Sturcture and bonding in homo- and heteronuclear molecules, including shapes of molecules (VSEPR Theory)

Chemical bond:

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms.

The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei or as the result of a dipole attraction.

Every system tends to be most stable and bonding nature's way of lowering the energy of the system to attain stability.

Kossel - Lewis approach to chemical bond formation:

Kossel and Lewis developed electronic theory of valence or theory of chemical bonding to explain the formation of chemical bond between the two atoms. According to the electronic theory of valence, every atom tries to attain octet configuration (presence of eight electrons) in its valence shell by losing or gaining or by sharing of electrons. This is known as the "Octet Rule".The elect rostatic forces of attraction that holds the two oppositely charged ions together are known as "electrovalent bond". Atoms attain stability by the means of bond formation. The process of bond formation is associated with the lowering of energy of the system. Only valence electrons participate in chemical bonding, but not inner electrons.

Octet rule:

Kossel and Lewis in 1916 developed and important theory of chemical combination between atoms known as **“electronic theory of chemical bonding”.**

According to this theory, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or sharing of valence electrons in order to have an Octet in their valance shells.

This is known as **octet rule.**

Atoms which have already 8 electrons (2 for He) in their outer level, these are very much reluctant to form a molecule i.e. they remain as a monoatomic state (He, Ne…)

When two atoms share one electron pair, they are called **single bond** and when two atoms share two pairs of electrons are called **double bond.**

Formal charge:

Formal charge = [Total number of valence electrons in the free atom]-[Total number of non-bonding (lone pair) electrons]-½ [total number of bonding (shared) electrons]

Ex: (i) CNO^- has three resonating structure

(a) $[C=N=O]^-$ Formal charge of C = (-2), N = (+1), O = (0)

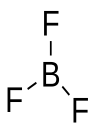
(b) $[C-N\equiv O]^-$ Formal charge of C = (-3), N = (+1), O = (+1)

(c) $[C\equiv N-O]^-$ Formal charge of C = (-1), N = (+1), O = (-1)

Among these structures (c) has the most favorable charge distribution.

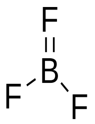
(ii) BF_3 has two resonating structure

(a)



B = 0
F = 0

(b)



B = -1
F = 0
F = +1 (pi bonded)

We conclude that structure (a) with smaller formal charge on the atoms should have lower energy and be dominating. However, small contribution form (b) accounts for the stability of the compound inspite of its electron deficient nature and for the shortness of the bonds.

Limitation of octet rule:

A few molecules had non-octet structures. Some important examples are: -

A) For 6 electrons around the central atom: A stable molecule as of beryllium chloride, $BeCl_2$, contains an atom with four electrons in its outer shell.

- $BeCl_2$ and $BeCl_3$both are electron deficient species.

B) 7 electrons around the central atom:

Example: ClO_2

C) 10 or more electrons around central atom: Non-metallic elements app III and higher periods react with electronegative elements to form structures in which the central atoms have 10 ,12 or even more electrons.

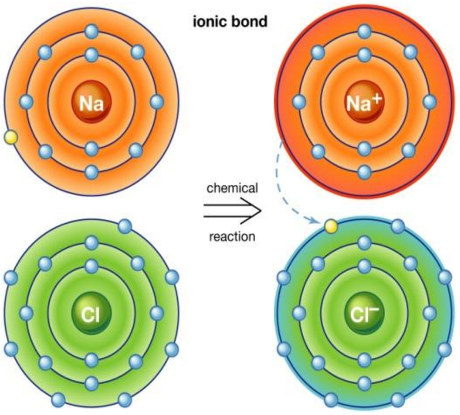
Example:PCl_5,SF_6 and H_2SO_4

The molecules with more than an octet of electrons are called **super octet structures.**

In elements C, N, O and F are strictly obeyed octet rule because only four orbitals are available (one 2s and three 2p) for bonding.

Ionic Bond or Electrovalent bond:

Electrovalent bonds are produced when electrons are transferred from atoms of one element to atoms of another element, producing positive and negative ions. The bond which is formed by the transfer of electrons between the atoms is called electrovalent bond or ionic bond. Electrovalent bonds are only formed between metals and non-metals. Electrovalent bonds are not formed between two non-metals.



In simple words electrovalent bond involves the transference of a certain number of electrons to another dissimilar atom which has a tendency to gain electrons so-that both acquire stable inert gas configurations. The electrostatic attraction always tends to decrease the potential energy. Hence, the potential energy of the system is much less than it was before the formation of an ionic bond.

Electronegativity and Ionic bonding:

(1) An Ionic bond is the bond formed by the complete transfer of valence electron to attain stability.

(2) This type of bonding leads to the formation of two oppositely charged ions – positive ion known as **cations** and negative ions are known as **anions**.

(3) The presence of two oppositely charged ions results in a strong attractive force between them. This force is an ionic or electrovalent bond.

(4) Ionic bonds form between atoms with large differences in electronegativity, whereas covalent bonds formed between atoms with smaller differences in electronegativity.

(5) The compound formed by the electrostatic attraction of positive and negative ions is called an ionic compound.

Property:

Due to the presence of a strong force of attraction between cations and anions in ionic bonded molecules, the following properties are observed:

1. The ionic bonds are the strongest of all the bonds.
2. The ionic bond has charge separation, and so they are the most reactive of all the bonds in the proper medium.
3. The ionic bonded molecules have high melting and boiling point.
4. The ionic bonded molecules in their aqueous solutions or in the molten state are good conductors of electricity. This is due to the presence of ions which acts as charge carriers.

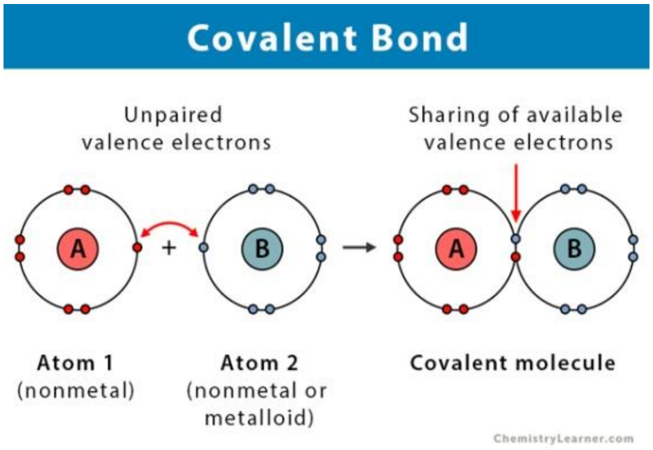
Covalent Bond:

Elements having very high ionisation energies are incapable of transferring electrons and elements having very low electron affinity cannot take up electrons. The atoms of such elements tend to share their electrons with the atoms of other elements or with other atoms of the same element in a way that both the atoms obtain octet configuration in their respective valence shell and thus achieve stability. Such association through sharing of electron pairs among different or same kinds is known as Covalent Bond.

Covalent bonding can be achieved in two ways:

(1) Sharing of electrons between atoms of the same kind e.g. Formation of H_2, Cl_2, O_2, etc.

(2) Sharing of electrons between atoms of different kind e.g. Formation of CH_4, H_2O, NH_3, etc.



Property:
If the normal valence of an atom is not satisfied by sharing a single electron pair between atoms, the atoms may share more than one electron pair between them. Some of the properties of covalent bonds are:

(1) Covalent bonding does not result in the formation of new electrons. The bond only pairs them.
(2) They are very powerful chemical bonds that exist between atoms.
(3) A covalent bond normally contains the energy of about ~80 kilocalories per mole (kcal/mol).
(4) Covalent bonds rarely break spontaneously after it is formed.
(5) Covalent bonds are directional where the atoms that are bonded showcase specific orientations relative to one another.
(6) Most compounds having covalent bonds exhibit relatively low melting points and boiling points.
(7) Compounds formed by covalent bonding don’t conduct electricity due to the lack of free electrons.

Covalent bonds are two types:

(A) **Polar covalent bond:**

This type of covalent bond exists where the unequal sharing of electrons occurs due to the difference in the electronegativity of combining atoms.

More electronegative atom will have a stronger pull for electrons. The electronegative difference between the atoms is greater than zero and less than 2.0. As a result, the shared pair of electrons will be closer to that atom.

Example, molecules forming hydrogen bonding as a result of an unbalanced electrostatic potential. In this case, the hydrogen atom interacts with electronegative fluorine, hydrogen, or oxygen.

(B) **Nonpolar Covalent bond**:

(C) This type of covalent bond is formed whenever there is an equal share of electrons between atoms. The electronegativity difference between two atoms is zero. It occurs wherever the combining atoms have similar electron affinity (diatomic elements).

Example, Nonpolar Covalent Bond is found in gas molecules like Hydrogen gas, Nitrogen gas, etc.

Ionic bond Vs Covalent bond:

Covalent Bonds	Ionic Bonds
A covalent bond is formed between two similar electronegative non-metals	This type of bond is formed between a metal and non-metal
Bonds formed from covalent bonding have a Definite shape	Ionic Bonds have No definite shape
Low Melting Point and Boiling Point	High Melting Point and Boiling Point
Low Polarity and more Flammable	High Polarity and less Flammable
Covalent Bonds are in Liquid or gaseous State at room temperature	At room temperature, Ionic Bonds have Solid-state.
Examples: Methane, Hydrochloric acid	**Example:** Sodium chloride, Sulfuric Acid

Bond length: Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

$$\text{Bond length (R)} = r_A + r_B$$

Where r_A = covalent radius of A atom, r_B = covalent radius of B atom.

- The Bond lengths are measured by spectroscopic x-ray diffraction and electron diffraction technique.

Covalent radius: The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule.

$$r_c = x/2$$

X=Bond length of a homo diatomic molecule (e.g. H_2,O_2 etc.)

r_c= Covalent radius of atom in a molecule.

Vander Waals radius: The Vander Waals radius is half of the distance between two similar atoms in separate molecules in a solid

Vander waals radius (r_{vdw}) = y/2 pm.

Y=internuclear distance between two atoms of different molecules when they are nearest to each other.

Bond angle:

The angle between the hybrid orbitals containing bonding electron pairs around the central atom in a molecule or complex ion.

It gives the idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape.

Factors affecting the magnitude of bond angles are

(i) Number of lone pairs of electrons on the central atom e.g

CH_4(no lp) > NH_3 (1 lp) >H_2O (2 lp)

(ii) Electronegativity: Bond angle decreases with decrease of electronegativity of central atom.

$H_2O>H_2S>H_2Se>H_2Te$

$NH_3>PH_3>AsH_3>SbH_3$

(iii)**Hybridisation:** The hybridization of c atom in CH_4, C_2H_4 and C_2H_2 is Sp^3, sp^2 and sp respectively. The bond angles are 109.5º, 120º and 180º respectively.

Bond energy:

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

Unit: $kJmol^{-1}$

- Larger the bond dissociation energy stronger will be the bond in the molecule.

Factors on which bond energy depends:

- **Bond length:** Shorter the bond length greater is the bond energy.

C-C<C=C< C≡C.

Factors affecting bond length are

(i)**Size of the atoms:** The bond length increases with increase in size of atoms HI>HBr>HCl>HF

(ii**) Multiplicity of bonds:** The bond length decreases with multiplicity of bonds

C-C<C=C< C≡C.

(iii) **Type of hybridization:** Greater the s character shorter is the hybrid orbital and hence shorter is the bond length e.g

CH(sp^3)>C-H(sp^2)>C-H (sp)

- **Size of bonded atom:** Shorter the size of bonded atoms, greater is the bond energy.So bond energy values decrease down the group.

Li-Li>Na-Na>K-K.

- **Bond order:** Bond energy increases as the bond order increases.
- **Electronegativity:** The greater the electronegativity difference between the bonded atom greater is the bond energy.

HF>HCl>HBr>HI

- **Number of lone pairs:** The greater the number of lone pairs on the bonded atoms, the greater is the repulsion between them. This results in a weaker bond. Hence bond energy decreases.
- **Hybridization:** The extent of overlapping in case of hybridized orbitals is greater than that of a hybridized orbital. Therefore, hybridized orbitals form stronger bonds and hence higher bond energy than the unhybridized orbitals. As the percentage of p character in the hybridized orbitals increases the bond energy increases.
- **Bond angle:** The greater the bond angle, the greater is the bond energy.

$BeF_2\,(180°) > BF_3\,(120°) > CCl_4\,(109°28')$

Bond order:

$$\text{Bond order} = \frac{(\text{Number of bonding electrons}) - (\text{Number of antibonding electrons})}{2}$$

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

- Isoelectronic molecules and ions have identical Bond orders.
- A molecule/ion is stable if $N_b > N_a$. If $N_b = N_a$, then bond order is zero, molecule does not exist.
- Bond dissociation energy depends on the bond order. Higheris the bond order higher is the bond dissociation energy.
- Bond order is inversely proportional to the bond length. Higher the bond order smaller is the bond length.

Resonance structure:

Whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the **canonical structures** of the hybrid which describes the molecule accurately. This is called **resonance.**

- Resonance is represented by a double headed arrow (↔).
- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure.
- Resonance averages the bond characteristics as a whole.
- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical form and for other functions of time in other canonical forms.
- There is no such equilibrium between the canonical forms as we have between tautomeric forms in tautomerism.
- The molecules as such as a single structure with is the resonance hybrid of the canonical forms and which cannot as such be defeated by a single Lewis structure.

- **Average bond order**$=\dfrac{\text{Number of bonds associated with central atom in molecule}}{\text{Total number of resonance structure}}$

Or, average bond order$=\dfrac{\text{Bond order in its resonance structure}}{\text{Number of such structures}}$

Or, average bond order$=\dfrac{\text{Number of bonds associated with molecules or ions}}{\text{Number of groups or atoms around central atom}}$.

Polarity of bonds/Dipole moment:

The dipole moment is equal to the product of the magnitude of electrical charge (*e*), in e.s.u and distance (*d*) between two different opposite charge in angstrom.

$$\boldsymbol{\mu = e \times d}$$

μ=(Charge on the electron) ×(Distance between the electron and the positive charge)

A) Determination of Dipole moment by Temperature method:

We know that, $P_i = a + \frac{b}{T}$, where, a and b are the constants and are given as

$$a = \frac{4}{3}\pi N \quad \text{and} \quad b = \frac{4}{9}\frac{\pi N}{k}\mu^2$$

Where, N= Avogadro's Number,
K= Boltzman's Constant
μ = Dipole moment, a= degree of polarizability.

If total, polarization P_1 and P_2 are determine at two different temperatures T_1 and T_2, respectively then

$$P_1 = a + \frac{b}{T_1} \quad \text{and} \quad P_2 = a + \frac{b}{T_2}$$

$$\therefore b = (P_1 + P_2)(\frac{T_1 T_2}{T_1 - T_2})\ldots\ldots\text{(i)}$$

The value of Dipole moment, μ is easily calculated from the value of 'b', i.e.,

$$b = \frac{4\pi N}{9k}\mu^2 \quad \text{or, } \mu = \sqrt{(\frac{9k}{4\pi N})b}$$

As, $k = 1.3805\times10^{-16}$ $erg.deg^{-1}$, $\pi = 3.14$, $N = 6.023\times10^{23}$, we get

$$\mu = \sqrt{\frac{9 \times 1.3805 \times 10^{-16} \times b}{4 \times 3.14 \times 6.023 \times 10^{23}}}$$

$$= 0.0128 \times 10^{-18}\sqrt{b}\ \text{esu.cm}$$

So, knowing 'b' from Eq. (i) we can calculate dipole moment easily.

B) Units of dipole moment:

CGS-Debye (D)
SI-Coulomb meter (Cm)
1D=0.334×10^{-29} coulomb meter

- As electronegativity difference increases in diatomic molecules polarity of bond between the atom increases and therefore magnitude of dipole moment increases.
- A**symmetrical molecule** is non-polar even though it contains polar bonds because the dipole moment of each Bond cancels to each other and hence the resultant dipole moment of molecule is zero.

Example: CO_2, BF_3, CCl_4 etc.

- **Unsymmetrical nonlinear** polyatomic molecules have net magnitude of dipole moment.

Example: H_2O, CH_3OH, NH_3 etc.

C) Applications of dipole moment:

- **To distinguish between polar and nonpolar molecules:** A molecule which has purely covalent bond is called non-polar molecule while that which contains polar covalent bonds is called polar molecule. On the basis of the dipole moment value of a given molecule, it is possible to predict whether the given molecule is polar or nonpolar in nature.

The molecules having some value of dipole moment (e.g. HCN, OCS, NH_3, PF_3, AsF_3, H_2O, H_2S, SO_2, NO_2, O_3, N_2O etc.) are polar while those having zero value of dipole moment (e.g. CO_2, BeF_2, H_2, N_2, CH_4, SF_6, CS_2, BF_3, SO_3, CF_4, CCl_4 etc.) are nonpolar. Greater is the value of dipole moment of a polar molecule, greater is the amount of ionic character in the polar covalent bond.

- **To calculate the percentage of ionic character in the polar covalent bond in a given molecule:**

Greater is the electronegativity difference between the bonded atoms in a polar molecule, greater is the value of dipole moment. Can we know that greater is electronegative difference, greater is percentage of ionic character in the bond linking the two atoms.

Percentage of ionic character in A-B bond in AB molecule = $\frac{\mathbf{100\times\mu_{exp}}}{\mathbf{\mu_{ionic}}}$ **%**

Here, μ_{exp}= Experimental (observed or actual) value of dipole moment of AB molecule, μ_{ionic}= Calculated (theoretical) value of dipole moment of AB molecule when this molecule is assumed to be completely ionic, i.e., an electron is completely transferred from less electronegative atom to more electronegative atom.

- **To predict the shape of a given molecule:**

i) **Monoatomic molecules,** like those of real gases, have no dipole moment and are nonpolar.

ii) **The homo nuclear diatomic molecules** (e.g. H_2, C_2, N_2, O_2, Cl_2 etc.) have zero dipole moment and hence have symmetrical shape.

iii) **The heteronuclear diatomic molecules** (e.g. HF, HCl, HBr, HI, CO, NO, ClF etc.)Have some value of dipole moment and hills have unsymmetrical dumbbell shape. Dipole moment is in order H-F > H-Cl > HBr > H-I.

iv) **Tri-atomic molecules** like CO_2, $BeCl_2$, $HgCl_2$ etc. zero dipole moment and hence are linear (symmetrical shape) in shape. **Tri-atomic molecules** like H_2O,H_2S,SO_2 etc. have some value of their dipole moment and hence have angular shape (unsymmetrical shape)

v) **Tetra atomic molecules** like BF_3, BCl_3, SO_3 etc. have zero dipole moment and have symmetrical trigonal geometry. Each of these molecules has three identical bonds. **Tetra atomic molecules** like NH_3,NF_3,PH_3,PCl_3 etc. has some value of the dipole moment and hence these molecules have trigonal pyramidal shape (unsymmetrical shape).Each of these molecules has three identical bonds. All these bonds are identical due to the unsymmetrical shape of the molecule the dipole moment of the three bonds are not able to cancel each other and hence the net dipole moment of these molecules is not equal to zero i.e. they have some value of dipole moment.

vi) **Penta atomic molecules** like CCl_4, CF_4, SiF_4, CH_4 etc. have zero dipole moment and hence have regular tetrahedral geometry. Each of these molecules has four identical bonds. **Penta atomic molecules like**CH_3Cl has some value of dipole moment and heels has unsymmetrical tetrahedral structure.

vii) A comparison of the dipole moments of NH_3 and NF_3 shows the effect of the lone pair in the determination of bond moments. For NH_3, μ=1.7D and for μ=0.2 D. This large difference between two is due to the effect of the LP present on N. In case of NH_3, the orbital dipole due to LP is in the same direction as the resultant bond moment of the N-H bonds, but in case of NF_3, it is in the opposite direction. Hence, the bond moment is nearly cancelled out.

viii) The trans isomers have zero dipole moment while cis isomers have certain dipole moment. The value of dipole moment also depends upon the orientation in distributed benzene, e.g. p-derivative with same group has dipole moment zero while ortho and meta derivatives have certain values.

- **To calculate the bond angle between two bonds in a molecule: The dipole moment 'M'of the molecule is given by**

$$\mu = 2m\cos\frac{\theta}{2}$$

Where 'm'is the bond moment and $\theta$is the angle between the two bonds.

- **To distinguish between *cis* and *trans* isomers:**

For *trans* isomers **μ=0**

For *cis* isomers **$\mu \neq 0$**

- **Prediction of position of substituents in di-substituted benzene from their given relative dipole moment values:**

i) For a molecule like C_6H_4XY, where X and Y are electron withdrawing in nature, the dipole moment order is observed as *ortho>meta>para.*

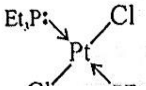
ii) If X is electron withdrawing in nature and Y is electron donating in nature, the order of dipole moment is *ortho<meta<para*.

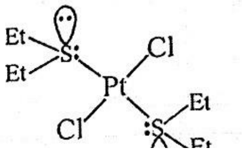
D) The molecule **Hydroquinone**is expected to have zero dipole moment value but it has the dipole moment value of 1.64 D. This is due to the presence of lone pair of O-atom which is not involved in resonance with benzene ring.

E) Sometimes the value of dipole moment is lessened by the mesomeric effect and becomes reversed in direction also.

F) The dipole-moment of ***p*-nitroaniline** is extraordinarily large to compare to the expected value. This is because +R effects of $-NH_2$group and -R effect of $-NO_2$ group are couple together and the overall effect enhances dipole moment value.

G) *trans*-$(Et_3P)_2PtCl_2$ has zero dipole moment value while *trans* $(Et_2S)_2PtCl_2$ has significant value of dipole moment.





The lone pairs on S atom are not oriented in a manner that their lone pair moments are cancelled by each other.

H) O_3molecule is also polar due to its lone pair moments and resultant lone pair moment is not zero.

I) Dipole moment order:

HF>HCl>HBr>HI
$CH_3Cl>CH_3F>CH_3Br>CH_3I$
$CH_3Cl>CH_2Cl_2>CHCl_3>CCl_4$

Types of chemical bonds:

- Electropositive element + electronegative element→Ionic bond/electrovalent /non-directional Bond
- Electronegative element + electronegative element→Covalent bond/directional Bond
- Electropositive element + electropositive element→ Metallic Bond
- **Ionic bonding** involves the complete transfer of one or more electrons from one atom to another. **Covalent bonding** involves the sharing of a pair of electrons between two atoms, and in **metallic bonding** the valency electrons are free to move throughout the whole crystal. These bonds are also called **primary bonding** and they are responsible for existence of molecules. Some other type of Bond like **hydrogen bond** and **Vander walls bonding** are responsible for modification of properties are called **secondary bonding.**

Ionic bond:

Bond formed by the complete reference of an electron from one account to another atom is known as electrovalent or ionic bond. The oppositely charged ions are held together by columbic forces.

General characteristics of ionic compound:

- **Melting point:** Ionic compounds have high melting point. In general, the greater the charge, the greater the electrostatic attraction (cation-anion interaction), the stronger the ionic bond, the higher the melting point. Smaller ions can pack closer to other than larger ions so the electrostatic attraction is greater, the ionic bond is stronger, the melting point is higher.
- **Hardness:** Ionic compounds are hard and brittle. Hardness increases with increase in charge on the ion for crystals of similar interionic distances for ionic compounds having similar structures. For a given charge hardness increases with decrease in inter ionic distance for crystal with similar structure.
- **Brittleness:** Ionic solids are brittle.
- **Solubility:** Ionic compounds dissolve in polar solvents, especially those that ionize, such as water and ionic liquids. They are usually appreciably soluble in other polar solvents such as alcohols, acetone and dimethyl sulfoxide (DMSO) as well. Ionic compounds trend not to dissolve in nonpolar solvents such as diethyl ether or petrol.

- **Conductivity:** Solid ionic compounds do not conduct electricity. This conduct electricity when in molten state or in aqueous solutions.

Factors governing the formation and stability of ionic compound:

- **Low ionization energy of the metal:** Lower the ionization energy, greater will be the tendency of the metal atom to form cation and hence, greater will be the tendency of formation of ionic bond.
- **High electron affinity of the other element (non-metal):** Higher the electron affinity hair will be the anion. Hence ease the formation of ionic bond. On moving down, a group the electron affinity decreases and therefore the tendency of ionic bond formation also decreases.
- **High lattice energy:** Lattice energy is directly proportional with the strength of ionic bond. Thus, an ionic lattice which have a higher lattice energy, haywire in thermal stability i.e. compounds melts at a higher temperature.

Lattice energy (U):

The minimum amount of potential energy released when definite number of opposite charges combine together to produce an ionic crystal is called its lattice energy. Alternately the lattice energy also defined as the amount of energy required to break a particular letter into its constituent's ion. It is expressed in **kj/mole** or **kcal/mole.**

Born-Lande equation:

The theoretical equation was proposed by Born and Lande by which we can determine the lattice energy of ionic crystal.

$$U=\frac{N_0AZ_+Z_-e^2}{4\pi\epsilon_0 r}\left(1-\frac{1}{n}\right)$$

Where, U=Lattice energy of ionic crystal.

No=Avogadro's constant whose value is 6.023×10^{23}

A=Madelung constant, where value depends on the geometrical structure of the ionic crystal.

Z_+=Charge of the cation

Z_-=Charge of the anion

r_0=Inter ionic distance

e=Electronic charge where value is 1.602×10^{-19}C

ε_0=Born exponential constant, which measure the repulsive forces, arise due to the presence of same ion.

From Bond-Lande equation we can write

- $U \propto Z_+Z_-$
- $U \propto 1/r$
- For a solid to be able to dissolve in a particular solvent its salvation energy must be greater than its lattice energy so that the latter may be overcome by the former.

Some conclusion of Born equation:

1. The higher the charge on cation and anion, the greater would be the magnitude of lattice energy and therefore, the greater would be the stability of the crtstal

$Na^+F^- < Mg^{2+}F_2^- < Mg^{2+}O^{2-}$

Thus, lattice energy of bivalent solids > bi-univalent solids > Uni-univalent solids

2. The lattice energy is inversely proportional to the inter-ionic distance e.g.

Lattice energy of lkali metal fluorides decreases in the order

LiF > NaF> KF>RbF>CsF

Size of M^+ ion $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Lattice energy of the halides of a given alkali metal decreases in the order.

LiF > LiCl> LiBr >LiI

For the same anion but different cation, the magnitude of lattice energy of ionic solids decreases, as the size of cation increases e.g

Lattice energy of LiF > CsF

Lattice energy of the oxides of alkaline earth metals also decrease on descending the group

BeO > MgO > CaO > SrO > BaO

Thus, in order to get high value of lattice energy, the size of cation (or anion) should be small and electric charges on the cation/anion should be high.

3. The lattice energy and hence stability of an ionic crystal is directly proportional to the Madelung constant which depends upon the coordination number of each ion and the geometric pattern of the ions in the crystal lattice of the crystal.

4. Estimation of heat of formation:

One very interesting case is the speculation of the first true compound of xenon. The compound $O_2^+PtF_6^-$ was known. Now, I. P of Xe is nearly the same as the I. P of O_2. Also, the sizes of Xe^+ and O_2^+ were similar. This gave rise to the idea that the compound $Xe^+PtF_6^-$ might have a lattice energy sufficient for its formation from Xe and PtF_6.

5. Explanation of the high oxidation states of metals:

Metals form many fluorides with oxidation states higher than usual. Similarity, iodides contain the metals in a respectively lower oxidation state. This can be explained in view of the high lattice energies of fluorides (small size of fluorides ion) as compared to the iodides.

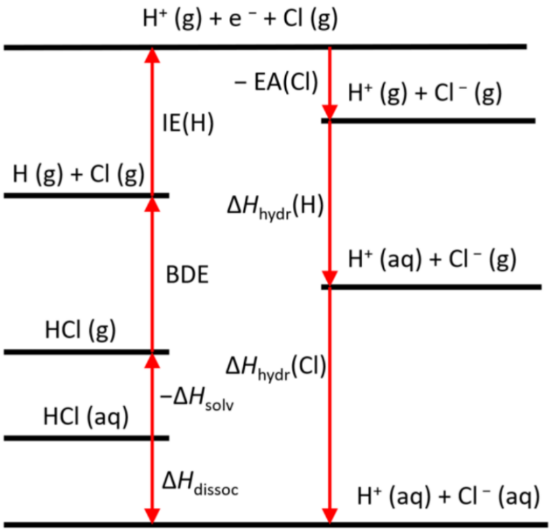
Hydration energy:

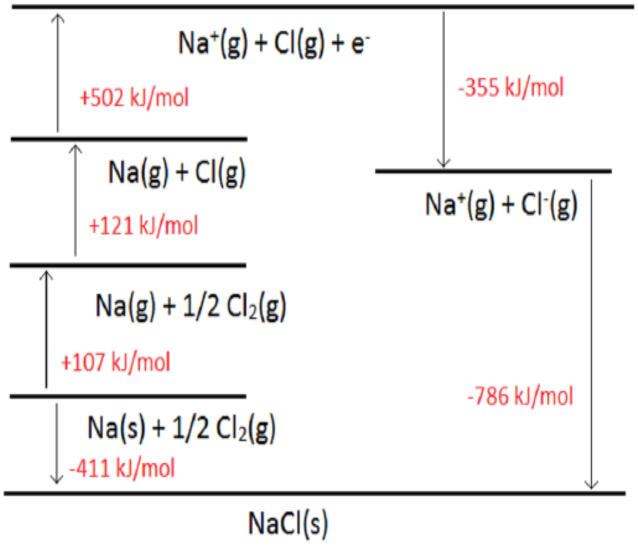
The amount of energy released when 1 mole gaseousion dissolve completely in water is called its hydration energy. The hydration energy depends on the ionic charge density i.e. the ratio of the amount of charge and its ionic radius.

$$\text{HE} \propto \text{Ionic charge density} \propto \frac{\text{Amount of Charge}}{\text{Ionic Radius}}.$$

Compound which has very high lattice energy compared to the hydration energy the compound is insoluble in water, whereas when the hydration energy is higher than the lattice energy, the compound is soluble in water.

Born-Haber cycle:





Application of Born Haber cycle:

- **The cycle helps us in understanding the stability of ionic compounds e.g.** Formation of Mg^{2+} and $O^{2-}$are very difficult as the process are endothermic but MgO is a stable ionic compound because of its very high lattice energy.
- The correct chemical formula of ionic compound can be justified from ΔH_f value. The chemical formula of sodium chloride is NaCl or $NaCl_2$, that can be verified from ΔH_f value. It is found that the ΔH_f is positive for $NaCl_2$ i.e. the crystallization process is

endothermic (non-spontaneous) but the ΔH_f is negative for NaCl i.e. the crystallization process is spontaneous. Show the correct formula of sodium chloride is NaCl not $NaCl_2$.

- The ΔH_f value is negative for CaF_2, but it does not exist, undergo easy disproportionation to give more stable CaF_2, whereΔH_f is also negative with higher in magnitude.

- **Estimation of proton affinity:**

The amount of energy released when a proton is added to the species in gaseous state is called its proton affinity. The proton affinity of ammonia can be determined from Born-Haber cycle of ammonium chloride. It is found that the proton affinity of H_2O is higher than the PH_3. So that the Phosphonium salts (PH_4^+) readily decomposed in presence of water.

The order of proton affinity is $H_2O > PH_3$.

- **Estimation of electron affinity:**

The electron affinity of electrons cannot be determined directly. By using Born-Haber cycle we can determine the electron affinity of the element.

- **Chemical reactivity of the metals:**

The noble metals like Pd, Pt, Ag, Au have a very high sublimation energy as well as very high ionization potential. So, these are chemically less reactive. On the other hand, alkali metals like Li, Na, K, Rb have a very e low sublimation energy and small ionization potential. Suggest that these are chemically more reactive.

Polarization of ions:

When two opposite charged ions (cation and anion) of the ionic molecule come closer to each other, the cation attracts the electron cloud of the outermost cell of the anion towards itself and hence, the symmetrical shape of the anion gets distorted (deformed or polarized). These phenomena are called polarization of ion.

- The effect of cation by which the shape of an iron is lost, called the polarizing power of cation. The property of a cation is its polarizing power which depends on its cationic charge density or ionic potential value.
- The effect of anion by which it lost its shape own, called polarizability of anion. Higher the size of anion higher will be its polarizability. Higher the polarizability of anion where will be the covalency.

Factors affecting the magnitude of polarizing power of a cation:

- Higher the charge, higher is the polarizing power of cation
- Smaller the size, higher the polarizing power of cation, higher will be covalent character in ionic bond.

- If Cations have same charge and almost same size, then cations having inert gas configuration (ns^2p^6), have less polarizing power than the cations having pseudo inert gas configuration ($ns^2p^6d^{10}$).

  Although $Hg^{2+}(5s^2p^6d^{10})$ and $Zn^{2+}(3s^2p^6d^{10})$ have the same charge and nearly the same size, yet Hg^{2+} ion has more polarizing power then Zn^{2+} ion.

Factors affecting the polarizability of an anion:

- As magnitude of negative charge on anion increases, the polarizability of anion also increases i.e. higher the negative charge on anion where is the polarizability of anion.
- As the size of anion increases, the polarizability of anion increases.

Consequence of polarization:

(i) Decrease of solubility in polar solvents: Thus AgI is much less soluble in water than AgF (or AgCl, AgBr). Lattice energy considerations alone cannot explain this. Here solubility decreases from fluoride to iodide due to increasing polarization of the anion and hence increasing covalence. The same explanation fits the series $HgF_2 > HgCl_2 > HgBr_2 > HgI_2$.

(ii) **Decrease of electrical conductance in fused state and tendency to ionize in solution:**

Eq. conductance in fused state: $LiCl > BeCl_2$; $NaCl > MgCl_2$

(iii) **Intensification of color:** Polarized anions seem to be responsible for colour in some compounds. As polarization increases from chloride to iodide, the colour of many metal halides are intensified. Thus, higher the covalent character higher is the tendency for a compound to be coloured.

Colourless	$HgCl_2$	AgCl	$SnCl_4$	$PbCl_2$
Coloured	HgI_2 (Red)	AgI (yellow)	SnI_4 (Red)	PbI_2 (golden yellow)

Fajan's rule:

Covalent character of ionic bond results by polarization of ions. The polarization of ions results in a high electron charge concentration between the two nuclei. It leads in the formation of a covalent bond with high degree of polarity (polar covalent bond). A polar covalent bond is more stable than a pure covalent or a pure ionic bond. The higher the degree of ionic polarization, the greater is the stability of the polar covalent bond. The rules regarding polarization are known as Fajans's rules.

According to Fajan's, higher the polarizing power of cation and higher polarizability of anion, more will be the covalent character in ionic molecule.

If ionic molecules follow the following conditions, will have more covalent character.

- Higher positive charge on cation
- Small size of cation

- The cation having pseudo inert gas configuration has more polarizing power than that of cations having inert gas configuration.

Difference between Ionic and Covalent character:

CovalentCharacter	Ionic character
• Small size cation	• Large size cation
• Large size anion	• Small size anion
• High charge of both ions	• Low charge of both ions
• Cation having a pseudo inert gas configuration i.e. total number of electrons is 18 in the valence shell.	• Cation having an inert gas structure in the valence shell.

Example: (i) The covalent character of molecules of chlorides increases as the order $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

$FeCl_3 > FeCl_2$, $SnCl_4 > SnCl_2$

(ii) Covalent character of calcium halide and hydrogen halides as follows

$CaF_2 < CaCl_2 < CaBr_2 < CaI_2$

$HF < HCl < HBr < HI$

(iii) Covalent character of the elements in same period is as follows

$LiCl < BeCl_2 < BCl_3 < CCl_4$

$CH_4 < NH_3 < H_2O < HF$

(iv) CuCl is more covalent than AgCl; AgI is covalent while NaI is ionic.

Note: Percentage of ionic character of polar covalent bond:

When the electronegativity difference between two atoms (A-B) is 1.7, the bond is 50% ionic and 50% covalent. If the electronegativity difference is less than 1.7 the amount of ionic character less than 50% and that of covalent is more.According to Hannay and Smith Equation

Percentage ionic character

$=16(X_A-X_B) + 3.5(X_A-X_B)^2$

Solubility of ionic compounds:

The solubility of ionic compounds depends upon several parameters like lattice energy, hydration energy, polarization, packing pattern, entropy etc.

Higher polarization will cause less solubility in polar solvent.

Examples:

- $AgF > AgCl > AgBr > AgI$
- $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$
- $HgF_2 > HgCl_2 > HgBr_2 > HgI_2$
- More the covalent character where will be the solubility in relatively non-polar solvent.

- With decreasing the hydration energy, the solubility decreases down the group.
- **When the lattice energy and hydration energy are dominating factors**:

$U \propto 1/(r_c+r_a)$

Where r_c and r_a are the radii of cation and anion respectively.

$\Delta H_s \propto$ **$1/r_{ion}$.**

a) If $r_c << r_a$ then $r_c+r_a=r_a$

$\Delta H_s \propto 1/r_c$, where ΔH_s is heat of dissolution.

Thus, with increase in radius of the cation down the group heat of dissolution becomes less and less negative. Hence, the solubility decreases down the group.

Examples:

- $LiClO_4 > NaClO_4 > KClO_4 > RbClO_4 > CsClO_4$
- $LiNO_3>NaNO_3>KNO_3>RbNO_3>CsNO_3$
- $NaI > LiI > KI > RbI > CsI$
- $LiBr > NaBr>KBr>RbBr>CsBr$
- $CaCrO_4>SrCrO_4>BaCrO_4$
- $BeCO_3>MgCO_3>CaCO_3>SrCO_3>BaCO_3$
- $BeSO_4>MgSO_4>CaSO_4>SrSO_4>BaSO_4$
- $CaSO_3>SeSO_3>BaSO_3$
- $BeX_2>MgX_2>CaX_2>SrX_2>BaX_2$.(Where X=Cl,Br,I)

Exceptions where $r_c<<r_a$ what solubility increases down the group, are given as follows:

- $CaC_2O_4<SrC_2O_4<BaC_2O_4<BeC_2O_4$($BeC_2O_4$ is the exception of this trend)
- $Li_2CO_3<Na_2CO_3<K_2CO_3<Rb_2CO_3<Cs_2CO_3$
- $NaHCO_3<KHCO_3<RbHCO_3<CsHCO_3$

b) **When r_c is nearly equals to r_a then the lattice energy parameter is deciding factor for solubility order.**

- $LiF<NaF<KF<RbF<CsF$
- $LiOH<NaOH<KOH<RbOH<CsOH$
- $Be(OH)_2<Mg(OH)_2<Ca(OH)_2<Sr(OH)_2<Ba(OH)_2$

Electrical conductivity and color of the ionic compound:

- As the polarization increases, the electrical conductivity decreases because ionization tendency decreases due to increase in the covalent character. Example $LiCl > BeCl_2$
- As the intensity of color in ionic compound increases with the increase in polarization.

Colorless compound: $AgCl$, $PbCl_2$, $HgCl_2$, $SnCl_4$

Colored compound: AgI (yellow), PbI_2 (yellow), HgI_2 (deep red), SnI_4 (orange red)

Covalent bond:

A type of chemical bond in which there is mutual sharing of electrons between two atoms is called covalent bond.

It is further classified into single, double and triple covalent bond with respect to mutual sharing of one, two and three bonds respectively.

Conditions for formation of covalent bond:

- Incomplete octet of atom.
- Almost equal electronegativity.
- Equal sharing of electrons.

Characteristics of covalent compounds:

- Gases, liquids or solids at room temperature.
- low melting point and boiling point because the molecules are held together in the solid crystal lattice by weak forces.
- Soluble in nonpolar solvents because the kinetic energy of the solvent molecules easily overcome the weak intermolecular forces.
- Insoluble in polar solvents.
- Generally covalent compounds are insoluble in water. Some of them (alcohol, amine) dissolved in water due to hydrogen bonding.
- Non-conductor of electricity.
- Exhibit isomerism.
- Give slow molecular reactions.

Polar covalent bond:

A covalent bond in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, what is called a polar covalent bond.

Such type of bonds found in Hetero-atomic molecules.

Examples: HCl, H_2O, NH_3 etc.

Greater the difference of electronegativity between two atoms, higher the polar nature of covalent bond.

Sidgwick Powell Theory:

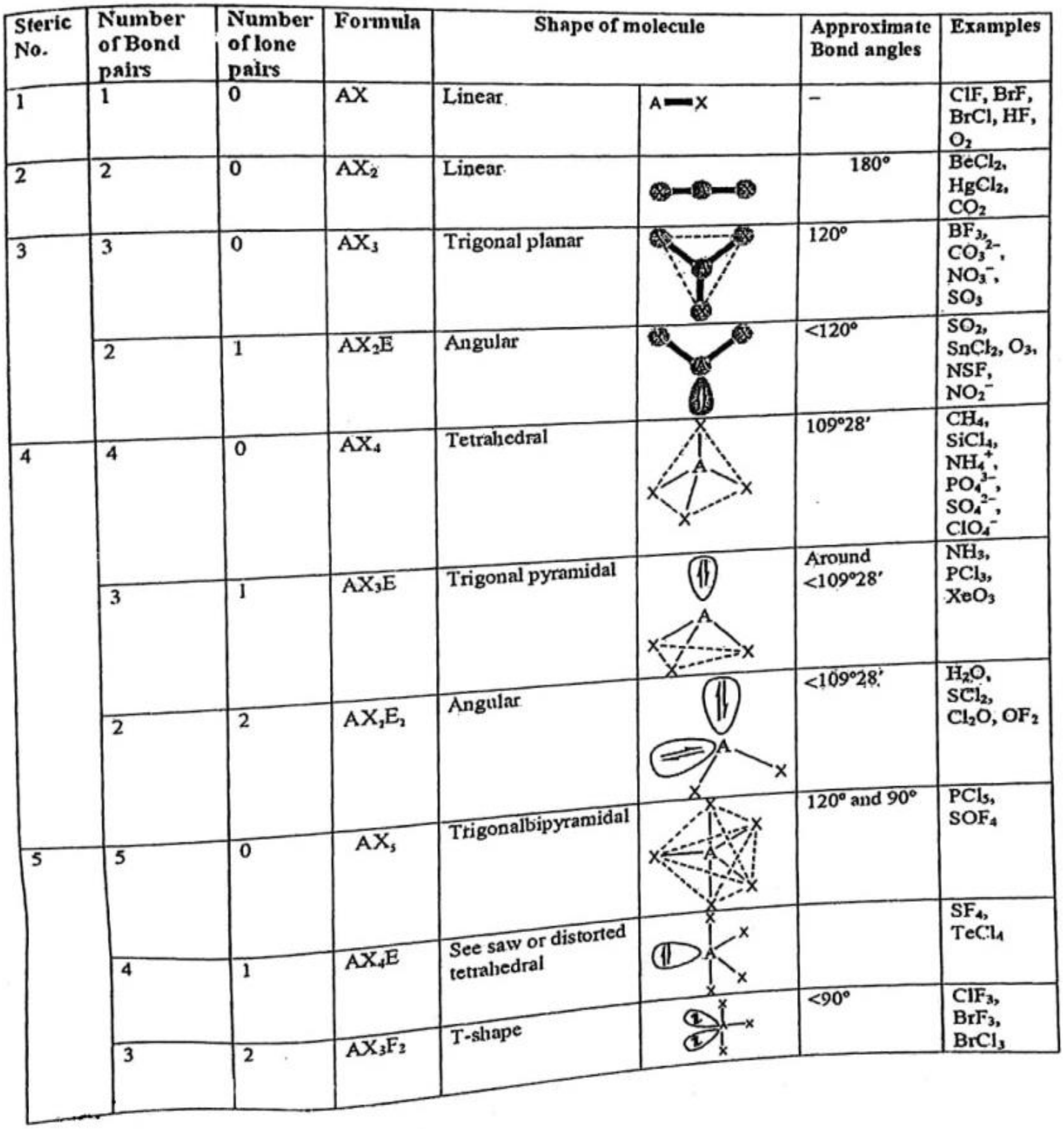
In 1940, Sidgwick and Powell reviewed the structure of molecules. This suggest that for molecules and ions that content single bonds, the approximate shape can be predicted from the number of electron pairs in the outer or valence shell of the central atom.

Number of electrons pair in outer shell	Shape of Molecule	Bond Angles
2	Linear	180°
3	Planner triangle	120°
4	Tetrahedron	109°28′
5	Trigonal bipyramidal	90° and 120°
6	Octahedral	90°
7	Pentagonal bipyramidal	72° and 90°

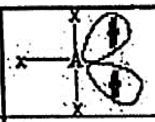
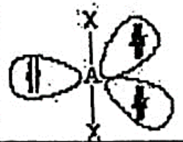
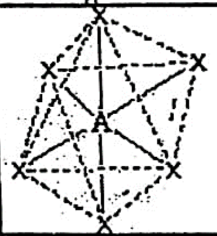
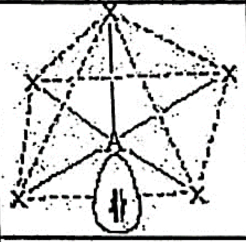
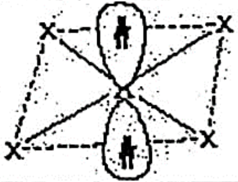
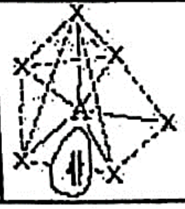
Valence shell electron pair repulsion (VSEPR) theory:

According to VSEPR theory

1. Electron pairs tend to minimize repulsions. Ideal geometries are as follows



Steric No.	Number of Bond pairs	Number of lone pairs	Formula	Shape of molecule		Approximate Bond angles	Examples
1	1	0	AX	Linear	A━X	–	ClF, BrF, BrCl, HF, O_2
2	2	0	AX_2	Linear		180°	$BeCl_2$, $HgCl_2$, CO_2
3	3	0	AX_3	Trigonal planar		120°	BF_3, CO_3^{2-}, NO_3^-, SO_3
	2	1	AX_2E	Angular		<120°	SO_2, $SnCl_2$, O_3, NSF, NO_2^-
4	4	0	AX_4	Tetrahedral		109°28′	CH_4, $SiCl_4$, NH_4^+, PO_4^{3-}, SO_4^{2-}, ClO_4^-
	3	1	AX_3E	Trigonal pyramidal		Around <109°28′	NH_3, PCl_3, XeO_3
	2	2	AX_2E_2	Angular		<109°28′	H_2O, SCl_2, Cl_2O, OF_2
5	5	0	AX_5	Trigonalbipyramidal		120° and 90°	PCl_5, SOF_4
	4	1	AX_4E	See saw or distorted tetrahedral			SF_4, $TeCl_4$
	3	2	AX_3F_2	T-shape		<90°	ClF_3, BrF_3, $BrCl_3$

							$BrCl_3$
5	2	3	AX_2F_3	Linear		180°	XeF_2, I_3^-
6	6	0	AX_6	Octahedral		90°	SF_6
	5	1	AX_5E	Square pyramidal		90°	ClF_5, BrF_5, ICl_5
	4	2	AX_4E_2	Square planar		90°	XeF_4
7	7	0	AX_7	Pentagonal bipyramidal		72° and 90°	IF_7
	6	1	AX_6E	Pentagonal pyramidal		Around 72° and 90°	$XeOF_5^-$, IOF_5^{2-}

2. Repulsions are of the order
LP-LP >LP-BP > BP-BP

(a) When lone pairs are present, the bond angles are smaller than predicted.

(b) Lone pairs choose the largest site e.g. equatorial in trigonal bipyramidal.

(c) If all sites are equal, lone pairs will be Trans to each other.

3. Double bonds occupy more space than single bonds.

4. Bonding pairs to electronegativity substituents occupy less space than those to more electropositive substituents.

Steps involved in predicting the shapes of molecules using VSEPR theory:

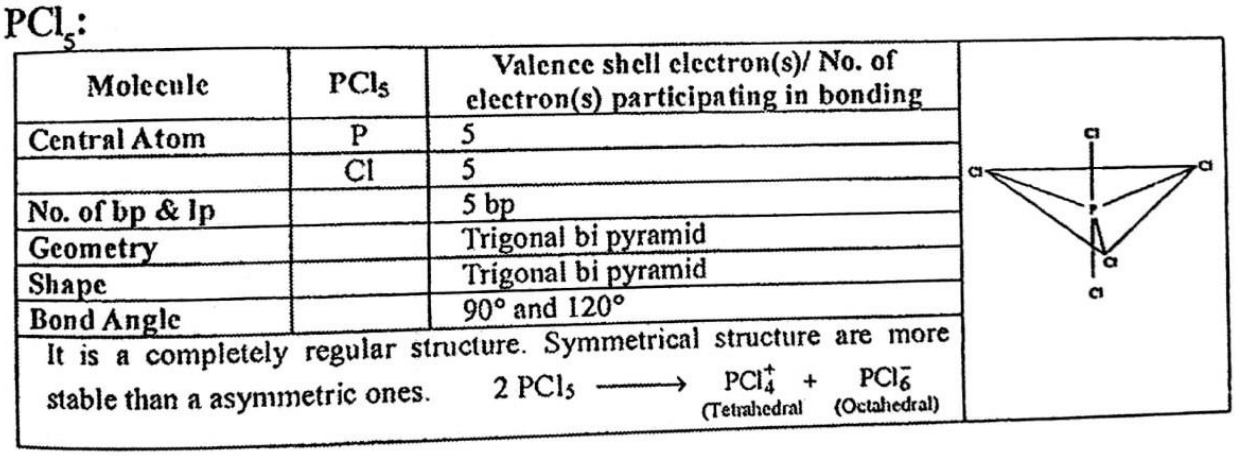
- **H=**S+½(E-V±C) **OR H=**lone pair of electrons+number of surrounding atoms

H=Hybridization
S= Number of atoms bonded with central atom
E= Valence electrons of central atom
V= Valency of central atom
C= Electrical charge on molecule,if molecule is ionic(+C for anion and -C for cation)

- Lone pairs of central atom (L)=½(E-valency of central atom±C)

Or,L=½(E-number of bonds around central atom±C)
Or,L=½(E-number of Bond pair of electrons around central atom±C)

PCl_5:



Molecule	PCl_5	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	P	5
	Cl	5
No. of bp & lp		5 bp
Geometry		Trigonal bi pyramid
Shape		Trigonal bi pyramid
Bond Angle		90° and 120°

It is a completely regular structure. Symmetrical structure are more stable than a asymmetric ones. $2\,PCl_5 \longrightarrow \underset{\text{(Tetrahedral}}{PCl_4^+} + \underset{\text{(Octahedral)}}{PCl_6^-}$

Modern theories of chemical bonding:

The theories of chemical bonding proposed by Kossel and Lewis are called as classical theories of bonding. This does not account the web mechanical or quantum mechanical principles. After the development of quantum mechanical description atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are valence bond theory (VBT) and Molecular Orbital Theory (MOT).

Valence Bond Theory (VBT):

This theory was proposed by Pauling in 1935 by which we can draw the geometrical structure of the molecule by considering the hybridization of the actual atom.

Hybridization:

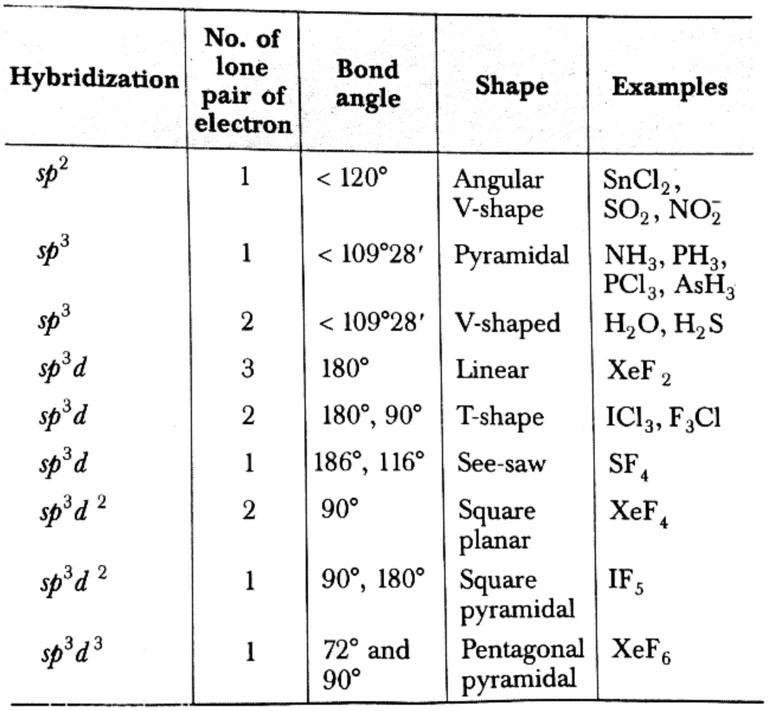
This is process where different atomic orbitals of comparable shape and energy are mixing to each other to produce an average energy orbital is called hybridization and the new orbitals are called hybrid orbitals.

In hybridization, positive and negative charge of a molecule, we take on central atom or surrounding atom, depends upon the electronegativity difference between two, which is more electronegative carry negative charge and vice versa.

Classification of hybridization:

a) Symmetrical hybridization (sp, sp^2, sp^3, sp^3d^2)

b) Unsymmetrical hybridization (sp^3d, sp^3d^3)



Hybridization	No. of lone pair of electron	Bond angle	Shape	Examples
sp^2	1	< 120°	Angular V-shape	$SnCl_2$, SO_2, NO_2^-
sp^3	1	< 109°28′	Pyramidal	NH_3, PH_3, PCl_3, AsH_3
sp^3	2	< 109°28′	V-shaped	H_2O, H_2S
sp^3d	3	180°	Linear	XeF_2
sp^3d	2	180°, 90°	T-shape	ICl_3, F_3Cl
sp^3d	1	186°, 116°	See-saw	SF_4
sp^3d^2	2	90°	Square planar	XeF_4
sp^3d^2	1	90°, 180°	Square pyramidal	IF_5
sp^3d^3	1	72° and 90°	Pentagonal pyramidal	XeF_6

The shapes of molecules are determined by the type of hybridization and number of bond/lone pair of electrons.

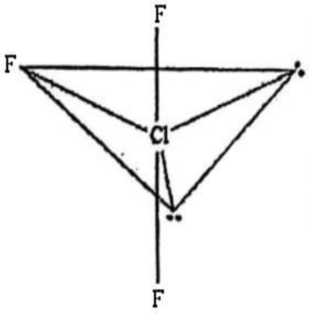
Postulates of VBT:

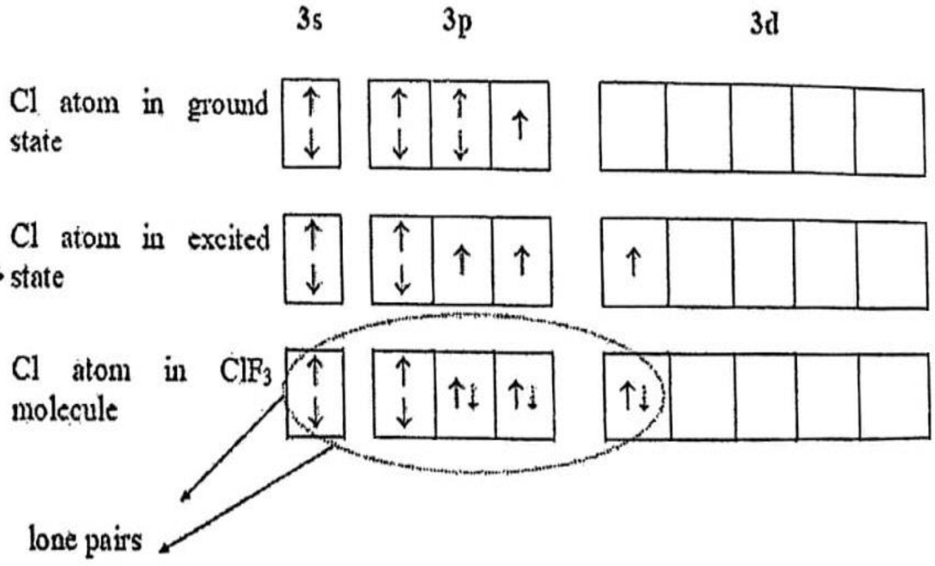
- A covalent bond is formed by the overlapping of two half filled valence atomic orbitals of two different atoms.
- The electrons in the overlapping orbitals get scared and confined between the nuclei of two atoms.
- The electron density between two bonded atoms increases due to overlapping. This confers stability to the molecule.
- Greater the extent of overlapping, stronger is the bond formed.
- The direction of the covalent bond is along the region of overlapping of the atomic orbitals i.e. covalent bond is directional.
- There are two types of covalent bonds based on the pattern of overlapping. They are i) σ-bond, ii) π-bond (the s orbitals can form only σ-bonds, where is the p, d, f orbitals can form both σ and π-bonds).

ClF_3

Cl → (E.C.) $3s^2\,3p^5\,3d^0$

Valence shell configuration

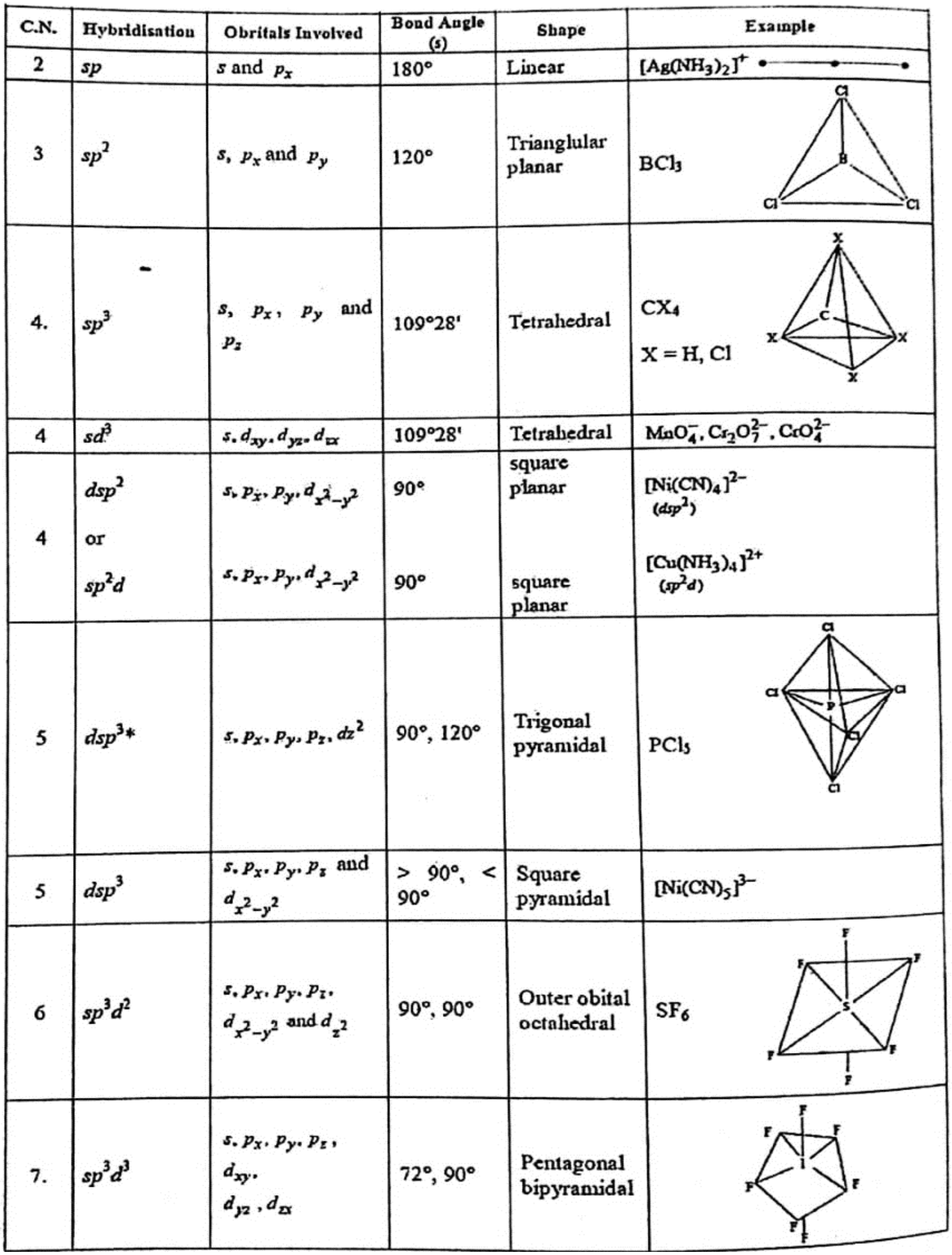




T-Shape

sp^3d Hybridisation

According to VBT, various type of hybridization gives different types of structure



C.N.	Hybridisation	Obritals Involved	Bond Angle (s)	Shape	Example
2	sp	s and p_x	180°	Linear	$[Ag(NH_3)_2]^+$
3	sp^2	s, p_x and p_y	120°	Trianglular planar	BCl_3
4.	sp^3	s, p_x, p_y and p_z	109°28'	Tetrahedral	CX_4 X = H, Cl
4	sd^3	$s, d_{xy}, d_{yz}, d_{zx}$	109°28'	Tetrahedral	MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-}
4	dsp^2 or sp^2d	$s, p_x, p_y, d_{x^2-y^2}$ $s, p_x, p_y, d_{x^2-y^2}$	90° 90°	square planar square planar	$[Ni(CN)_4]^{2-}$ (dsp^2) $[Cu(NH_3)_4]^{2+}$ (sp^2d)
5	dsp^3*	s, p_x, p_y, p_z, dz^2	90°, 120°	Trigonal pyramidal	PCl_5
5	dsp^3	s, p_x, p_y, p_z and $d_{x^2-y^2}$	> 90°, < 90°	Square pyramidal	$[Ni(CN)_5]^{3-}$
6	sp^3d^2	s, p_x, p_y, p_z, $d_{x^2-y^2}$ and d_{z^2}	90°, 90°	Outer obital octahedral	SF_6
7.	sp^3d^3	s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}	72°, 90°	Pentagonal bipyramidal	

Limitation of VBT:

- Since the electron constituting the covalent bond must come from different source, VBT does not explain co-ordinate bonds.
- VBT predicts O_2 to be diamagnetic. Since all electrons taking part in bonding should be paired to occupy low lying symmetric orbital. But experiments show O_2 to be paramagnetic.
- This theory does not consider formation of odd electron, molecule or ions (such as H_2^+) where no pairing of electron is possible.

Stability of compound with participation of d-orbital is always lower than those compound in which d-orbital is not present in hybridization. Because stability is inversely proportional with energy.

Molecular orbital theory:

A) Basic features of MOT:

- **When atoms come in equilibrium distance,** their valence shell A.O's coming together to form a new sets of MO's. So A.O's are mono-atomic but MO's are polyatomic.
- **When atom combine**, they always come in a pair AO's maybe pure or may be hybridized.
- To form an effective MO's the AO's satisfy the following condition

They have a same symmetry

They have a comparable energy

They have to allow for overlapping

- The bonding molecular orbitals are presented by σ, Π and δ etc. Whereas the corresponding antibonding molecular orbitals are represented by $\sigma *$, Π* and δ*.
- The shape of the molecular orbitals formed depends upon the type of the combing atomic orbitals.
- The number of MO's is equal to the number of AO's combined together. Half of the MO's have a higher in energy called antibonding MO's (ABMO).

BMO $(\psi_g)=N(\psi_a+\psi_b)$

ABMO $(\psi_u)=N(\psi_a-\psi_b)$

B) Bond strength: p-p >s-p > s-s

For tri-atomic molecules, other the BMO and ABMO, a new MO is formed called non-bonding MO and the energy order is BMO < non-bonding MO < ABMO.

Electron filled up into the MO's according to the Afbau principle, Pauli exclusion principle and Hund's rule i.e. lower energy MO filled up first where as higher energy MO's fill up at the end.

MO electronic distribution:

$$\sigma_{1s}\ \sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}\sigma_{2p_x}\ (\pi_{2p_y}\pi_{2p_z})\ (\pi^*_{2p_y}\pi^*_{2p_z})\ \sigma^*_{2p_x}$$

From MO electronic distribution we can determine the bond order by the following,

Bond order = ½(number of bonding MO's - number of antibonding MO's)

Information convey by bond order:

1. If the value of bond order is positive, it indicates a stable molecule and if the value of bond order is negative or zero, it means that the molecule is unstable and is not formed.
2. Dissociation energy of the molecule is directly proportional to the bond order of the molecule. In other words, greater the bond order greater is the dissociation energy.
3. Greater the bond order shorter will be the bond length.
4. Knowing the bond order, the number of covalent bonds between the atoms in the molecule can be predicted. Bond order of a molecule is equal to the number of covalent bonds between the atoms in the molecule.
5. If the es are paired, the substance is diamagnetic and in case there are unpaired electrons in the molecule, the substance is paramagnetic. If bond order is fractional, the molecule will definitely be paramagnetic. However, if the bond order is whole number, the molecule may or may not be paramagnetic.

Molecular properties like magnetic behavior of the species can be determined from the MO electronic distribution.

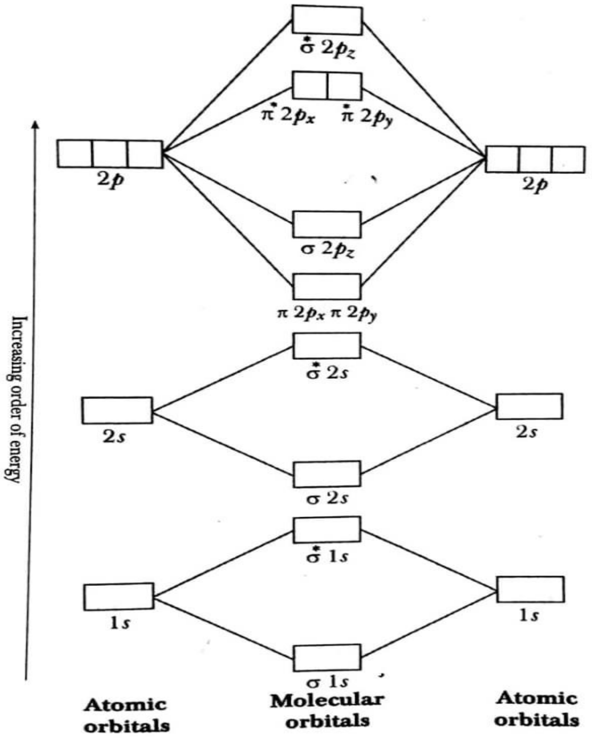
Magnetic moment (μ)=$\sqrt{n(n+2)}$ **BM**

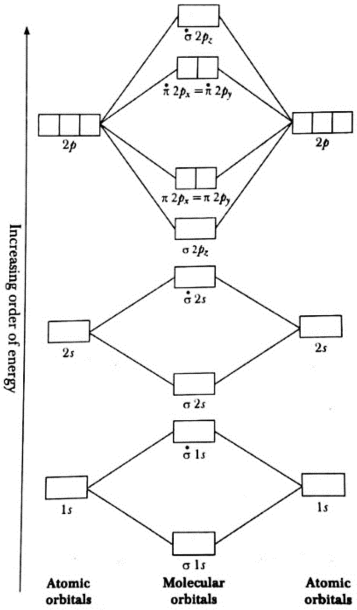
Where n= Number of unpaired electrons.

If total number of electrons in a molecule ≤14, the energy level of MO's follows this sequence

$$\sigma_{1s}\,\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}\ \ (\pi_{2p_x}\pi_{2p_y})\ \sigma_{2p_z}(\pi^*_{2p_x}\pi^*_{2p_y})\ \sigma^*_{2p_z}$$

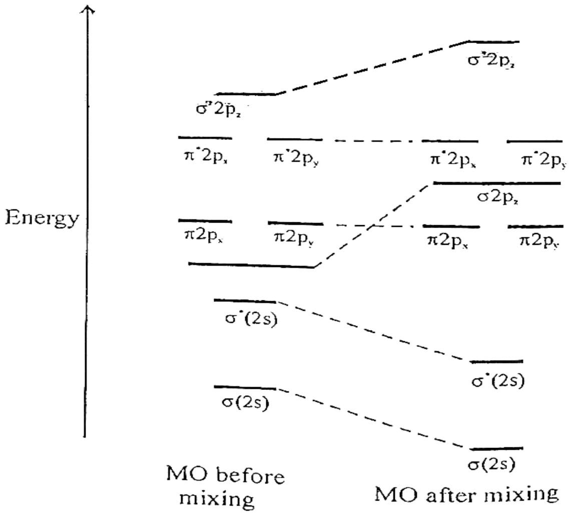
If total number of electrons in molecule >14, then the energy sequence of energy of molecular orbitals in MO diagram will be





$$\sigma_{1s}\,\sigma^{*}_{1s}\sigma_{2s}\sigma^{*}_{2s}\sigma_{2p_z}\,(\pi_{2p_x}\pi_{2p_y})\,(\pi^{*}_{2p_x}\pi^{*}_{2p_y})\,\sigma^{*}_{2p_z}$$

If the difference between 2s and 2p atomic orbital are small, this is a possibility of the mixing of these orbitals to form mixed atomic orbitals. This would be comparatively more stable.



Isoelectronic species have the same shape and same bond order e.g. CO and NO^+ or CO_3^{2-} and NO_3^-.

CO: C=$1s^22s^22p^2$, O= $1s^22s^22p^4$

A total of 10 outer electrons are to be accommodated in the MO of CO. The MO electronic configuration

= $kk\sigma(2s)^2\sigma *(2s)^2\pi(2p_x)^2\pi(2p_y)^2\sigma(2p_z)^2$

Bond order = ½(8-2) = 3

NO$^+$: kk$\sigma(2s)^2\sigma*(2s)^2\sigma(2p_z)^2\pi(2p_x)^2\pi(2p_y)^2$

Bond order = ½(8-2) = 3

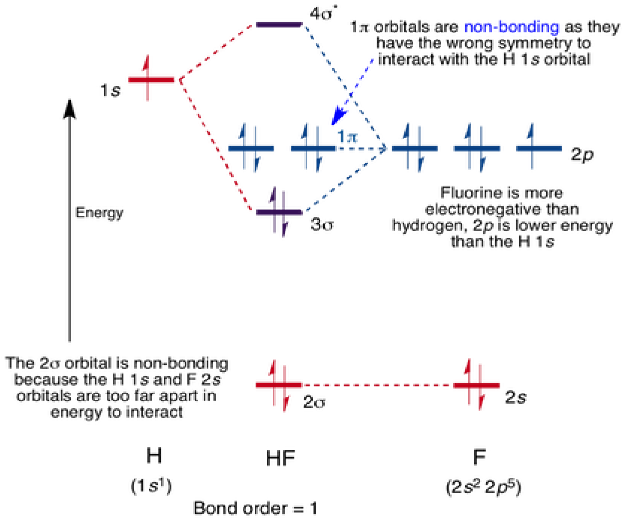
CN$^-$: kk$\sigma(2s)^2\sigma*(2s)^2\pi(2p_x)^2\pi(2p_y)^2\sigma(2p_z)^2$

Bond order = ½(8-2) = 3

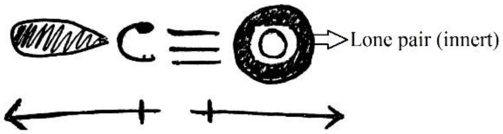
HF: The 2s AO of the F atom does not interact with 1s AO of H atom because of its low energy and is retained as atomic orbital. Only the 2pz orbital of f atom has proper symmetry and energy to interact with 1s orbital of H atom to form σ(sp) MO. The σ(sp) is the only MO formed in HF molecule. This is bonding orbitals with 2 es. The rest of the es remain in their MOs. The MO formed in the case of HF molecule will not be symmetrical.

HF: KK$(2s)^2\sigma(sp)^2(2p_x)^2(2p_y)^2$

HCl: KL$(3s)^2\sigma(sp)^2(3p_x)^2(3p_y)^2$



CO has negligible dipole moment: the dipole moment of CO is very low. This cannot be explained by VBT, but explained by MOT. The σ-bond moment is partially cancelled by lone pair moment which is situated on carbon atom.



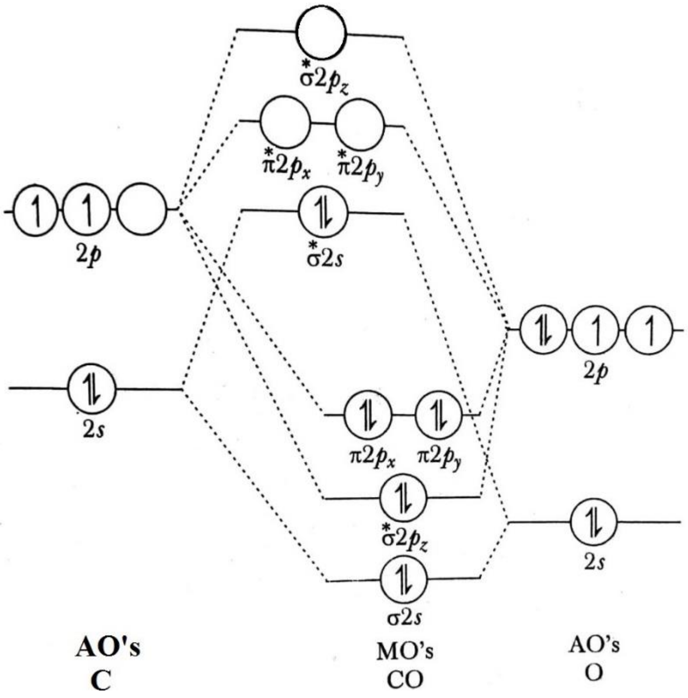
Ligand:

Any species which is able to donate its electron pair to the transition metal and form a stable complex is called ligand.

CO contains two lone pairs, one of the O-atom which is highly stable (not available for donation) but the other lone pair which is placed in C atom is highly reactive, easily available for donation to the transition metal. So that CO is a very good ligand, but CO is a poor Lewis base fails to you donate its lone pair to the Lewis acid.

Actually, CO is a week σdonor, the stability of metal carbonyls comes due to the formation of dπ-pπback bonding. Here field metal d orbital overlap with the low-lying empty $\pi^*_{2p_y}$ or $\pi^*_{2p_z}$of CO. So that the metal ligand bond order increases as well as stability also increases.

MO picture:



Common features between valence bond theory and molecular orbital theory:

- Both the theories are the interpretation of covalent bonds.
- According to both theories the atomic orbitals of the two atoms mast overlap to form a covalent bond. The atomic orbitals overlapping each other must have the same symmetry and must be of same energy.
- According to both, the electronic charge resides in the region between the atomic nuclei.
- The basic principles involved in the distribution of electrons are similar. Thus, an orbital, whether atomic or molecular cannot have more than two electrons. They are field in order of increasing energy.
- Both the theory postulates that a covalent bond poses directional properties.

Hydrogen bonding: The electrostatic attraction between a hydrogen atom, covalently bonded to a highly electronegative (O, N, F) atom and a lone pair of electrons of another electronegative atom (F, O, N) in different or same molecule is called hydrogen bonding.

Nature of hydrogen bonding:

Since the hydrogen bond is formed by the most electronegative elements only, it is considered that its nature is dipole-ion, dipole-induced dipole or dipole-dipole interaction.

Conditions for hydrogen bonding:

- High electronegativity of atom bonded to hydrogen.
- Small size of electronegative atom.

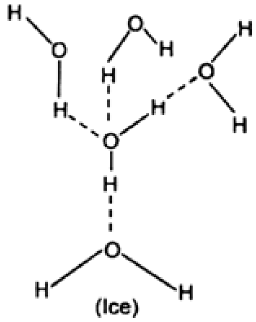
Types of hydrogen bond:

- Intermolecular hydrogen bonding
- Intramolecular hydrogen bonding

Intermolecular hydrogen bonding:

This type of hydrogen bonding takes place between hydrogen and electronegative element in the different molecules of the same substances for different substances. The compounds with intermolecular hydrogen bonding have high melting point, boiling point, viscosity, surface tension etc.

- **Carboxylic acid diereses in gaseous state due to hydrogen bonding.**
- **In gaseous state several polymeric forms of the HF molecules exist in which the monomers are held together through hydrogen bonding.**
- Trimethylamine has a higher relative molecular weight than dimethylamine. Yet trimethylamine has a lower boiling point (4 °C) as it is not associated through hydrogen bonds (no H atom joined only to N); dimethylamine, hydrogen bonded, boils at 7 °C.
- **Ice** contains extensive hydrogen bonding. Each oxygen atom is surrounded tetrahedrally by four hydrogen atoms-two H atoms by usual covalent bonds, the other two by hydrogen bonds. When ice melts, some of these hydrogen bonds break, the water molecules can now come closer. Hence the volume decreases on melting. When water at 0°C is heated, breaking of such ordered H-bonds still continues up to about 4°C and the contraction caused is greater than thermal expansion. So, the volume goes on decreasing up to this point. Normal expansion of volume on heating starts only after this temperature. Consequently water has its higher density at 4 °C.



(Ice)

Intramolecular hydrogen bonding:

This type of hydrogen bonding occurs when polar hydrogen and electronegative atom are present in the same molecule, i.e. hydrogen bonding within a molecule called intramolecular hydrogen bonding. Due to this the molecules present in discrete unit and not in associated form. Intramolecular hydrogen bonding has no effect on physical properties like melting point, boiling point, viscosity, surface tension, solubility etc.

- Intramolecular hydrogen bonding provides the extra stability to a molecule through chelation.

The necessary conditions for the formation of intramolecular hydrogen bonding:

- The ring formed as a result of hydrogen bonding should be planner.
- 5 or 6 membered rings should be formed.
- Interacting atoms should be placed in such a way that there is minimum strain during the ring closer.

Note: HF_2^- (or KHF_2) exists but HCl_2^- (or $KHCl_2$) does not because there is H bonding in HF but not in HCl.

Van der waals bonding:

Van der waals forces is a general term used to define the attraction of intermolecular forces between molecules. There are two kinds of Van der Waals forces: weak London dispersion forces, stronger dipole-dipole forces.

(i) **Dipole-dipole interaction:** These interactions are present in polar substances like NH_3, SO_2, HF, HCl etc. In these types of polar molecules, which though neutral have permanent dipoles, the Van der waals forces are due to electrical interaction between dipoles. The magnitude of this type of interaction depends upon the dipole moment of the molecule, the greater the dipole moment, the greater is the dipole dipole interaction.

(ii) **Induced dipole-induced dipole interactions London interaction:** These interactions are present in non-polar molecules Cl_2, I_2, O_2, N_2 and monoatomic molecules such as He, Ne, Ar etc. The electrostatics forces of attraction between induced dipoles and original dipoles are known as London forces.

(a) The magnitude of vander waals forces increases as the number of electrons in a molecules increases with the increase in vander waals forces the boiling points of the molecules also increases.

(b) Larger the molar mass, the stronger is the vander waals forces and hence boiling point also increases.

(c) Vander waals forces are only short range forces.

(d) The forces are much weaker than covalent and hydrogen bonds. Bond energies per mole involved in covalent bond hydrogen bond and the vander waals attraction are 200-400, 10-40 and 2-20kJ respectively.

(d) Strength of bonds: Ionic bond> covalent bond > Metallic bond > H-bond.

Co-ordinate Bond:

Co-ordinate bond is a type of alternate covalent bond that is formed by sharing of electron pair from a single atom. Both shared electrons are donated by the same atom. It is also called dative bond or dipolar bond.

Co-ordinate covalent bonds are usually formed in reactions that involve two non-metals such as a hydrogen atom or during bond formation between metals ions and ligands.

Characteristics of Coordinate Covalent bond:

(1) In this type of bonding, the atom that shares an electron pair from itself is termed as the donor.

(2) The other atom which accepts these shared pair of electrons is known as a receptor or acceptor.

(3) The bond is represented with an arrow →, pointing towards acceptor from the donor atom.

(4) After sharing of electron pain each atom gets stability.

(5) This type of bonding is central to the Lewis theory.

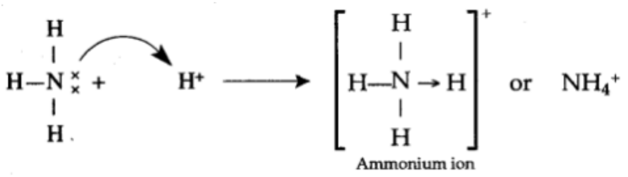
(6) Getting a good understanding of co-ordinate covalent bonds can help in properly designing complex organic molecules.

Property:

1. These have lower melting and boiling points than ionic compounds.
2. Some of these compounds exhibit isomerism.
3. Sharing of electrons takes place in a definite direction, hence, it is a directional bond.
4. It is weaker than Ionic bonding.

Examples:

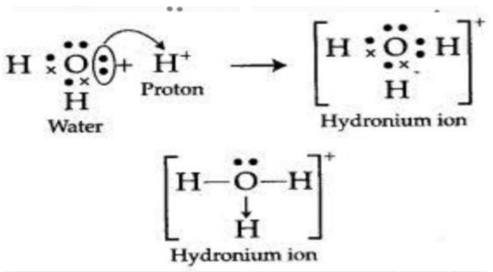
(1) **Formation of Ammonium ions:**



The nitrogen atom in Ammonia donates its electron pair to the empty orbital of H^+ ion thus nitrogen is donor, H^+ is acceptor and a co-ordinate bond is formed.

(2) **Formation of Hydronium ion:**

An oxygen atom in water donates its one pair of electrons to the vacant orbital of H^+ ion thus a dative bond is formed oxygen atom is donor atom and H^+ acceptor atom.



Metallic bonds: Metals are made up of positive ions packed together, usually in one of the three following geometrical arrangements- (i)face centred cubic (fcc) (ii) hexagonal close packed (hcp) (iii) body centred cubib(bcc)

(a) Metallic bonds are weaker than covalent bonds because the valency electrons in a metallic bond, being mobile, do not experience very strong force of attraction towards the nuclei.

(b) Alkali metals have only a single electron in the valance shell, therefore, only half of the outermost energy level band is occupied by electrons and even on slightest excitations, these electrons can move to higher energy levels in this bond. The mobility of these electrons make the alkali metals good conductor of electricity.

(c) In case of alkaline earth metals the outermost orbital is fully filled with two electrons so that no vacant energy level of the energy band is available for the electrons to jump to. However, at the equilibrium intermolecular distance, the 3s energy band and the 3p energy band overlap so that some of the vacant energy levels of 3p band and the filled energy levels of the 3s band fall in the same energy range, consequently, the 3s electrons can be easily excited to the 3p energy levels in this range. The resulting mobility of electrons makes the alkaline earth metals good conductor of electricity.

Hydrogen Bridge bonds in diborane:

Diborane

Figure 1. The structure of diborane

If we consider the molecule B_2H_6 (diborane Figure 1), there are 12 valence electrons at our disposal for chemical bonding (B has 3, and H has 1, so 2xB + 6xH =12). Each terminal B–H bond is a standard vanilla two electron bond, and there are four of these, thus accounting for a total of eight electrons. This leaves a total of four electrons to share between the two bridging H atoms and the two B atoms. Consequently, two B–H–B bridging bonds are formed, each of which consists of two electrons (Figure 2), forming what are called three center-two-electron bonds (i.e., 3 atoms share 2 electrons) – sometimes called ‘banana’ bonds, as they are not linear but curved. Each B atom is, approximately, sp^3 hybridized, and if we consider just one of the B atoms, two of the four sp^3 hybrid orbitals form s bonds to the terminal H atoms (1s orbitals). That leaves two B sp^3 hybrid orbitals, one of which contains an electron, one of which is empty. For each bridge therefore, one sp3 orbital from each of the B atoms combines (Figure 3) with the 1s orbital of the bridging H atom to form three new molecular orbitals (MOs) – as always, n atomic orbitals (AO) form n MOs. One B atom gives its remaining valence electron to one bridge, and the other B atom gives to the other. Each bridge, therefore, has two electrons, which fill our new MO scheme starting with the lowest energy bonding MO.

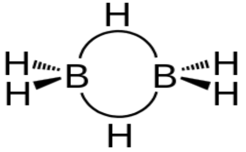


Figure 2: The terminal B-H bonds and the bridging B-H-B bonds each contain two electrons.

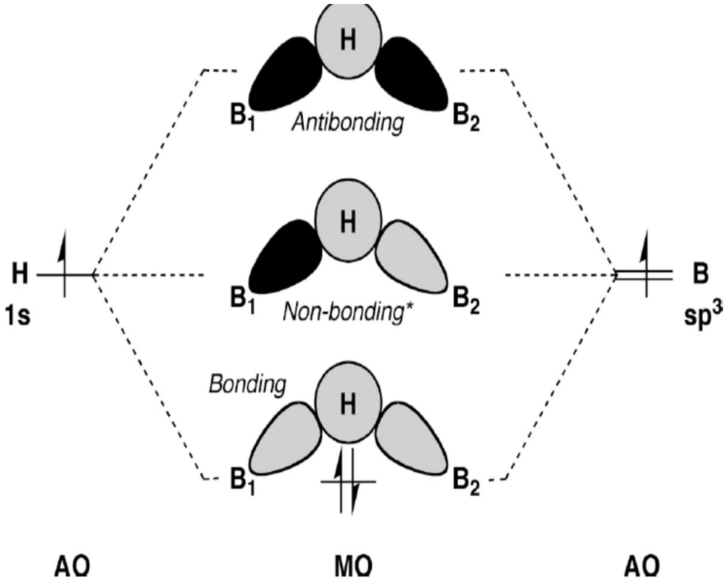


*Figure 3. The MO scheme for one of the B–H–B bridging three center two electron bonds. *This picture is still a simplification of the actual MO scheme. The non-bonding orbital is actually of slightly lower energy than shown and so has slight bonding character. This arises from the fact that the orbitals involved in the terminal B–H bonding have the correct symmetry to overlap with the bridging bond orbitals, resulting in a stabilization of the 'non-bonding' orbital.*