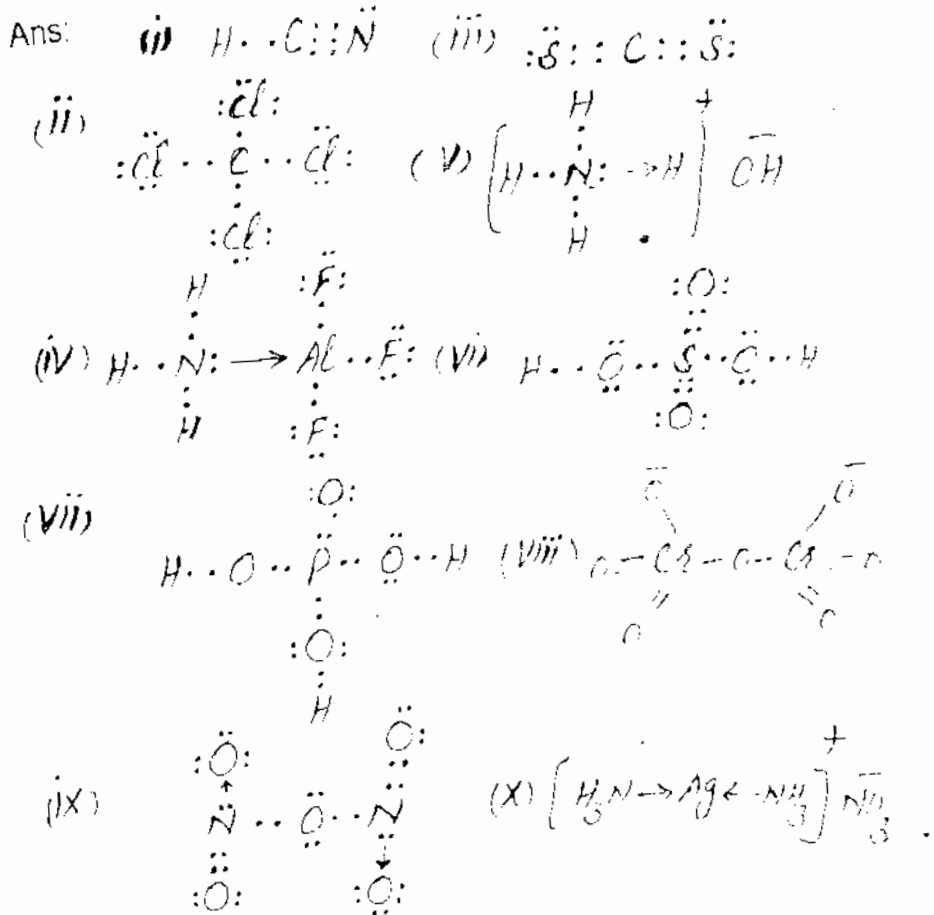
Q 5. Explain the following terms: electronegativity, electron affinity, bond enthalpy. How these quantities are related to each other? What factors are responsible for the variation in these quantities?

Ans: See previous page.
I respond: what do you understand by the term electronegativity? How does it vary in the periodic table? How does it affect the bond strength?

Ans: See page No. 250, 251, 252, 253

Q. 6. Write the Lewis structures for the following compounds:

- (i) HCN (ii) CCl_4 (iii) CS_2 (iv) $\text{H}_3\text{N} \rightarrow \text{AlF}_3$
 (v) NH_4OH (vi) H_2SO_4 (vii) H_3PO_4 (viii) $\text{K}_2\text{Cr}_2\text{O}_7$
 (ix) N_2O (x) $\text{Ag}(\text{NH}_3)_2\text{NO}_3$

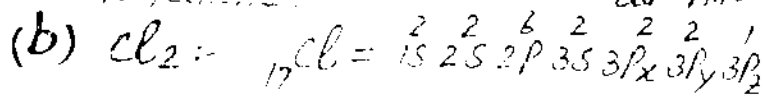


Q.7. (a) Explain qualitatively the valence bond theory. How does it differ from molecular orbital theory?

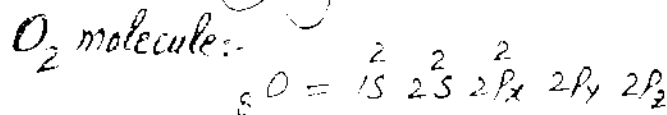
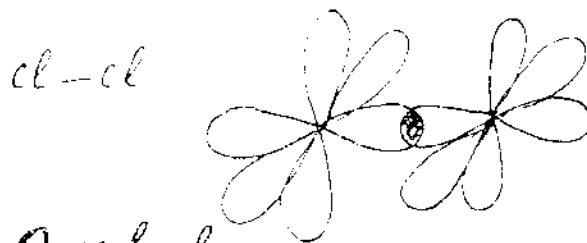
(b) How the bonding in the following molecules can be explained with respect to valence bond theory? Cl_2 , O_2 , N_2 , HF , H_2S .

According to valence bond theory, the atomic orbitals overlap to form a bond. The electron density is maximum b/w two nuclei and bond axis. There is no concept of antibonding in VBT. In VBT, molecular orbitals

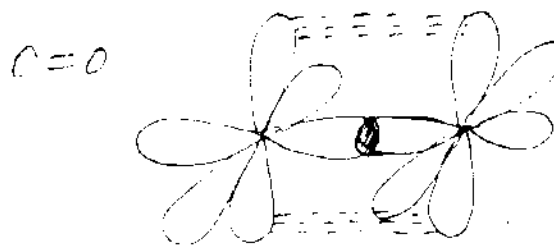
According to molecular orbital theory, atomic orbitals overlap to form bonding molecular and Anti-bonding molecular orbitals. The Electron density is maximum in bonding region. ~~an~~ ⁱⁿ MOT, molecular orbitals lose their shape. ~~NOT~~ Explain the Paramagnetic nature of O_2 , while VBT do not.



The Cl_2 molecule has a Sigma bond due to linear overlap of partially filled orbitals.



O_2 molecule has a double bond (one σ and one π)



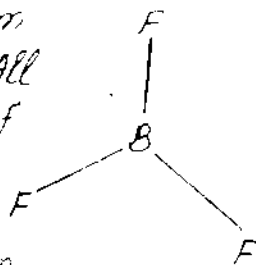
For other molecules - See page No

Q 8. Explain VSEPR theory. Discuss the structures of CH_4 , NH_3 , SO_2 , SO_3 with reference to this theory.

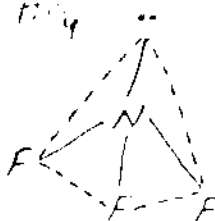
Ans: See page No. 241, 242, 243, 244

Q 9. The molecules NF_3 , BF_3 and ClF_3 all have molecular formula of the type XF_3 . But they have different structural formulas. Keeping in view VSEPR theory sketch the shape of each molecule and explain the origin of differing in shapes.

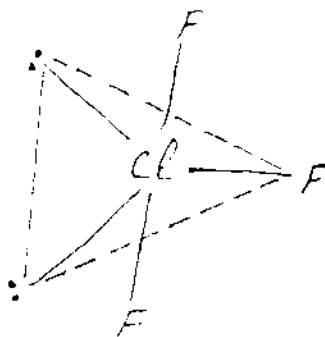
Answer:- (i) In BF_3 , the central atom boron contains three electron pairs. All three pairs are bonding. Thus shape of BF_3 is triangular planar. Each angle is of 120° . It is shown in fig.



(ii) In NF_3 , the central atom Nitrogen contains four electron pairs. Three are bonding electron pairs and one is lone pair of electrons. Thus according to VSEPR theory the shape of NF_3 will be tetrahedral.

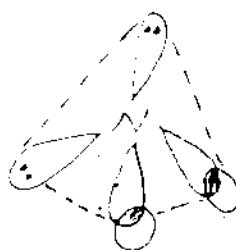


(iii) In ClF_3 the central atom Chlorine contains five electron pairs. Three pairs are bonding and two are lone pairs of electrons. Thus according to VSEPR theory the molecule ClF_3 has a T-shaped structure.

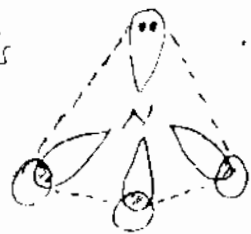


Q.10. The species NH_2^- , NH_3 , NH_4^+ have bond angles of 105° , 107.5° and 109.5° respectively. Justify these values by drawing their structures.

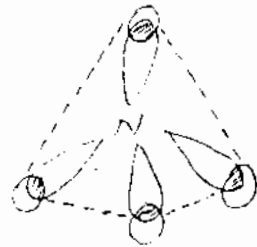
Answer:- (i) In NH_2^- , nitrogen atom forms two covalent bonds with two Hydrogen atoms. Nitrogen has two lone pairs of electrons. These lone pairs of electrons repel each other thus angle H-N-H decreases from 109.5° to 105° .



(ii) In NH_3 , nitrogen forms covalent bonds with three hydrogen atoms. There is one lone pair of electrons on nitrogen atom. The lone pair of electron repels bond pairs of electrons. Thus angle H-N-H decreases from 109.5° to 107° .



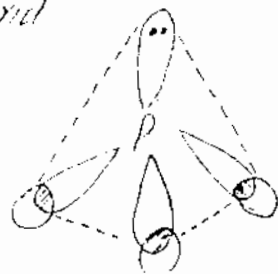
(iii) In NH_4^+ , nitrogen forms three covalent bonds and one coordinate bond. There is no lone pair of electrons on nitrogen. So NH_4^+ ion has perfect tetrahedral structure. All bond angles are equal to 109.5° .



- Q11. (a) Explain atomic orbital hybridization with reference to sp^3 , sp^2 and sp modes of hybridizations for PH_3 , C_2H_4 and C_2H_2 . Discuss geometries of CCl_4 , PCl_5 and H_2S by hybridization of central atoms.
- (b) The linear geometry of BeCl_2 suggests that central Be atom is sp -hybridized. What type of hybridization a central atom undergoes, when the atoms bonded to it are located at the corners of (a) an equilateral triangle (b) a regular tetrahedron and (c) triangular bipyramide?

Answer:- For C_2H_4 and C_2H_2 See page No. 272, 273

Hybridization for PH_3 :- In PH_3 , phosphorus shows sp^3 hybridization. Four sp^3 hybrid orbitals are required. Three sp^3 hybrid orbitals form σ -bonds with 1s orbitals of three H-atoms. In fourth sp^3 hybrid orbital one lone pair of electrons is present. Due to repulsion between lone pair and bond pairs, the angle H-P-H decreases from 109.5° to 107° .

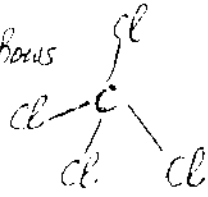


These Notes Have been Prepared
and Developed By

ADNAN SHAFIQUE

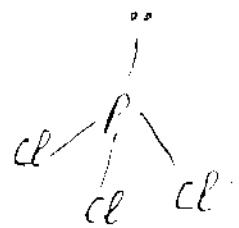
www.guldasta.pk

Geometry of CCl_4 :- In CCl_4 , Carbon shows sp^3 hybridization. Four sp^3 hybrid orbitals are formed. They overlap with p-orbitals of four Cl-atoms. So structure of CCl_4 is perfect tetrahedral. Each angle is 109.5° .



Geometry of PCl_3 :-

In PCl_3 , Phosphorus shows sp^3 hybridization. Four sp^3 hybrid orbitals are formed. They form three σ -bonds with p-orbitals of three Chlorine atoms. In the fourth sp^3 hybrid orbital a lone pair of electrons is present.



Due to lone pair-bond pair repulsion angle decreases from 109.5° to 107° .

Geometry of H_2S :- In H_2S , Sulphur shows sp^3 hybridization. Four sp^3 hybrid orbitals are formed. Two sp^3 orbitals overlap with 1s orbitals of two H-atoms. In the remaining two sp^3 orbitals, two lone pairs of electrons are present. Due to lone pair-lone pair repulsions, angle HSH decreases from 109.5° to 104.5° .



- (b):- when atoms are located at the corners of equilateral triangle, then central atoms sp^2 -hybridization.
 (ii) when atoms are located at the corners of regular tetrahedron, then central atom shows sp^3 -hybridization
 (iii) When atoms are located at the corners of a triangular bipyramide, then central atom shows dsp^2 hybridization

Q12. (a) Give the basis of the molecular orbital theory and discuss the molecular orbital configurations of the following molecules?

(i) He_2 (ii) H_2 (iii) O_2 (iv) N_2 (v) CO

(b) How does molecular orbital theory explain the paramagnetic character of O_2 , O_2^+ and O_2^- species?

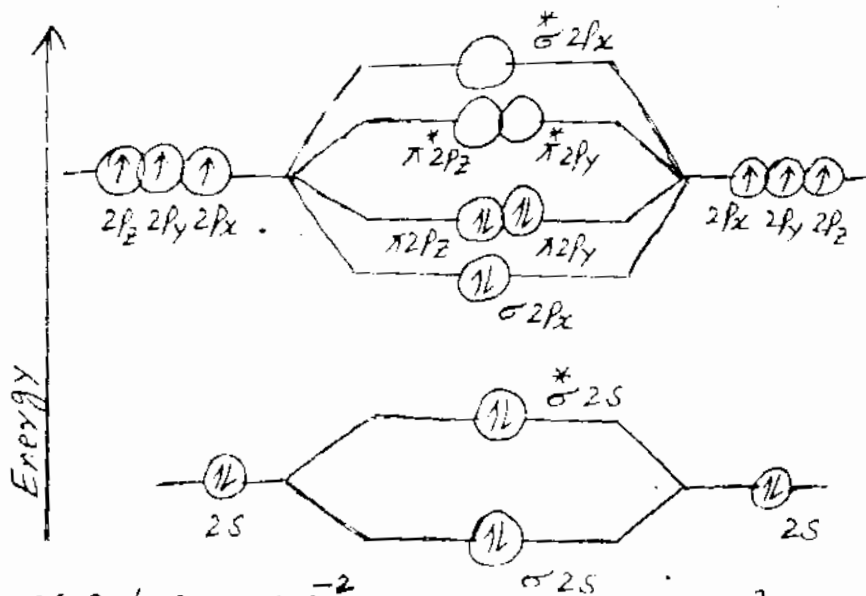
Answer:- see page No 278 . 279

M-O diagram of O_2^{+2}

The M-O diagram of O_2^{+2} is shown below. The electronic configuration of O_2^{+2} is

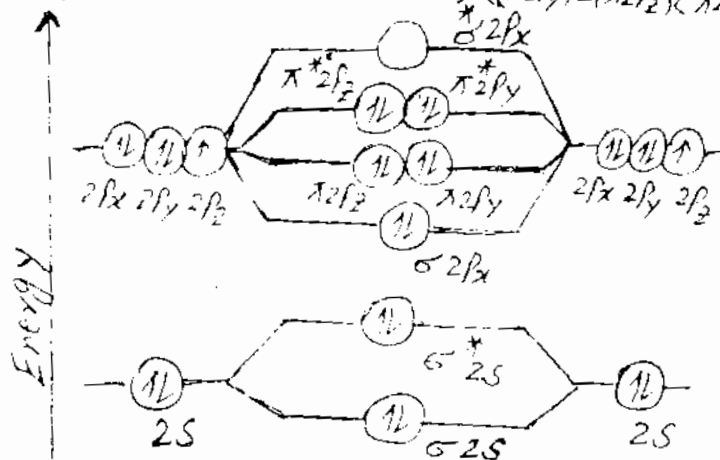
$$[KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2]$$

The bond order of $O_2^{+2} = \frac{6-0}{2} = 3$



M-O diagram of O_2^{-2} :- The M-O diagram of O_2^{-2} is shown below. The electronic configuration of O_2^{-2} is as

$$[KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2(\pi^* 2p_y)^2(\pi^* 2p_z)^2]$$



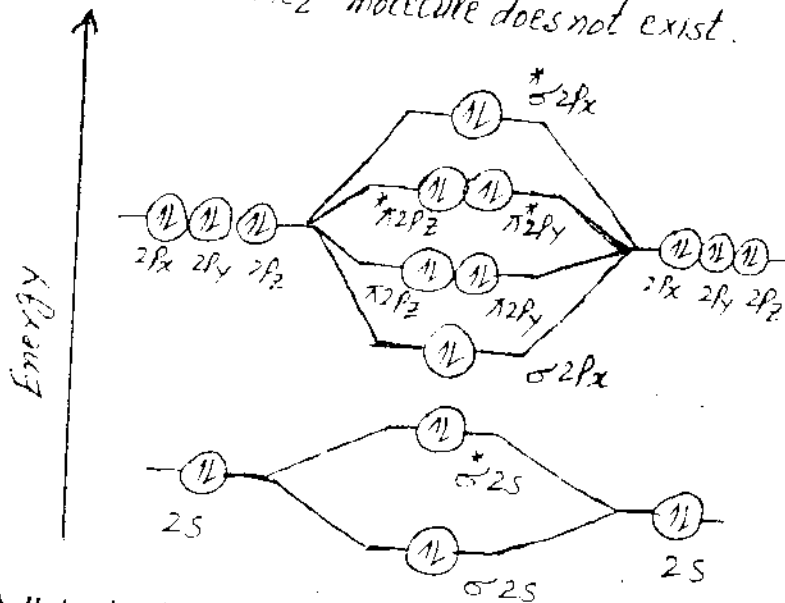
- (b) The M.O diagram of O_2 shows that two unpaired electrons are present in O_2 . So it is Paramagnetic. The M.O diagrams of O_2^{+2} and O_2^{-2} show that they have no unpaired electrons. Thus O_2^{+2} and O_2^{-2} are diamagnetic.

- Q13. a) Sketch the molecular orbital pictures of
 (i) $\pi 2p_y$ and $\pi^* 2p_y$ (ii) O_2 , O_2^{+2} , O_2^{-2} (iii) He_2 and Ne_2
 b) Sketch the hybrid orbitals of the species, PCl_3 , SF_6 , $SiCl_4$ and NH_4^+

Answer:- see page No 276, 277.

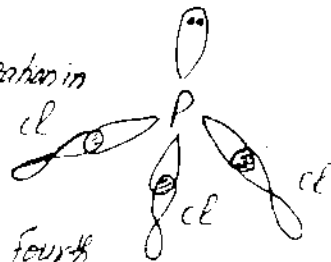
Molecular orbital Picture of Ne_2 :-

The M.O picture of Ne_2 (Neon molecule) is shown below. The bond order = $\frac{8-8}{2} = 0$. Because bond order of Neon is zero. So Ne_2 molecule does not exist.



(b) Hybrid orbital of PCl_3 :-

Phosphorous shows sp^3 hybridization in PCl_3 . The four sp^3 hybrid orbitals are formed. These form σ bonds with P-orbitals of three chlorine atoms. In fourth



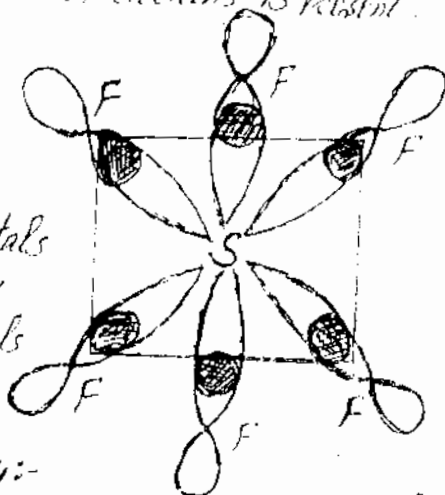
sp^3 hybrid orbital lone pair of electrons is present.

Hybrid orbital of SF_6 :-

In SF_6 , Sulphur shows

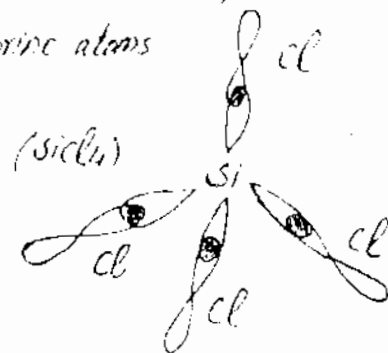
d^2sp^3 hybridization.

Six d^2sp^3 hybrid orbitals are formed. They all six overlap with p-orbitals of six-fluorine atoms.



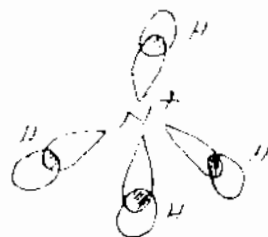
Hybrid orbital of $SiCl_4$:-

In $SiCl_4$, Silicon shows sp^3 hybridization. Four sp^3 hybrid orbitals are formed. They overlap with four p-orbitals of four Chlorine atoms.



Hybrid orbital of NH_4^+

In NH_4^+ , Nitrogen shows sp^3 hybridization. Nitrogen forms three covalent bond with three H-atoms and one coordinate bond with H^+ ion.



- Q.14.a) Define bond energy. Explain the various parameters which determine its strength.
- (b) How do you compare the bond strengths of
- (i) Polar and non-polar molecules. (ii) σ and π bonds?
- (c) Calculate the bond energy of H-Br. The bond energy of H-H is 436 kJ mol^{-1} and that of Br-Br is 193 kJ mol^{-1} .

Answer:- (a) see page No. 280, 281

(b)(i) A covalent bond between two alike atoms is called non-polar covalent bond. e.g. $\text{Cl}-\text{Cl}$, $\text{Br}-\text{Br}$.
A covalent bond between two unlike atoms is called polar bond. e.g. $\text{H}^{\delta+}-\text{Cl}^{\delta-}$, $\text{H}^{\delta+}-\text{Br}^{\delta-}$. In a polar bond the shared pair of electrons is slightly shifted towards more electronegative (E.N) atom. So atoms have partial positive and partial negative charges. Thus atoms are attracted due to extra electrostatic (dipole-dipole) forces. Hence a polar bond is stronger than a non-polar bond.

(ii) A bond formed by head to head or linear overlap of two partially filled orbitals is called σ -bond.

A bond formed by parallel overlap of two partially filled p-orbitals is called π -bond. In σ -bond, overlapping of orbitals is symmetrical on the bond axis. In a π -bond overlapping of orbitals is spread above and below the bond axis. So σ -bond is stronger than a π -bond. & ✓

(c) Bond energy of $\text{H}-\text{H} = 436 \text{ kJ mol}^{-1}$

$$\text{Bond energy of H-H per molecule} = \frac{436}{6.02 \times 10^{23}} = 7.24 \times 10^{-22} \text{ kJ}$$

$$\text{Bond energy of 1 atom of hydrogen} = \frac{7.24 \times 10^{-22}}{2} = 3.62 \times 10^{-22} \text{ kJ}$$

Bond energy of $\text{Br}-\text{Br} = 193 \text{ kJ mol}^{-1}$

$$\text{Bond energy of Br-Br per molecule} = \frac{193}{6.02 \times 10^{23}} = 3.20 \times 10^{-22} \text{ kJ}$$

$$\text{Bond energy of 1 atom of Bromine} = \frac{3.20 \times 10^{-22}}{2} = 1.60 \times 10^{-22} \text{ kJ}$$

$$\text{Bond energy of 1 molecule of H-Br} = 3.62 \times 10^{-22} + 1.60 \times 10^{-22} = 5.22 \times 10^{-22} \text{ kJ}$$

$$\text{Bond energy of H-Br per mole} = 5.22 \times 10^{-22} \times 6.02 \times 10^{23} = 314.2 \text{ kJ mol}^{-1}$$

- Q.15. (a) Define dipole moment. Give its various units. Find relationship between Debye and mc. How does it help to find out the shapes of molecules?
- (b) The bond length of H-Br is 1.4×10^{-10} m. Its observed dipole moment is 0.79 D. Find the percentage ionic character of the bond. Unit positive charge = 1.6022×10^{-19} C and $1 \text{ D} = 3.336 \times 10^{-30}$ mc

Answer: (a) See page No. 284, 285, 286

(b) Bond length of HBr, $\ell = 1.4 \times 10^{-10}$ m, $\mu_{\text{obs}} = 0.79 \text{ D}$
Unit positive charge, $q = 1.6022 \times 10^{-19}$ C

% ionic character = ?

$$\mu_{\text{ionic}} = q \times \ell = 1.6022 \times 10^{-19} \times 1.4 \times 10^{-10} = 2.24 \times 10^{-29} \text{ C m}$$

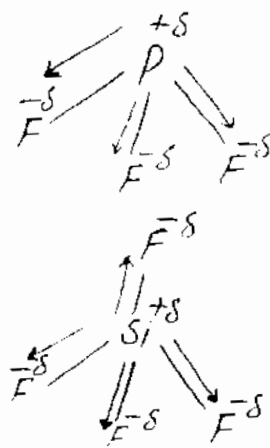
$$\mu_{\text{ionic}} = \frac{2.24 \times 10^{-29}}{3.336 \times 10^{-30}} = 6.72 \text{ D}$$

$$\begin{aligned} \% \text{ ionic character of H-Br} &= \frac{\mu_{\text{obs}}}{\mu_{\text{ionic}}} \times 100 \\ &= \frac{0.79}{6.72} \times 100 = 11.7\% \end{aligned}$$

- Q16. PF_3 is a polar molecule with dipole moment 1.02 D and thus the P-F bond is polar. Si is in proximity of P in the periodic table. It is expected that Si-F bond would also be polar, but SiF_4 has no dipole moment. Explain it?

Answer:- PF_3 is a pyramidal molecule

like NH_3 . All three P-F bonds are polar. Their polarity is not cancelled. So PF_3 has a net dipole moment of 1.02 D. On other hand SiF_4 is a perfect tetrahedral molecule. All four Si-F bonds are polar but their polarity is cancelled out. Hence net dipole moment of SiF_4 is zero.

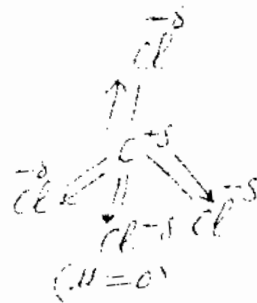


Q17. Which of the following molecules will be polar or non-polar, sketch the structures and justify your answer.

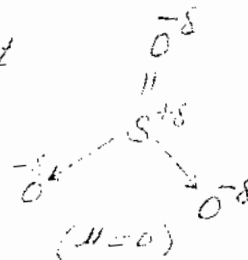
- (i) CCl_4 (ii) SO_3 (iii) SF_4 (iv) NF_3 (v) PF_5
(vi) SO_2 (vii) SF_6 (viii) IF_7

Answer:-

(i) CCl_4 :- The CCl_4 molecule is perfect tetrahedral. All C-Cl bonds are polar. Their polarities cancel each other. Thus net dipole moment is zero. So CCl_4 is a non-polar molecule.



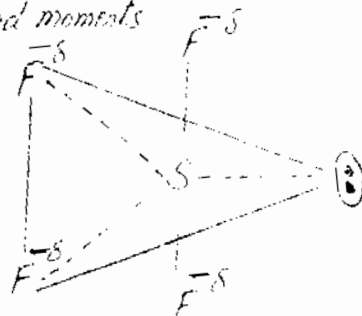
(ii) The SO_3 molecule is plane triangular. All bonds are polar but their polarities cancel each other. Thus net dipole moment is zero. So SO_3 is a non-polar.



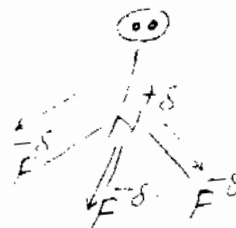
(iii) SF_4 :- The molecule SF_4 is trigonal bipyramidal. All four

S-F bonds are polar. Their bond moments do not cancel each other.

Hence net dipole moment of SF_4 is not zero. Therefore SF_4 is a polar molecule.

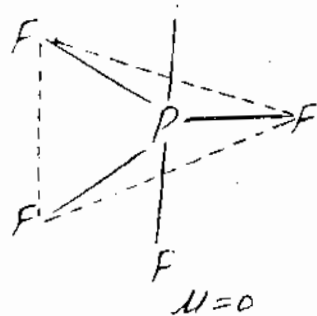


(iv) NF_3 :- The molecule NF_3 is trigonal pyramidal. All N-F bonds are polar. Their bond moments do not cancel each other. So net dipole moment is not zero. Hence NF_3 is a polar molecule.

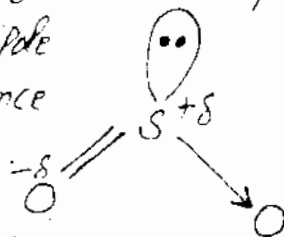


(v) PF_5 :- The molecule PF_5 is trigonal bipyramidal. All P-F bonds are polar. Their bond moments cancel each other. So net dipole moment is zero.

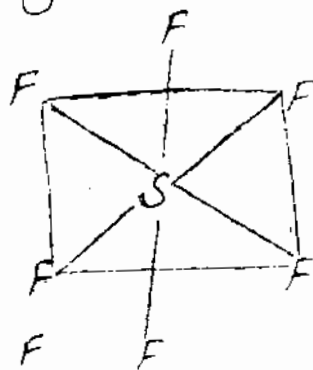
Hence PF_5 is a non polar molecule



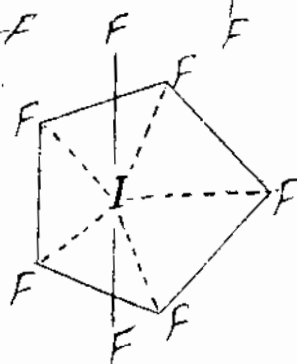
(vi) SO_2 :- The molecule SO_2 is a angular V-shaped. Two bond moments do not cancel each other. Thus net dipole moment is 1.6D. Hence SO_2 is a polar



(vii) SF_6 :- The molecule SF_6 is octahedral. All bond moments cancel one another. Thus net dipole moment is zero. Hence SF_6 is a non-Polar molecule.



(viii) IF_7 :- The molecule IF_7 is Pentagonal bipyramidal. All I-F bond moments cancel each other. So net dipole moment is zero. Hence IF_7 is a non-Polar



Q18. Explain the following with reasons:

- Bond distance is the compromise distance between two atoms.
- The distinction between a coordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+ , H_3O^+ and CH_3NH_3^+ .
- The bond angles of H_2O and NH_3 are not 109.5° like that of CH_4 . Although, O- and N-atoms are sp^3 hybridized.
- π -bonds are more diffused than σ -bonds.
- The abnormality of bond length and bond strength in HI is less prominent than that of HCl .
- Solid sodium chloride does not conduct electricity, but when electric

current is passed through molten sodium chloride or its aqueous solution, Electrolysis takes place.

(vii) The melting points, boiling points, heat of vaporization and heats of sublimations of electrovalent compounds are higher as compared with those of covalent compounds.

Answer:-(i) When two atoms come close to make a bond, then their attraction increases and P.E decreases. At a certain distance atomic attraction is maximum and energy is minimum. It is compromise distance between two atoms. Here bond formation takes place.

If atoms come further closer, then nuclear repulsions takes place and energy of system increases. Here bond formation does not occur. Hence bond distance is the compromise distance between two atoms.

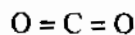
(ii) In a covalent bond two atoms provide shared pair of electrons. In a coordinate covalent bond only one atom provides a shared pair of electrons. If a molecule contains some covalent bonds and one coordinate bond then there is no difference between their bond length and bond energy. e.g. in NH_4^+ ion all four bonds are taken equally. It is the reason that distinction between covalent and coordinate covalent bond vanishes after their formation.

(iii) In NH_3 and H_2O there is sp^3 hybridization like CH_4 . Four sp^3 hybrid orbitals are formed. The angle between sp^3 orbitals should be 109.5° . But we know that NH_3 has one lone pair and H_2O has two lone pairs of electrons. There is repulsion between lone pairs and bonding pairs of electrons. Due to lone pair-bond pair repulsion the bond angles in NH_3 and H_2O are not 109.5° like CH_4 , which has no lone pair of electrons.

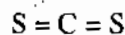
σ -bond is formed by the end-to-end overlapping of Partially filled orbitals of two atoms. Electron density is between two nuclei ~~at intermediate~~.
 π -bond is formed by the sideway overlapping of Partially filled co-planar orbitals of two atoms. Electron density is above and below the bond axis. So π -bond electron cloud is more expanded than that of σ -bond. So π -bond is more diffused than σ -bond.

- (v) In case of HI, the calculated bond strength or bond energy is 291 kJ/mol while observed bond energy is 299 kJ per mole. The small difference of 8 kJ is due to the difference of electronegativity between two bonded atom and less ionic characters. In case of HCl, the observed bond energy is 431 kJ/mol and calculated bond energy is 337 kJ per mole. The difference of both bond energies is 96 kJ/mol. Greater difference is due to the presence of greater ionic characters and greater difference of electronegativity.

- (vi) CO_2 and CS_2 are triatomic molecules. These molecules have linear structure. The polarity of molecules is cancelled out and resultant dipole moment is zero.

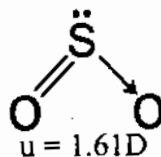


$$\mu = 0.0\text{D}$$



$$\mu = 0.0\text{D}$$

SO_2 is also triatomic molecule but it has angular shape. Polarity is not cancelled out.



- (vii) Melting and boiling points of ionic or electrovalent compounds are usually high. In ionic compound, strong interionic forces are present. Large amount of energy is required to break these forces. Ionic compounds are solid in nature while covalent compounds are usually found in solids, liquids and gases. Covalent compounds have less attractive forces between atoms.

گلدستہ ڈاٹ پی کے کی جانب سے خوش آمدید

السلام علیکم ورحمۃ اللہ وبرکاتہ

مختصر تعارف

کافی عرصہ سے خواہش تھی کہ ایک ایسی ویب سائٹ بناؤں جس پر طالب العلموں کیلئے کچھ تعلیمی مواد جمع کر سکوں۔ اللہ تعالیٰ نے توفیق دی اور میں نے ایک سال کی محنت کے بعد ایک سائٹ ”گلدستہ ڈاٹ پی کے“ کے نام سے بنائی جو کہ قرآن و حدیث، اصلاحی، دلچسپ، تاریخی قصے واقعات، اردو انگلش تحریریں، شاعری و اقوال زریں، F.Sc اور B.Sc کے مضامین کے آن لائن نوٹس، اسلامک، تفریحی، معلوماتی وال پیپرز، حمد و نعت، فرقہ واریت سے پاک اسلامی بیانات، پنجابی نظمیں و ترانے اور کمپیوٹر و انٹرنیٹ کی دنیا کے بارے میں ٹپس، آن لائن کمائی کرنے کے مستند طریقہ کار۔ کے ساتھ ساتھ اور بھی بہت سی چیزوں پر مشتمل ہے۔ اور انشاء اللہ میں مزید وقت کے ساتھ ساتھ اضافہ کرتا جاؤں گا۔ آپ کی قیمتی رائے کی ضرورت ہے۔ **عمران شفیق**

اہم نوٹ

ذیل میں جو نوٹس مہیا کیے گئے ہیں وہ کئی گھنٹوں کی لگاتار محنت کے مرتب ہوئے ہیں۔ اور آپ کو بالکل مفت مہیا کر رہے کیے جا رہے ہیں۔ آپ سے ان کی قیمت صرف اتنی سی متوقع ہے کہ ایک بار **دروڈ ابراہیمی** اپنی زبان سے ادا کر دیں۔

اللَّهُمَّ صَلِّ عَلَى مُحَمَّدٍ وَعَلَى آلِ مُحَمَّدٍ كَمَا صَلَّيْتَ عَلَى
إِبْرَاهِيمَ وَعَلَى آلِ إِبْرَاهِيمَ إِنَّكَ حَمِيدٌ مُجِيدٌ



اللَّهُمَّ بَارِكْ عَلَى مُحَمَّدٍ وَعَلَى آلِ مُحَمَّدٍ كَمَا بَارَكْتَ عَلَى
إِبْرَاهِيمَ وَعَلَى آلِ إِبْرَاهِيمَ إِنَّكَ حَمِيدٌ مُجِيدٌ