UNIT - 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Chemical bond :- The binding force which holds together the constituting units (atoms, ions etc) in a molecule is called chemical bond.

KOSSEL LEWIS APPROACH TO CHEMICAL BONDING :-/

OCTET RULE :- A number of attempts were done to explain the formation of chemical bond, but it was only in 1916 that W. Kossel and G.N. Lewis independently succeded in giving a satisfactory explanation. Since their theory was based on the electrons present in valence shell, so it is c/d as electronic theory of valency.

Nobel gas atoms (He, Ne, Ar, Kr, Xe and Rn) possess $ns^2 np^6$ as valence shell configuration (except He $= 1s^2$) Now atoms of noble gases have little or no tendency to combine. Where as all other atoms have less than 8 $\bar{e}s$ to their outermost shell. So in 1916 G.N Lewis and Kossel stated that the stability of noble gas elements is due to presence of 8 $\bar{e}s$ in their valence shell or 2 $\bar{e}s$ (duplet) in case of He. On the basis of above observation, Kossel and Lewis proposed that, the atoms of different elements take part in chemical combination in order to complete their octet or duplet. This is K/as **OCTET RULE** or **ELECTRONIC THEORY OF VALENCY**.

Thus according to electronic theory of valency atoms take part in chemical combination in order to complete their octet and to acquire nearest noble gas configuration. The atoms acquire noble gas configuration either by transfer of valence $\bar{e}s$ from one atom to another by mutual sharing of $\bar{e}s$. Thus depending upon mode of acquiring noble gas configuration there are 3 common types of bond.

(i) Ionic bond (ii) Covalent bond (iii) Co-ordinate bond

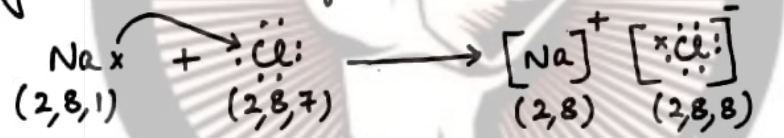
In addition to these 3 main types of chemical bonds, the atoms in a metal are linked by metallic bonds while hydrogen bond and vanderwaals forces arise because of intermolecular forces of attraction in the covalent molecules.

* IONIC BOND OR ELECTROVALENT BOND :-

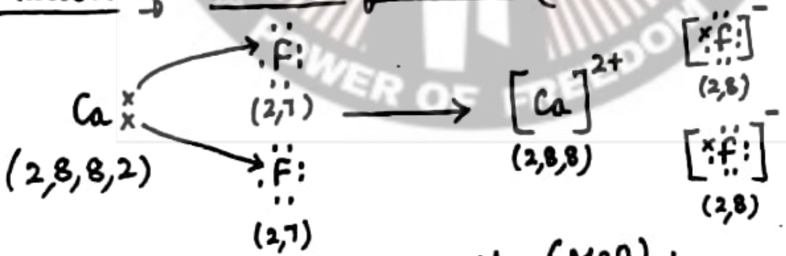
The bond formed by complete transference of ē from one atom to another so that both of them acquire nearest noble gas configuration is called ionic bond. It is formed by atoms having large electronegativity difference. The atom which loses ē acquire +ve charge and which gain ē acquire negative charge. The +vely and -vely charged ions are held together by the strong electrostatic force of attraction.

Examples :-

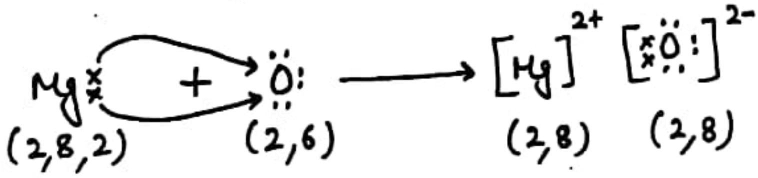
1. formation of NaCl :- Sodium atom (z=11) has one valence ē (2,8,1). IIIly chlorine atom (z=17) has 7 valence ēs (2,8,7). Sodium atom loses its only valence ēs and changes Na⁺ ion (cation). This ē is taken up by chlorine atom which changes to Cl̄ ion (anion). But these ions are mutually attracted to form NaCl as shown below :-



ⓑ formation of Calcium fluoride (CaF_2) :-



ⓒ formation of magnesium oxide (MgO) :-



⇛ factors influencing formation of Ionic bond ?

1. **Low ionization energy** :- One of the atom forming ionic bond should possess low I.E because lower the I.E, easier will be the loss of $\bar{e}$.
e.g I.E of Na, K, Mg, Ca are very low and ∴ easily form ionic bond.

2. **High electron affinity** :- During ionic bond formation, one atom has to gain $\bar{e}$s. This atom should have high $\bar{e}$ affinity. Higher the $\bar{e}$ affinity, more the tendency to form ionic bond.

3. **Lattice energy** :- The energy released when required no. of gaseous +ve and -ve ions combine to form 1 mole of solid ionic compound.
e.g Lattice energy of NaCl is 788 $KJ\ mol^{-1}$

Higher the value of lattice energy released, of an ionic compound, the greater will be the stability of ionic compound and hence more easily it will be formed.

Lattice Energy depends upon -

(i) **Charge on the ion** :- Higher the charge on ions, greater is the force of attraction and large is amount of energy released.

(ii) **Size of the ions** :- Smaller the size, lesser will be the inter nuclear distance and ∴ greater will be the force of attraction and hence more will be the energy released e.g Size of Na^+ is smaller than K^+ and ∴ Na^+ forms stronger ionic bond with Cl^- than K^+.

General Characterstics of Ionic Compounds :-

1. **Physical state** :- Ionic compounds generally exists as crystalline solids in which oppositely charged ions are closely packed.
2. **Melting and boiling pt.** → They possess high m.pt and b.pt.
3. **Solubility** :- They are soluble in water but insoluble in organic solvents.
4. **Conductivity** :- These conduct electricity in fused state and in aqueous form but insulators in solid state.

⇛ **COVALENT BOND** :- Different theories have been given to explain the formation of Covalent bond.

I Lewis - Langmuir theory :-
II Valence Bond theory
III Molecular Orbital theory

I **LEWIS - LANGMUIR THEORY** :- Acc. to Lewis in 1916, the bond formed by mutual sharing of electrons between atoms of same or different elements having small electronegativity difference is c/d covalent bond.

The no. of ēs contributed by each element is called its covalency. Shared ē pair contribute towards the stability of both the combining atoms.

Types of Covalent bond :-

1. Single Covalent bond :- If one ē pair is shared b/w 2 atoms, then bond formed is called single Covalent bond.

e.g formation of H_2 molecule :-

$$H\cdot + \cdot H \longrightarrow (H{:}H) \text{ or } H-H$$

2. Double Covalent bond :- If ē pairs are shared b/w 2 atoms, then bond formed is called double Covalent bond.

e.g formation of O_2 molecule

$$\ddot{O}: + :\ddot{O} \longrightarrow (\ddot{O}::\ddot{O}) \text{ or } \ddot{O}=\ddot{O}$$

3. Triple Covalent bond :- If three ē pairs are shared b/w 2 atoms, then bond formed is called triple covalent bond.

e.g formation of N_2 molecule

$$:N\vdots + \vdots N: \longrightarrow (:N\vdots\,\vdots N:) \text{ or } :N\equiv N:$$

⇒ **Conditions necessary for formation of Covalent bond :-**

1. **High ionigation energy** :- Atoms having high I.E cannot lose electron and ∴ favour covalent bond.

2. **Equal Electronegativity** :- Combining atoms should have either same electronegativity or should have only small electro-vity difference.

⇒ **Lewis Representation of simple molecules and ions :-**

Various steps are as follows -

Step I :- Count the number of the valence $\bar{e}$s of the atoms involved in a particular molecule or ion and add them up.

Step II :- If the species is a cation (+vely charged), subtract the no. of $\bar{e}$s corresponding to the +ve charge from the total.

Step III :- If the species is an anion (-vely charged), add the no. of $\bar{e}$s corresponding to the -ve charges to the total.

Step IV :- from the species, select the central atom which is generally the least electro-ve in nature. Now write the skeletal structure on the basis of an intelligent guess. Please remember that the monoatomic atoms (H, F, Cl etc.) always occupy the terminal positions.

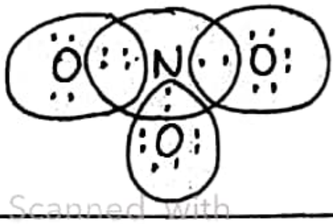
Step V :- Initially place one shared $\bar{e}$ pair b/w every pair of atoms to represent a single bond. The remaining $\bar{e}$s may account for either multiple bond or they may act as lone pairs.

Q Write Lewis dot structure of nitrate ion (NO_3^-) ?

Sol **Step 1** :- Total no. of valence $\bar{e}$s of $N + 3(O) = 5 + 18 = 23$

Step 2 :- Add 1 $\bar{e}$ ∵ the species is anion i.e $23 + 1 = 24$

Step 3 The skeletal st. is O N O
O



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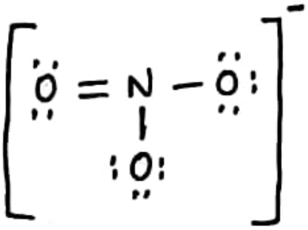
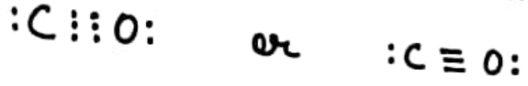


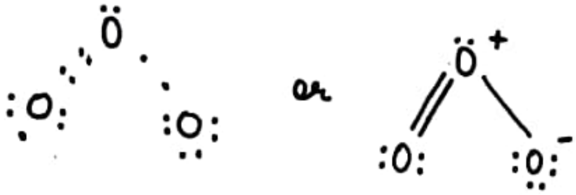
Molecule / ion **Lewis representation**

1. CO

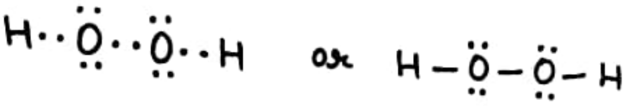


2. O_2

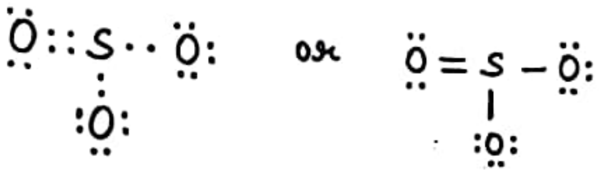
3. O_3



4. H_2O_2



5. SO_3



6. HNO_2

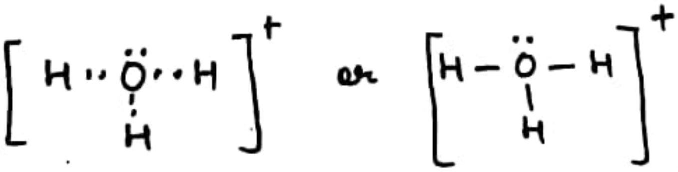
7. HNO_3

8. NO_2^-

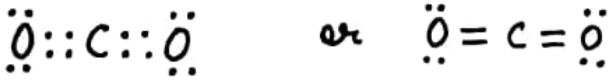
9. NO_3^-

10. O_2^{2-}

11. H_3O^+



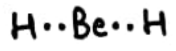
12. CO_2

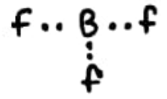


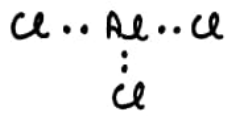
⇒ Limitations of Octet rule / Lewis Concept :-

1. Octet rule doesnot apply to hydrogen as hydrogen shares only one ē to acquire stable conf. of He. So hydrogen acquires duplet.

2. It fails to explain the formation of ē - deficient molecules like $BeCl_2$, BF_3, $AlCl_3$ etc.

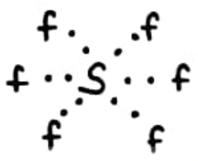




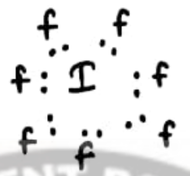


3. It fails to explain formation of ē - rich molecules like PF_5, SF_6 etc.

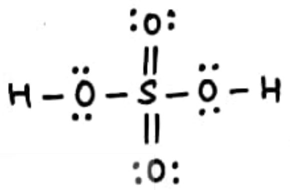
PF_5
10 ēs around Central atom



SF_6
12 ēs around C.A

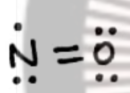


IF_7
14 ēs around C.A

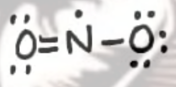


H_2SO_4
12 ēs around C.A

4. It fails to explain certain molecules containing odd ēs.



(NO)



(NO_2)

5. It fails to explain formation of compounds by noble gases.
e.g XeF_2, XeF_4

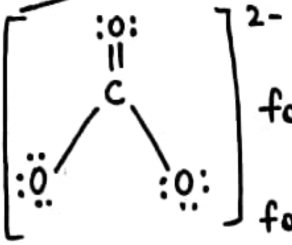
⇒ CONCEPT OF FORMAL CHARGE :-

In polyatomic ions, the net charge is the charge on the ion as a whole and not on the individual atoms present in the ion. If needed charges can be assigned to individual atoms / ions. These are called formal charges.

$$\text{formal charge on an atom/ion} = \left[\begin{array}{c}\text{Total no. of valence ēs}\\ \text{in the atom}\end{array}\right] - \left[\begin{array}{c}\text{Total no. of ēs of l.p's}\\ \text{(non-bonding ēs)}\end{array}\right] - \frac{1}{2}\left[\begin{array}{c}\text{Total no. of shared ēs}\\ \text{(bonding ēs)}\end{array}\right]$$

Q Write the formal charges on atoms in

(i) Carbonate ion



formal charge on C-atom = $4-0-\frac{1}{2}\times 8 = 0$

formal charge on double bonded O-atom
$= 6-4-\frac{1}{2}\times 4 = 0$

formal Charge on single bonded O-atoms
$= 6-6-\frac{1}{2}\times 2 = -1$

(ii) Nitrite ion :- $\left[\ddot{\text{O}}=\overset{+}{\ddot{\text{N}}}-\ddot{\text{O}}:\right]$

formal charge on N-atom = $5-2-\frac{1}{2}\times 6 = 0$
formal charge on double bonded O-atom = $6-4-\frac{1}{2}\times 4 = 0$
formal charge on single bonded O-atom = $6-6-\frac{1}{2}\times 2 = -1$

⇒ POLARITY OF COVALENT BOND :-

Polar Covalent bond :- When a covalent bond is formed between 2 dis-similar atoms having small electro-vity difference then shared ē pair gets slightly displaced towards more electro-ve atom and thus the more electro-ve element acquires partial -ve charge and other element acquires partial +ve charge. This type of bond is c/d polar covalent bond. Greater the electro-vity diff. more is the polarity of bond. e.g HF molecule

Non-Polar Covalent bond :- Covalent bond formed by atoms of same elements is called non-polar Covalent bond because in this case, the shared ē pair lies exactly b/w the 2 combining atoms because of their same electro-vity. Due to their same electro-vity neither of atom acquired any charge.
e.g Covalent bond in H_2, O_2, N_2, Cl_2 etc.

Note: Ionic bond is an extreme case of covalent bond. More the electro-vity difference, higher the polarity of Covalent bond and greater will be the ionic character. If E-vity difference b/w 2 atoms is 1.7, then bond is said to have 50% ionic and 50% covalent character.

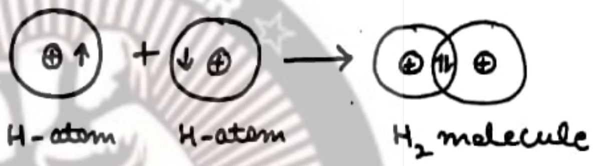
⇒ Valence Bond theory / Orbital overlap Concept of coval bond / Quantum theory of Covalency :-

The valence bond theory was introduced by Heitler and London in 1927 and developed by Pauling and Slater.

Acc. to this theory, a covalent bond is formed by partial overlap of 2 half filled orbitals containing $\bar{e}$s with opposite spins. The partial overlap means that a part of $\bar{e}$ cloud of each of 2 half-filled atomic orbitals becomes common. Hence probability of finding $\bar{e}$s is maximum in the region of overlap. After overlap, the 2 atomic orbitals merge into each other resulting in the formation of molecular orbitals or covalent bond. Greater the overlapping of atomic orbitals, stronger is the bond formed.

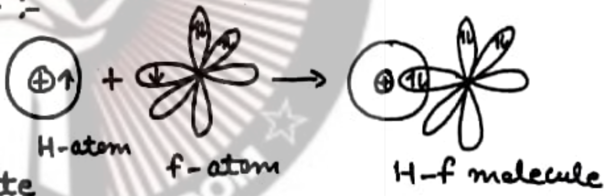
e.g formation of H_2 molecule :-

When 2 H-atoms having $\bar{e}$s with opposite spins come close to each other, their S-orbitals overlap with each other resulting in formation of H_2 molecule.



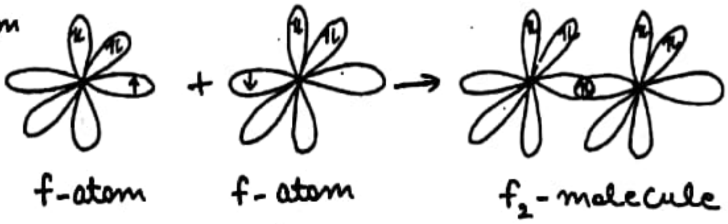
e.g formation of Hf molecule :-

Here half-filled 1S-atomic orbital of H-atom overlap with half filled $2p_3$ atomic orbital with $\bar{e}$ of opposite spin.



e.g formation of f_2 molecule :-

Here half filled 2p orbital of one f-atom overlap with half filled 2p orbital of other f-atom thus forming f_2 molecule.

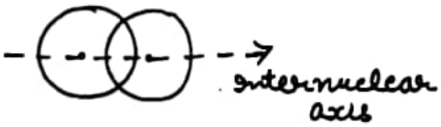


⇒ **Sigma (σ) and Pi (π) bonds / Type of covalent bond on the basis of Overlap** :- Depending upon mode of overlap, Covalent bonds are of 2 Types -

1. **Sigma (σ) bond** :- Covalent bond formed by head on over-lapping of half filled atomic orbitals along the internuclear axis is called σ - bond. This type of overlap is called axial overlap.

formation of σ - bond involves following types of overlap.

e.g **S - S overlap** :- It involves bond formed by partial overlap of 1S-orbital of one atom with 1S - orbital of other atom. e.g H_2 molecule

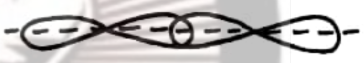


S-S overlap

(ii) **S - p overlap** :- It involves bond formed by the partial overlap of half-filled S-orbital of one atom with half-filled p-orbital of other atom. e.g Hf molecule

S-p overlap

(iii) **p - p overlap** :- It involves the bond formed by overlap of partially filled p-orbitals of one atom with partially filled p-orbital of 2nd atom along internuclear axis e.g f_2 molecule



p-p overlap

2. **Pi (π) bond** :- Bond formed by sideways (or side wise) over-lapping of half-filled atomic orbitals is called π - bond. Overlapping occurs at 2 places, one above the internuclear axis and other below the internuclear axis.

π - bond can never be formed unless accompained by σ - bond. The only type of overlapping is p - p overlapping.

P - P overlapping