UNIT 05

Chemical Bonding & Shape of MOLECULES

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Valency

Electronic theory of valency:-

↳ In 1916, Lewis and ~~Kossel~~ Kossel purposed a theory on the basis of valence electrons to explain the concept of valency. The main postulates (or assumptions) of this theory are:-

i. The Outermost orbit of an atom is called Valence Shell and Corresponding electrons are known as Valence electrons.
ii. Only the valence electrons can participate in a Chemical Combination.
iii. The Capacity of atoms to take part in chemical Combination depends upon no. of valence electrons.
iv. The Combination of atoms takes place by transferring mutual sharing and donating of one or more valence electrons to adjust their electronic configuration like nearest noble (inert) gas.
v. The no. of electrons Lost, gained or shared by atom during chemical combination is called Valency of that element.
vi. Atoms having 8 electrons (octet) in their Outermost Shell are more stable. This is the stable state of chemical combination.
vii. The attractive forces which hold the various constituents (atom, ion) together in different chemical species are called chemical bonds.
viii. Formation of a chemical bond is accompanied by Overall decrease in energy due to redistribution of electrons.

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Octet Rule:-

↳ All noble gases except He, have 8 electrons in their valence shell. They are chemically inert (or stable). The atoms of elements other than noble gases tend to attain 8 electrons in their valence shell. The principle of attaining 8 electrons to acquire the stable electronic configuration is called octet rule.

Inert gases:-

↳ Atoms of elements other than nobel gases have less electrons than 8 and they acquire to attain octet by transferring or sharing or donating electrons.

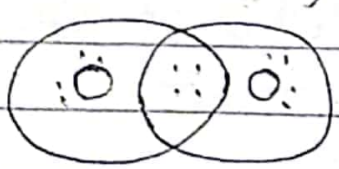
Lewis structure (or electron dot formula):-

↳ G.N. Lewis, an amerıcan scientist introduced a simple notation of valence electrons in atoms. This notation is called electron dot formula and the notation of a compound showing chemical bonds between atoms including electrons dots of these atoms is called Lewis structure.

For example:-

The electron dot formula of oxygen atom is $\cdot\ddot{O}\cdot$ 2,6

The Lewis structure of oxygen molecule is



or. $\ddot{O}=\ddot{O}$

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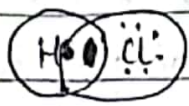
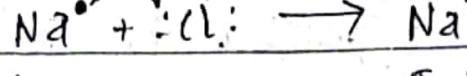
Similarly: Lewis structure of HCl,

 or $H-\ddot{Cl}:$ or $H-Cl$

Lewis Structure of NaCl:



$Na^{\bullet} + :\ddot{Cl}: \longrightarrow Na^{+}[:\ddot{Cl}:]^{-}$

(2,8,1) (2,8,7) Ionic or electrovalent bond

Note:-
Transfer of one electron is shown by using single-barbed (fish-hook) arrow (⇀) & a pair of electron by two-barbed arrow (→).

Chemical Bonds:-

↳ The attractive forces that holds together the constituent particles (ions or atoms or molecules) in a chemical species is known as chemical bond. There are three types of chemical bonds:-

1) Ionic bond (or electrovalent bond)
2) Covalent bond
3) Covalent co-ordinate bond.

Note:-

Range of weaker bond

weaker → Van der Waal > Hydrogen > metallic > co-ordinate > Covalent > Ionic ← Stronger

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[1] Ionic bond:-

↳ The electrostatic force of attraction caused by complete transfer of 1 or more valence electrons from the electro positive species to the electronegative species which holds the oppositely charged ions together, is called Ionic or electrovalent bond. This bond is formed between metal and non-metals. The no. of valence electrons involved in the formation of ionic bond is called electrovalency. The compound formed as a result of complete transfer of electrons from one atom to another atom is known as ionic compound. During the formation of an ionic bond one of the atom forms positive ion and other forms negative ion. The strong electrostatic force of attraction develops between cation and anion.

for example:- NaCl is an ionic compound. Sodium atom has one valence electron while chorine has 7 valence electrons. During the chemical combination, Sodium Loses one electron and chlorine gains one electron to form Na^+ and Cl^-. They acquire octet state.

★ Conditions for formation of ionic Compounds:-

1) Ionic bond is formed between metals and non-metals.
2) One atom should have Low value of ionization potential whereas the other atom should have high value of electron

affinity.

☆ Characteristics of ionic Compounds:-

i. State:-

↳ All ionic compounds exist in solid crystalline state at ordinary temperature because, there is strong electrostatic force of attraction between ions.

ii. Density, melting point & boiling point:-

↳ The density of ionic compounds is high because the force of attraction is strong and ions are arranged orderly in closed packed crystal form. Similarly, melting and boiling points of ionic solid are also high because large amount of heat energy is required to rupture the ionic bond.

iii. Solubility:-

↳ Ionic compounds are soluble in polar solvents like water but they are insoluble in non-polar solvents like benzene, ether, alcohol etc. Water is a polar solvent and its dielectric constant value is 82.

iv. Brittleness:-

↳ The ions of ionic crystals are orderly arranged when the crystal is hammered, the identical charged ions are brough in close with each other and the repulsive forces result

in the breaking of the crystals.

V. Electrical Conductivity:-

↳ At molten State and in aqueous ~~States~~ solution, ionic Substances contains '+ve' and '-ve' ions. These ions carry electric charges. Therefore, ionic Compounds Can Conduct electricity at molten and aqueous States. But ionic compounds cannot Conduct electricity at Solid States because ions are not mobile at solid state.

Vi. Reactions:-

↳ Reaction between ionic compounds solutions is fast because there are free ions in their aqueous solution.

Vii. Ionic Compounds are non-directional (or non-polar):-

↳ Ionic Compounds are non-polar in nature. The attractive force which binds oppositely charged ions acts equally in all directions of ionic compounds. Therefore ionic compounds are non-directional in nature.

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[2] Covalent bond:-

↳ The chemical linkage formed by mutual sharing of valence electrons between combining atoms of same or different element is called Covalent bond.
It is denoted by a dash line (—). The no. of electrons contributed by both atoms for sharing are equal which is known as covalency. The compounds formed by covalent bond is called Covalent bond Compound.
The covalent bond is formed between two similar elements having high electronegativity.
For e.g:- In hydrogen molecule, the Lewis structure of Hydrogen molecule is

H(—)H or H — H.

In Oxygen molecule, there are two covalent bonds between two Oxygen atoms. The Lewis structure of O_2 is $:\ddot{O}=\ddot{O}:$
In a nitrogen molecule, there are three covalent bonds, $\ddot{N}\equiv\ddot{N}$
Again, HCl is a covalent compound. Hydrogen atom has one valence electron and chlorine atom has seven valence electrons.
A covalent bond is formed between Hydrogen atom and Chlorine atom, Then Hydrogen attains duplet and Chlorine attains octet as $H^{\cdot} + :\ddot{Cl}: \rightarrow H-\ddot{Cl}:$

Water is also covalent compound, The Lewis structure

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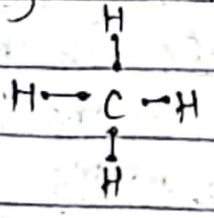
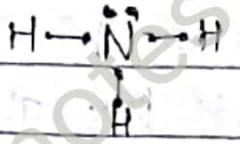
Of water molecule is;

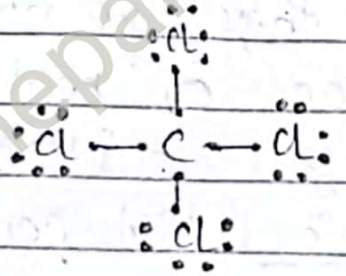
Similarly, Methane is also covalent compound. The Lewis structure of Methane molecule is;



Ammonia is also Covalent Compound. The Lewis structure of ammonia is;

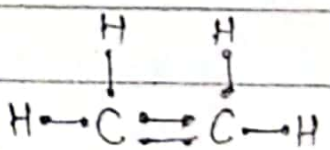


Carbon tetrachloride (CCl_4) is covalent compound. The Lewis Structure is,

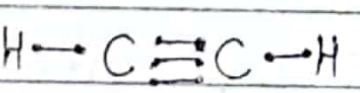


The Lewis structure of ethane and ethyne is;

Ethene (C_2H_4):-



(ii) Ethyne (C_2H_2)



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★ properties (or Characteristics) of covalent Compounds:-

i. Covalent Compounds may exist in all three physical states (solids, liquid or gaseous).

ii. The density, melting and boiling point of covalent Compounds are lower than ionic compounds. Because Covalent Compounds are held together by a weak force called vander-wall's force of attraction, which can be easily overcome by heat (except graphite & diamond).

iii. Covalent Compounds are usually insoluble in polar Solvents like water but they are soluble in non-polar Solvents like alcohol, ether, CS_2, $CHCl_3$, benzene, etc.

iv. Covalent Compounds are bad Conductor of electricity because they do not form ions in their aqueous solution or molten state (except graphite, alcohol's, carboxylic acids).

v. Rate of reaction between Covalent compounds is slow.

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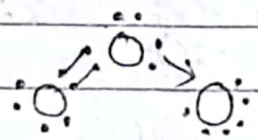
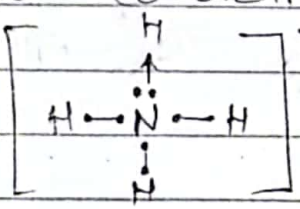
[3.] Co-ordinate Covalent bond:-

↳ The chemical bond formed by donating a lone pair of electrons from donor to acceptor is called co-ordinate covalent bond or it is also called Sami-polar or dative bond. In other words, covalent bond formed by sharing of electrons but the shared paired of electrons is contributed by only one atom. The co-ordinate covalent bond is denoted by an arrow '→' pointing towards the acceptor species. The valancy due to formation of co-ordinate covalent bond is called co-ordinate covalency and the corresponding compounds are called co-ordinate covalent compounds.
The co-ordinate covalent bond is weaker than ionic bond but stronger than covalent bond.
Examples of co-ordinate covalent compounds are:-
O_3, NH_4^+, SO_2, SO_3, CO_3^{--}, $(NH_4)_2CO_3$, Na_2CO_3, NO_2, etc.

Ozone is co-ordinate covalent molecule. It's Lewis structure is;



Ammonium (NH_4^+) ion is co-ordinate covalent species:-



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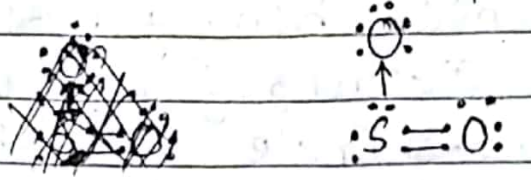
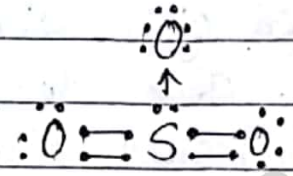
SO_2 is Co-ordinate Covalent Compound. It's lewis Structure is;



SO_3 is a Co-ordinate Covalent Compound. It's Lewis Structure is;

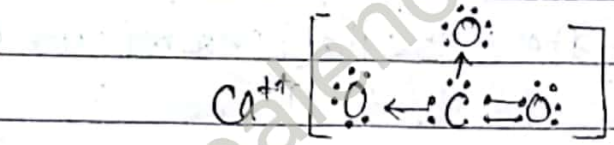


$CaCO_3$ is also a Co-ordinate Covalent Compound.

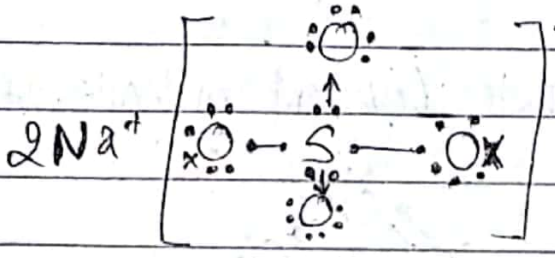
$CaCO_3 \xrightarrow{\text{ionization}} Ca^{++} + CO_3^{--}$

The Lewis structure will be;

Note:-
$C + 2e^- \rightarrow C^{--}$



Sodium thiosulphate is a co-ordinate Covalent Compound. (Na_2SO_4)



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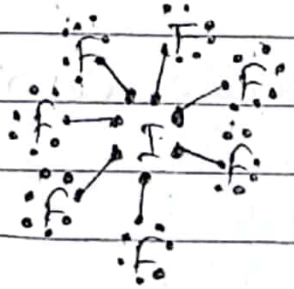
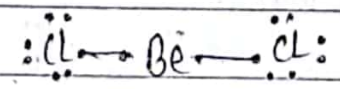
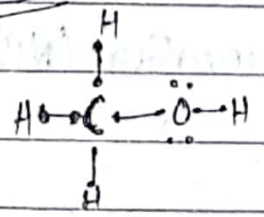


$BeCl_2$



CH_3OH



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Hydrogen Bonding:-

↳ The force of attraction which binds hydrogen atom of one molecule with more electronegative atom like F, N, O, etc. of another molecule or same molecule is called hydrogen bonding.
Hydrogen bond is a weak bond which is much weaker than a covalent bond. The bond length of hydrogen bond is the larger than that of a covalent bond. Hydrogen bond is denoted by a dotted line (------).

* Why is hydrogen bond formed (or How does hydrogen bond originate?)

↳ If hydrogen atom is linked with more-electronegative atom like F, N, O to form a covalent compound, the shared pair of electrons are displaced towards more electronegative atom. The partial displacement of bonding electrons towards the more electronegative atom causes the development of a partial negative charge (δ^-) on the atom and a partial positive charge (δ^+) on the hydrogen atom. Thus, the molecule becomes polar.
The electrostatic force of attraction between positively charged hydrogen atom of one molecule with the (-ve)ly charged atom of neighbouring molecule results in the formation of hydrogen bond as in hydrogen fluoride molecules.

$$H^{\delta+}-F^{\delta-} \cdots\cdots H^{\delta+}-F^{\delta-} \cdots\cdots H^{\delta+}-F^{\delta-}$$

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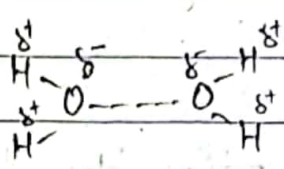
Types of Hydrogen bondings:- They are of two types:-

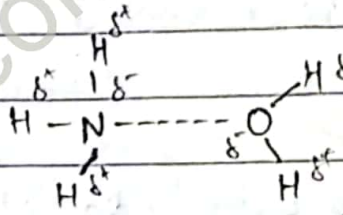
[1] Intermolecular Hydrogen bonding:-

↳ The hydrogen bond formed between two different molecules of the same compound or different compounds is known as inter-molecular hydrogen bonding. For e.g:- hydrogen bond in ammonia molecule and water molecule

(a) Water

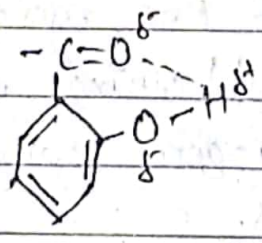


(b)

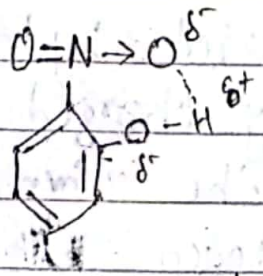


[2] Intramolecular hydrogen bonding:-

↳ The hydrogen bond formed between the hydrogen atom and the highly electronegative atom like F, N, O present in the same molecule is called intramolecular hydrogen bonding. This type of bond is normally observed in the organic compounds. The effect of such type of hydrogen bond on the physical properties is negligible. For e.g:- Intramolecular H-bonding is formed in following compounds.



Salicylic acid (O-hydroxy benzoic acid)



Orthonitrophenol

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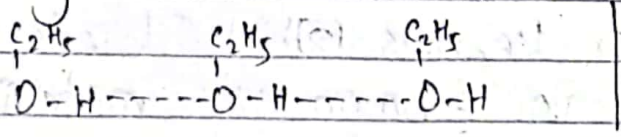
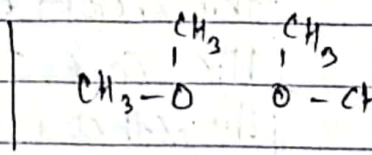
Application (or effect of Hydrogen bond on physical properties:-

↳ Hydrogen bonding brings variation on the physical properties like melting point, boiling point, solubility, surface tension, viscosity and physical state.

i. Melting & boiling point:-

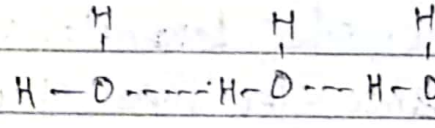
↳ The stronger the hydrogen bonding, greater will be the intermolecular attraction. Therefore, larger heat energy is required to separate these molecules before they melt or boil due to intermolecular hydrogen bonding. two or more molecules of a compound exist as associated molecules. The boiling point of ethyl alcohol (C_2H_5OH) is more than dimethyl ether (CH_3-O-CH_3) having same molecular mass. Ethyl alcohol forms intermolecular hydrogen bond but dimethyl other does not.



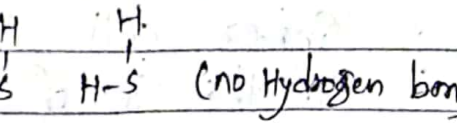


ii. Physical state:-

↳ Water exists in liquid state at ordinary temperature, but hydrogen sulphide exists in gaseous state though both oxygen & sulphur lie in the VI group of periodic table.



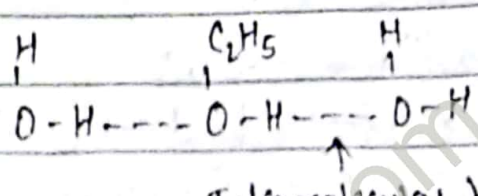
But



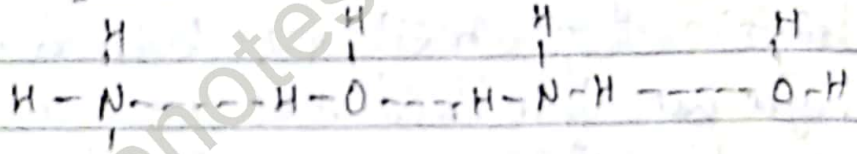
(no Hydrogen bond)

iii. Solubility of covalent Compounds:-

↳ The covalent compounds like ethyl alcohol (C_2H_5OH), ethanoic acid (CH_3COOH) are soluble in polar solvent like water due to formation of intermolecular hydrogen bond between water molecule and their molecules.



Similarly, NH_3 is soluble in water.



iv. Metallic bond:-

↳ The simultaneous force of attraction between the mobile electrons and the positive charged metallic core or kernels which binds the metal atoms together is known as metallic bond. It is very strong and a special type of bond. The metallic bond can be explained in terms of electron sea model theory.

According to this theory, metal consists of a three dimensional network of positively charged ions which include nucleus and core electrons in the inner cell called kernel. The kernels are immersed in the sea of mobile valence electrons. Thus metallic

bond can be defined as simultaneous force of attraction between the mobile valence electrons and the positive kernels.

The arrangement of metal atoms is:

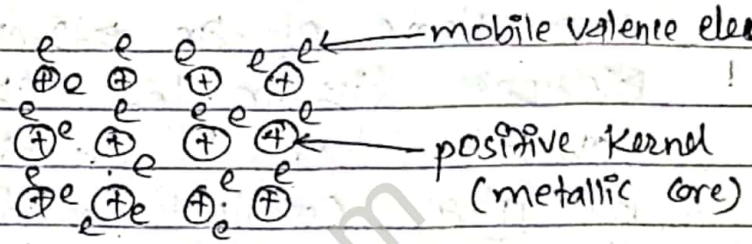


fig:- electron sea model.

Following properties of metals can be explained in light of metallic bond.

[1] Metals are hard in nature:-

↳ The strength of metallic bond increases with increasing the number of mobile valence electrons. For e.g:- iron, Copper, Gold, Silver are harder than Na, K, Li, Ca etc.

[2] Metals are good conductor of heat & electricity:-

↳ This is due to presence of mobile valence electrons.

[3] Metals possess metallic Lusture:-

↳ The mobile electrons absorb the light & get vibrated which immediately emit radiation.

[4] Metals are melleable & Ductile:-

↳ Metallic bonds are non-directional in nature. metal can be beaten into thin sheets and into wires. Since there is uniform charge distribution, on applying the stress on the metals the position of kernels is changed without destroying the crystals.

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Directional properties of Covalent Bond:-

↳ The Covalent bond is formed due to the mutual Sharing of valence electrons between combining atoms. If a Covalent bond is formed between two atoms of an Element, the shared pair of Electrons lie in the centre. Such type of Covalent bond is called non-polar Covalent bond. But if a Covalent bond is formed by sharing the Electrons of two different (hetero) atoms, the shared pair electrons will slightly be shifted towards the atom with more Electronegativity. Due to this, there is development of a partial negative charge on an atom having more Electronegativity and partial positive charge on another atom.

The appearance of a small positive charge (δ^+) on the atom having Less Electronegativity and a Small negative charge (δ^-) on the atom having high Electronegativity due to displacement of shared pair of Elections towards more Electronegative atom is called polarity, and the Covalent bond which has polar character or ionic character is called polar Covalent bond.

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Dipole moment:-

↳ The extent (or degree) of ionic character or polarity in a covalent bond is expressed in terms of dipole moment (μ). It is defined as the product of the magnitude of the charge developed (e) on any one atom and the distance of separation between the charges (d).

Mathematically,

$$\text{Dipole moment } (\mu) = e \times d$$

Dipole moment depends upon electronegativity difference of the two atoms forming the bonds. The dipole moment is a vector quantity and is represented by an arrow ($\longrightarrow$) showing the direction from positive end to negative end of the dipole.

For E.g:- $H \longrightarrow F$, $\mu = 1.91$ D

The unit of Dipole moment is Debye (D).

Note:- $1\,D = 10^{-18}$ esu cm $= 3.338 \times 10^{-30}$ Coulomb m

Greater the electronegativity difference, greater the charge separation and hence greater the ionic character in the covalent bond. and the value of dipole moment will also be greater.

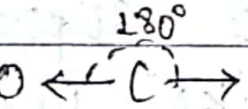
Application of Dipole moment:-

1. Distinction of polar & non-polar molecules:-

↳ If net dipole moment of a molecule is zero, the molecule is non-polar. If net dipole moment of a molecule is non-zero, the molecule is polar.
For e.g:- H_2, N_2, O_2 ($\mu = 0$), These are non-polar &
HCl, H_2O, H_2S ($\mu \neq 0$), These are polar molecules.

2. Shape of a molecule:-

↳ Dipole moment is used to find the shape of polyatomic molecules. If net dipole moment of a molecule is zero, the shape of the molecule is linear. In CO_2 molecule, there are two C=O bonds. Each C=O bond is a polar bond. This means each bond has certain dipole moment 2.3 D. Since the net dipole moment of CO_2 molecule is zero because the two dipoles are acting in opposite direction. Hence, CO_2 molecule is a linear with bond angle 180°.



3. Ionic Character of a molecule:-

↳ Greater the difference in electronegativity of bonded atoms, higher will be the ionic character of the compound.

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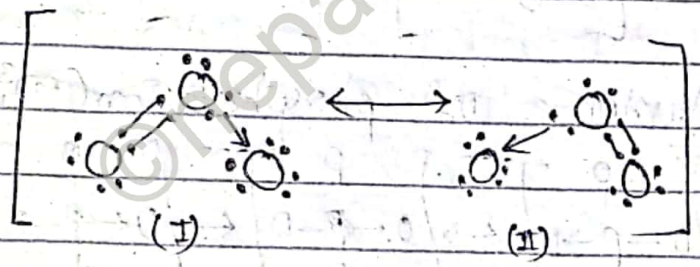
Resonance Structures (or Canonical Structures):—

↳ Some molecule can be represented by two or more Lewis structures or electronic structures having equivalent energy. The phenomenon of representation of a molecule or ion by two or more Lewis structures having equivalent energy is known as resonance. Such different structures are called resonance structures. The actual structure is called resonance hybrid of other structures which have most stability. A straight double headed arrow (↔) between resonance structures is written.

* The alternative structures and resonance hybrid structure of Ozone molecule are as:-

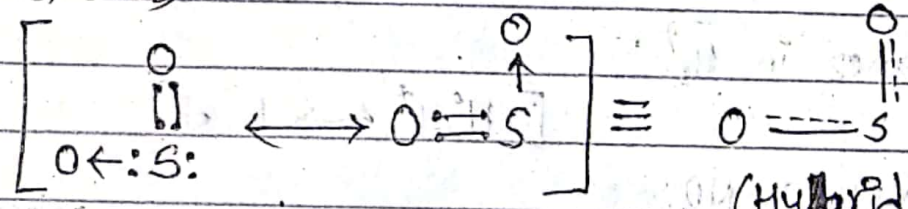


(I) (II)

Resonating (Canonical) Structures

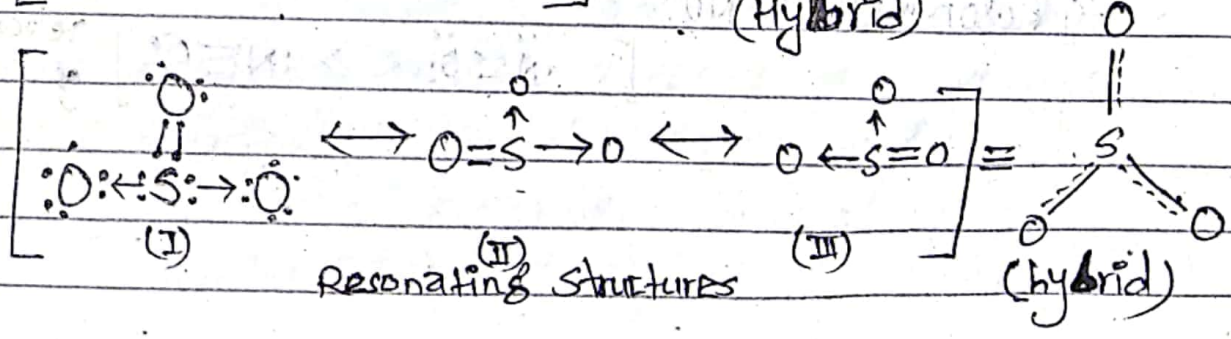
Resonance hybrid Structure

* Similarly, (SO_2):-



(Hybrid)

* (SO_3):-

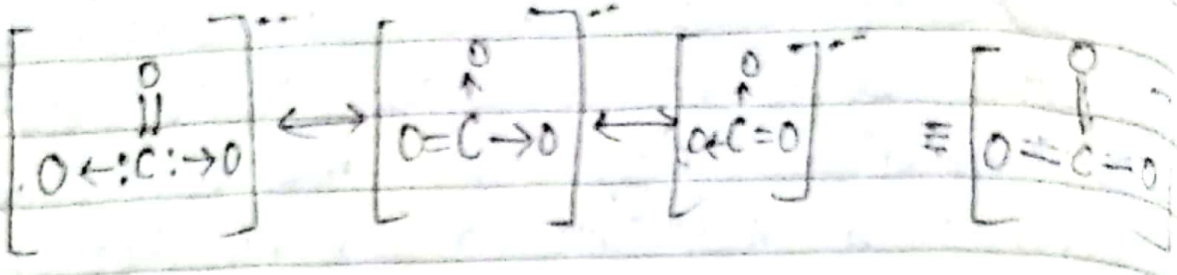


(I) (II) (III)

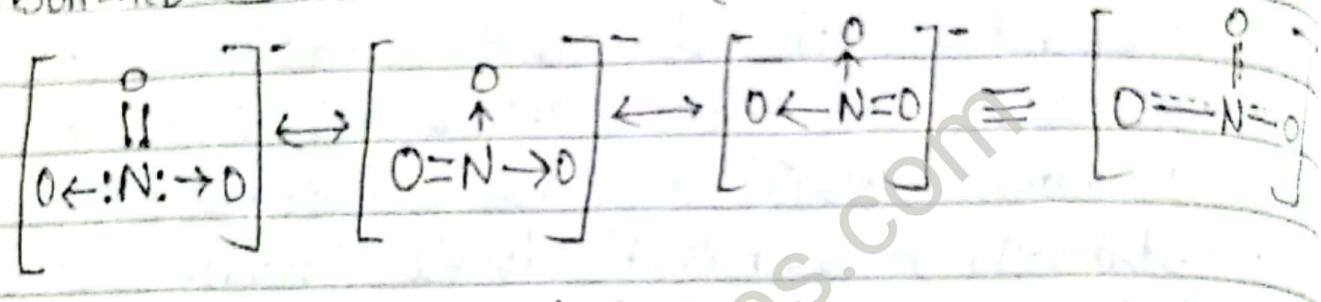
Resonating structures

(hybrid)

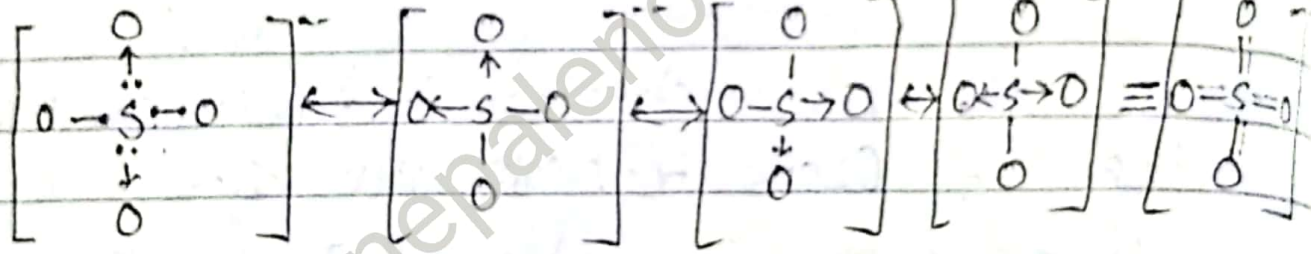
Resonance in CO_3^{2-} ion:-



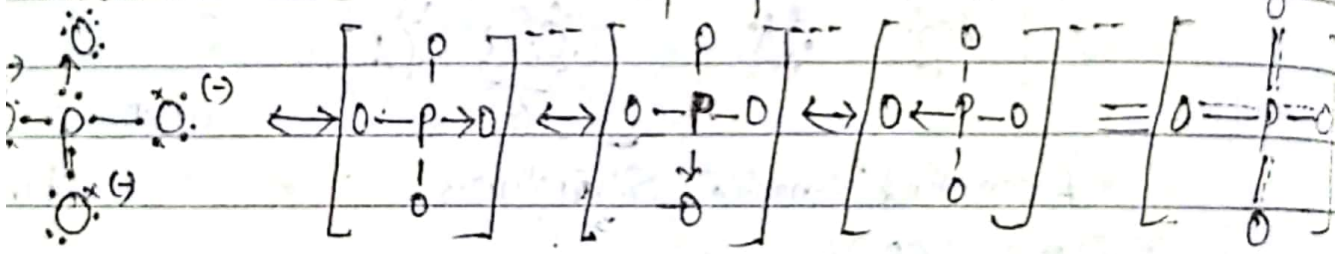
Resonance Structure of Nitrate (NO_3^-):-



Resonance Structures of SO_4^{2-}



Resonance Structures of phosphate Ion (PO_4^{3-}):-



Resonance in H_2^+ :-

$$[H^{\bullet}H^{+} \longleftrightarrow H^{+}\cdot H]$$

Resonance in NO :-

$$[\ \cdot\ddot{N}{=}\ddot{O}: \longleftrightarrow :N{\equiv}\dot{O}^{\bullet}\ ]$$ delocalisation of odd-electron

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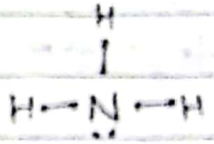
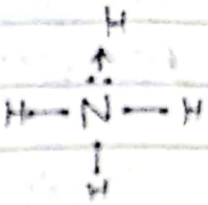
Q.N. Write down the Lewis structures of following species.-

(a) NH_3 molecule:-

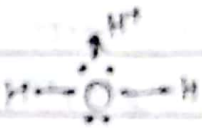


(b) Ammonium ion (NH_4^+):-



(c) Water molecule (H_2O):-

(d) Hydronium ion (H_3O^+)



(e) Sodium Chloride (salt):-

$Na^{(+)}$ $:\ddot{Cl}:^{(-)}$ or $Na^+ Cl^-$

Types of Solids:

↳ On the basis of bond present in solid, they are of five categories:

i. Ionic Solids
ii. Covalent Solids (or Atomic Solids)
iii. Molecular Solids
iv. Metallic Solids

[1] Ionic Solids:-

↳ These solids in which constituent particles are ions, are known as Ionic Solids. The oppositely charged ions of such solid are held together by electrostatic force of attraction. The ionic solids are hard & they do not conduct electricity because ions in (in solid state)

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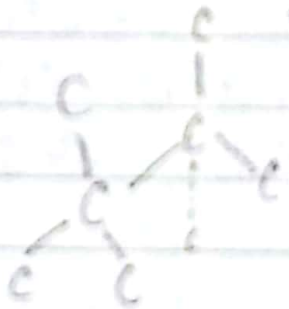
crystal Lattice are Strongly binded and restrict their mobility from one side to another side but aqueous or molten state they conduct electricity. The ionic solids are brittle and have high M.p & B.p.
Example:: NaCl, CaCl$_2$, KCl, ZnS are ionic solids.

[ii] Covalent Solids:-
↳ Those solids in which constituent particles are atoms are known as Covalent solids. The atoms of Covalent solids are held together by Covalent bond. The Covalent solids are also called giant molecules.
For example: graphite, diamond, etc.
The atoms are linked to each other by covalent bonds to form interlocked network solid.

Structure of Diamond is:-



[iii] Molecular Solids:-
↳ Those solids in which constituent particles are molecules are known as molecular solids. In this type of solid the molecules are held together by Vander Waal's force of attraction, eg ice, sugar

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[iv] Metallic solids:-

↳ Those solids in which constituent particles are metal atoms are known as metallic solids. The metals atoms are held together by metallic bond or simultaneous force of attraction between metallic kernel and valence electrons.

For e.g:- Iron, Silver, gold, Sodium, etc

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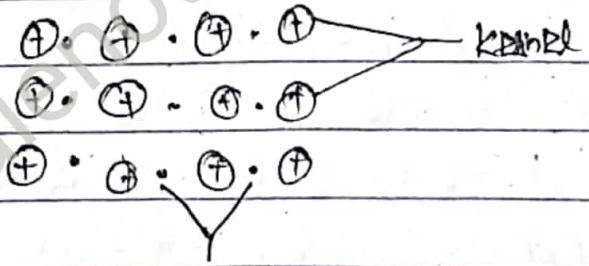
Metallic bond:-

↳ Metallic bond is a special type of bond exists only in Metals. In this theory inner shell electrons and nucleus is taken as positively charged core or kernels. It is consider that valence electrons of Metals form a sea of electrons & positively charged core immersed in it.

Metallic bond is the simultaneous force of attraction between positively charged kernels & sea of electrons which is responsible for binding the metal atoms together.

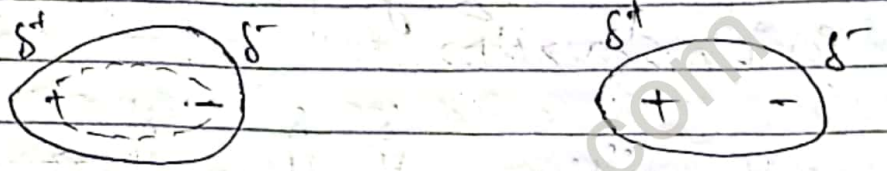


Vander Wall's force:-

↳ Vander Waal purposed that there is a force of attraction between the non-polar molecules. This force is called vander Waal force. Vander Waal force aries due to unsymmetrical distribution of electronic clouds. and separation of charge and formation of electric dipole. Due to unsymmetrical distribution of electron around the nucleus instantaneous dipole. Hence vander Waal's bond of force is defined as the force of attraction betwe

the instantaneous dipole and induced instaneous dipole which is responsible for binding the different molecular layers.

It is a weak force than other force it exists in solid Co, iodine crystal etc.



(Instantaneous dipole) (Induced Instantaneous dipole)

fig:- Vander Waal's force.

Ionic Character in Covalent bond:-

↳ When covalen bond is formed between two different combining atoms having different electronegativity then the bonding pair of electrons are not lie exactly mid way between the two atoms. In facts pair of electrons shifts towards more electronegative atom. The atom having more electronegativity bears partial negative charge and that having less electronegativity bears partial positive charge. Such molecules are said to be polar molecules & bond is said to polar covalent bond.
Hence, the covalent bond between two different atoms having different electronegativity is said to be polar covalent bond.

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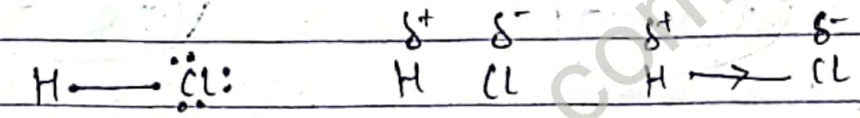
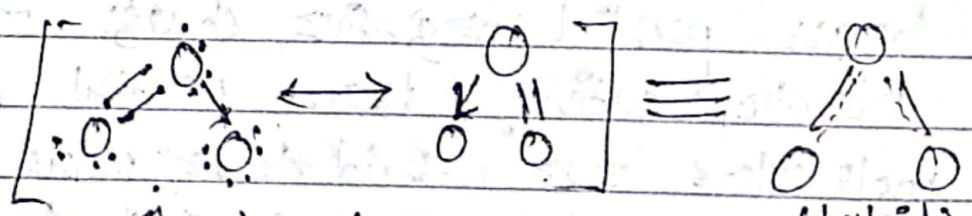
For Example:
In HCl, molecule hydrogen & chlorine has different electronegativity in which chlorine is more electronegative than hydrogen & shared pair of electrons lies more towards chlorine. Therefore, chlorine atom aquires slightly negative charge and hydrogen atom aquire slightly positive charge & H–Cl bond is ionic in character.



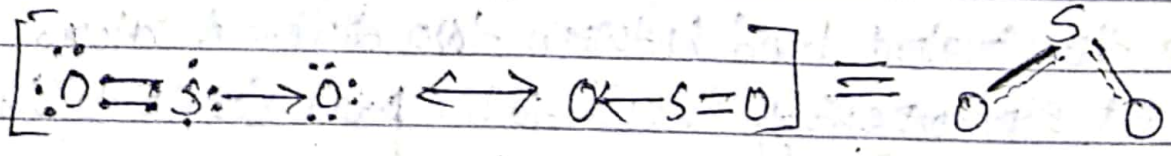
RESONANCE:-

↳ A single molecule can be represented by writing more than two Lewis structure. Due to delocalization of π-electrons pairs is called resonance. Each structure formed by resonance is called resonating structure & all the resonating structure can be represented by a single form of structure known as resonance hybrid.

* Resonance structure of ozone:- (O_3):-



* Resonance structure of SO_4:-



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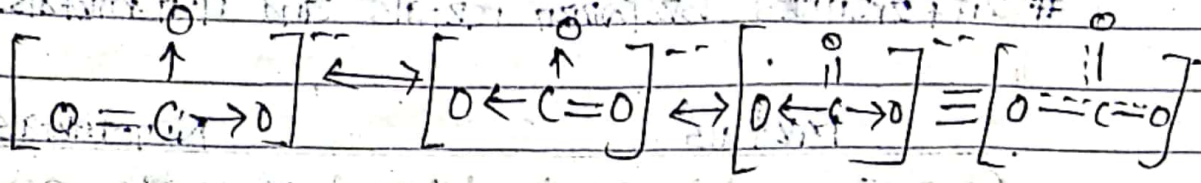
Resonance Structure of CO_3^{--}



Crystalline Solids:-

S.N.	Types	Constituent particles	Force of attraction	Examples
①	Ionic Solid	Ions.	Ionic bond/ Electrovalent bond	NaCl, KCl, $CaCl_2$
②	Covalent solid	Atoms	Covalent bond	Graphite, diamond
③	Molecular solid	Molecules	Vander waal's bond	dry ice, solid iodine
④	Metallic solid	Metal atom	metallic bonding	Cu, Au, Fe, Ag