

Chapter 3 Chemical Bonding

Atoms of different elements *excepting* noble gases do not have complete octet so they combine with other atoms to form chemical bond. The force which holds the atoms or ions together within the molecule is called a **chemical bond** and the process of their combination is called **Chemical Bonding**. It depends on the valency of atoms.

Cause and Modes of chemical combination

Chemical bonding takes place due to *acquire a state of minimum energy and maximum stability* and to *convert atoms into molecule to acquire stable configuration of the nearest noble gas*. We divide atoms into three classes,

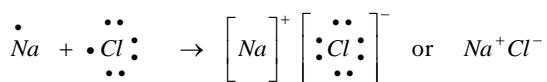
- (1) Electropositive elements which give up one or more electrons easily. They have low ionisation potentials.
- (2) Electronegative elements, which can gain electrons. They have higher value of electronegativity.
- (3) Elements which have little tendency to lose or gain electrons.

Different types of bonds are formed from these types of atoms.

Atoms involved	Type
$A + B$	Electrovalent
$B + B$	Covalent
$A + A$	Metallic
Electrons deficient molecule or ion (Lewis acid) and electrons rich molecule or ion (Lewis base)	Coordinate
H and electronegative element (F, N, O)	Hydrogen

Electrovalent bond

An electrovalent bond is formed when a metal atom transfers one or more electrons to a non-metal atom.



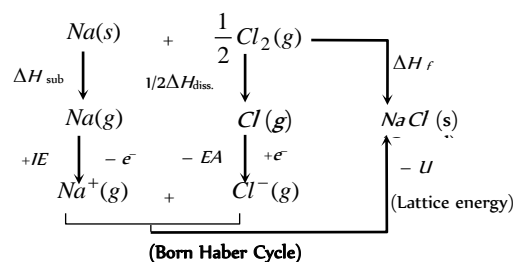
Some other examples are: MgCl , CaCl , MgO , NaS , CaH , AlF , NaH , KH , K_2O , KI , RbCl , NaBr , CaH etc.

(1) Conditions for formation of electrovalent bond

- (i) The atom which changes into cation (+ive ion) should possess 1, 2 or 3 valency electrons. The other atom which changes into anion (–ve ion) should possess 5, 6 or 7 electrons in the valency shell.
- (ii) A high difference of electronegativity (about 2) of the two atoms is necessary for the formation of an electrovalent bond. *Electrovalent bond is not possible between similar atoms.*
- (iii) *There must be overall decrease in energy i.e., energy must be released. For this an atom should have low value of **ionisation potential** and the other atom should have high value of **electron affinity**.*

(iv) *Higher the lattice energy, greater will be the case of forming an ionic compound. The amount of energy released when free ions combine together to form one mole of a crystal is called **lattice energy (U)**.* Lattice energy = $\frac{K}{r^+ + r^-}$; $r^+ + r^-$ is internuclear distance.

The energy changes involved in the formation of ionic compounds from their constituent elements can be studied with the help of a thermochemical cycle called **Born Haber cycle**.



According to Hess's law of constant heat summation, heat of formation of an ionic solid is net resultant of the above changes.

$$\Delta H_f = \Delta H_{\text{Subl.}} + \frac{1}{2}\Delta H_{\text{diss.}} + IE - EA - U$$

(2) Characteristics of electrovalent compounds

(i) Electrovalent compounds are generally crystalline in nature. The constituent ions are arranged in a regular way in their lattice.

(ii) Electrovalent compounds possess high melting and boiling points. Order of melting and boiling points in halides of sodium and oxides of II^+ group elements is as,



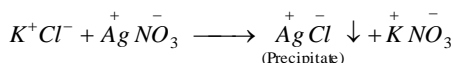
(iii) Electrovalent compounds are hard and brittle in nature.

(iv) Electrovalent solids do not conduct electricity. While electrovalent compounds in the molten state or in solution conduct electricity.

(v) Electrovalent compounds are fairly soluble in polar solvents and insoluble in non-polar solvents.

(vi) The electrovalent bonds are non-rigid and non-directional. Thus these compounds do not show space isomerism e.g. geometrical or optical isomerism.

(vii) Electrovalent compounds furnish ions in solution. The chemical reaction of these compounds are known as ionic reactions, which are fast.



(viii) Electrovalent compounds show isomorphism.

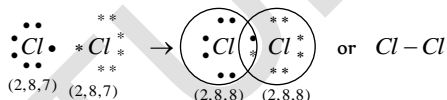
(ix) Cooling curve of an ionic compound is not smooth, it has two break points corresponding to time of solidification.

(x) Ionic compounds show variable electrovalency due to unstability of core and inert pair effect.

Covalent bond

Covalent bond was first proposed by **Lewis** in 1916. The bond formed between the two atoms by mutual sharing of electrons so as to complete their octets or duplets (in case of elements having only one shell) is called **covalent bond or covalent linkage**. A covalent bond between two similar atoms is non-polar covalent bond while it is polar between two different atoms having different electronegativities. Covalent bond may be single, double or a triple bond. We explain covalent bond formation by Lewis octet rule.

Chlorine atom has seven electrons in the valency shell. In the formation of chlorine molecule, each chlorine atom contributes one electron and the pair of electrons is shared between two atoms. Both the atoms acquire stable configuration of argon.



Some other examples are : $\text{H}_2\text{S}, \text{NH}_3, \text{HCN}, \text{PCl}_3, \text{PH}_3, \text{C}_2\text{H}_2, \text{H}_2, \text{C}_2\text{H}_4, \text{SnCl}_4, \text{FeCl}_3, \text{BH}_3$, graphite, BeCl_2 etc.

(1) Conditions for formation of covalent bond

(i) The combining atoms should be short by 1, 2 or 3 electrons in the valency shell in comparison to stable noble gas configuration.

(ii) Electronegativity difference between the two atoms should be zero or very small.

(iii) The approach of the atoms towards one another should be accompanied by decrease of energy.

(2) Characteristics of covalent compounds

(i) These exist as gases or liquids under the normal conditions of temperature and pressure. Some covalent compounds exist as soft solids.

(ii) Diamond, Carborandum (SiC), Silica (SiO_2), AlN etc. have giant three dimensional network structures; therefore have exceptionally high melting points otherwise these compounds have relatively low melting and boiling points.

(iii) In general covalent substances are bad conductor of electricity. Polar covalent compounds like HCl in solution conduct electricity. Graphite can conduct electricity in solid state since electrons can pass from one layer to the other.

(iv) These compounds are generally insoluble in polar solvent like water but soluble in non-polar solvents like benzene etc. some covalent compounds like alcohol, dissolve in water due to hydrogen bonding.

(v) The covalent bond is rigid and directional. These compounds, thus show isomerism (structural and space).

(vi) Covalent substances show molecular reactions. The reaction rates are usually low.

(vii) The number of electrons contributed by an atom of the element for sharing with other atoms is called **covalency** of the element. Covalency = $8 - [\text{Number of the group to which element belongs}]$. The variable covalency of an element is equal to the total number of unpaired electrons in s , p and d -orbitals of its valency shell.

The element such as P , S , Cl , Br , I have vacant d -orbitals in their valency shell. These elements show variable covalency by increasing the number of unpaired electrons under excited conditions. The electrons from paired orbitals get excited to vacant d -orbitals of the same shell.

Four elements, H , N , O and F do not possess d -orbitals in their valency shell. Thus, such an excitation is not possible and variable valency is not shown by these elements. This is reason that NCl_4 exists while NCl_5 does not.

(3) **The Lewis theory** : The tendency of atoms to achieve eight electrons in their outermost shell is known as Lewis octet rule.

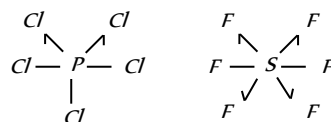
Lewis symbol for the representative elements are given in the following table,

	1	2	13	14	15	16	17
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Lewis symbol	\times	$\bullet \times$	$\cdot \times \cdot$	$\cdot \times \cdot$	$\cdot \times \cdot$	$\cdot \times \cdot$	$\cdot \times \cdot$

(4) **Failure of octet rule** : There are several stable molecules known in which the octet rule is violated i.e., atoms in these molecules have number of electrons in the valency shell either short of octet or more than octet.

$\text{BeF}_2, \text{BF}_3, \text{AlH}_3$ are electron-deficient (Octet incomplete) hence are Lewis acid.

In PCl_5 , P has 10 electrons in valency shell while in SF_6 , S has 12 electrons in valency shell. **Sugden** introduced singlet linkage in which one electron is donated (Instead of one pair of electrons) to the electron deficient atom so that octet rule is not violated. This singlet is represented as (\rightarrow) . Thus, PCl_5 and SF_6 have structures as,



(5) **Construction of structures for molecules and poly atomic ions** : The following method is applicable to species in which the octet rule is not violated.

(i) Determine the total number of valence electrons in all the atoms present, including the net charge on the species (n).

(ii) Determine $n = [2 \times (\text{number of H atoms}) + 8 \times (\text{number of other atoms})]$.

General formula	Molecular geometry	Dipole moment	Example
AX	Linear	May be non zero	HF, HCl
AX_2	Linear Bent or V-shape	Zero Non zero	CO_2, CS_2 H_2O, NO_2
AX_3	Triangular planar Pyramidal T-shape	Zero Non zero Non zero	BF_3 NH_3, PCl_3 ClF_3
AX_4	Tetrahedral	Zero	CH_4, CCl_4

AX_5	Square planar	Zero	XeF_4
	See saw	Non zero	$SF_4, TeCl_4$
AX_6	Trigonal bipyramidal	Zero	PCl_5
	Square pyramidal	Non zero	$BrCl_5$
AX_7	Octahedral	Zero	SF_6
	Distorted octahedral	Non zero	XeF_6
AX_7	Pentagonal bipyramidal	Zero	IF_7

(2) Every ionic compound having some percentage of covalent character according to Fajan's rule. The percentage of ionic character in compound having some covalent character can be calculated by the following equation.

$$\text{The \% ionic character} = \frac{\text{Observed } \mu}{\text{Theoretical } \mu} \times 100.$$

(3) The trans isomer usually possesses either zero dipole moment or very low value in comparison to *cis*-form



Fajan's rule

The magnitude of polarization or increased covalent character depends upon a number of factors. These factors are,

(1) **Small size of cation** : Smaller size of cation greater is its polarizing power i.e. greater will be the covalent nature of the bond.

(2) **Large size of anion** : Larger the size of anion greater is its polarizing power i.e. greater will be the covalent nature of the bond.

(3) **Large charge on either of the two ions** : As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases with the result its ability for forming the covalent bond increases.

(4) **Electronic configuration of the cation** : For the two ions of the same size and charge, one with a pseudo noble gas configuration (i.e. 18 electrons in the outermost shell) will be more polarizing than a cation with noble gas configuration (i.e., 8 electron in outer most shell).

Valence bond theory or VBT

It was developed by Heitler and London in 1927 and modified by Pauling and Slater in 1931.

(1) To form a covalent bond, two atoms must come close to each other so that orbitals of one overlaps with the other.

(2) Orbitals having unpaired electrons of anti spin overlaps with each other.

(3) After overlapping a new localized bond orbital is formed which has maximum probability of finding electrons.

(4) Covalent bond is formed due to electrostatic attraction between radii and the accumulated electrons cloud and by attraction between spins of anti spin electrons.

(5) Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy and the stability of bond will also be high.

(6) The extent of overlapping depends upon: Nature of orbitals involved in overlapping, and nature of overlapping.

(7) More closer the valence shells are to the nucleus, more will be the overlapping and the bond energy will also be high.

(8) Between two sub shells of same energy level, the sub shell more directionally concentrated shows more overlapping. Bond energy : $2s-2s < 2s-2p < 2p-2p$

(9) *s*-orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, *p*-orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping. Overlapping of different type gives sigma (σ) and pi (π) bond.

Sigma (σ) bond	Pi (π) bond
It results from the end to end overlapping of two <i>s</i> -orbitals or two <i>p</i> -orbitals or one <i>s</i> and one <i>p</i> -orbital.	It result from the sidewise (lateral) overlapping of two <i>p</i> -orbitals.
Stronger	Less strong
Bond energy 80 <i>kcal</i> s	Bond energy 65 <i>kcal</i> s
More stable	Less stable
Less reactive	More reactive
Can exist independently	Always exist along with a σ -bond
The electron cloud is symmetrical about the internuclear axis.	The electron cloud is above and below the plane of internuclear axis.

Hybridization

The concept of hybridization was introduced by Pauling and Slater. Hybridization is defined as the intermixing of dissimilar orbitals of the same atom but having slightly different energies to form same number of new orbitals of equal energies and identical shapes. The new orbitals so formed are known as **hybrid orbitals**.

Characteristics of hybridization

(1) Only orbitals of almost similar energies and belonging to the same atom or ion undergoes hybridization.

(2) Hybridization takes place only in orbitals, electrons are not involved in it.

(3) The number of hybrid orbitals produced is equal to the number of pure orbitals, mixed during hybridization.

(4) In the excited state, the number of unpaired electrons must correspond to the oxidation state of the central atom in the molecule.

(5) Both half filled orbitals or fully filled orbitals of equivalent energy can involve in hybridization.

(6) Hybrid orbitals form only sigma bonds.

(7) Orbitals involved in π bond formation do not participate in hybridization.

(8) Hybridization never takes place in an isolated atom but it occurs only at the time of bond formation.

(9) The hybrid orbitals are distributed in space as apart as possible resulting in a definite geometry of molecule.

(10) Hybridized orbitals provide efficient overlapping than overlapping by pure *s*, *p* and *d*-orbitals.

(11) Hybridized orbitals possess lower energy.

How to determine type of hybridization : The structure of any molecule can be predicted on the basis of hybridization which in turn can be known by the following general formulation,

$$H = \frac{1}{2}(V + M - C + A)$$

Where H = Number of orbitals involved in hybridization viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridization will be sp , sp , sp , spd , spd , spd respectively.

V = Number electrons in valence shell of the central atom,

M = Number of monovalent atom

C = Charge on cation,

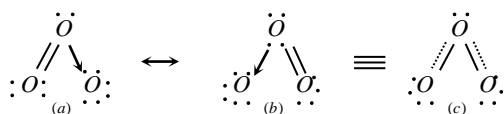
A = Charge on anion

Resonance

The phenomenon of resonance was put forward by **Heisenberg** to explain the properties of certain molecules.

In case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecule. The actual structure is in between of all these contributing structures and is called **resonance hybrid** and the different individual structures are called **resonating structures** or **canonical forms**. This phenomenon is called **resonance**.

To illustrate this, consider a molecule of ozone O_3 . Its structure can be written as



As a resonance hybrid of above two structures (a) and (b). For simplicity, ozone may be represented by structure (c), which shows the resonance hybrid having equal bonds between single and double.

Resonance is shown by benzene, toluene, O , allenes ($>C=C=C<$), CO , CO_2 , CO_3^{2-} , SO , NO , NO , while it is not shown by H_2O , H_2O , NH , CH , SiO .

As a result of resonance, the bond lengths of single and double bond in a molecule become equal e.g. $O-O$ bond lengths in ozone or $C-O$ bond lengths in CO_3^{2-} ion.

The resonance hybrid has lower energy and hence greater stability than any of the contributing structures.

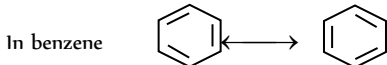
Greater is the number of canonical forms especially with nearly same energy, greater is the stability of the molecule.

Difference between the energy of resonance hybrid and that of the most stable of the resonating structures (having least energy) is called resonance energy. Thus,

Resonance energy = Energy of resonance hybrid – Energy of the most stable of resonating structure.

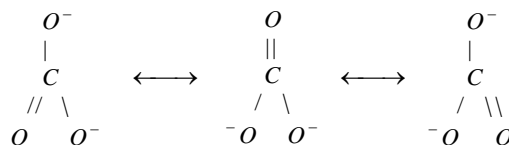
In the case of molecules or ions having resonance, the bond order changes and is calculated as follows,

$$\text{Bond order} = \frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of resonating structures}}$$



$$\text{Bond order} = \frac{\text{double bond} + \text{single bond}}{2} = \frac{2 + 1}{2} = 1.5$$

In carbonate ion



$$\text{Bond order} = \frac{2 + 1 + 1}{3} = 1.33$$

Bond characteristics

(1) Bond length

"The average distance between the centre of the nuclei of the two bonded atoms is called bond length".

It is expressed in terms of Angstrom ($1 \text{ \AA} = 10^{-10} \text{ m}$) or picometer ($1 \text{ pm} = 10^{-12} \text{ m}$).

In an ionic compound, the bond length is the sum of their ionic radii ($d = r_+ + r_-$) and in a covalent compound, it is the sum of their covalent radii (e.g., for HCl , $d = r_H + r_{Cl}$).

Factors affecting bond length

(i) The bond length increases with increase in the size of the atoms.

For example, bond length of $H-X$ are in the order, $HI > HBr > HCl > HF$.

(ii) The bond length decreases with the multiplicity of the bond. Thus, bond length of carbon-carbon bonds are in the order, $C \equiv C < C = C < C - C$.

(iii) As an s-orbital is smaller in size, greater the s-character shorter is the hybrid orbital and hence shorter is the bond length.

For example, $sp^3 C-H > sp^2 C-H > sp C-H$

(iv) Polar bond length is usually smaller than the theoretical non-polar bond length.

(2) Bond energy

"The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called **bond dissociation energy** or simply **bond energy**". Greater is the bond energy, stronger is the bond. Bond energy is usually expressed in kJ mol^{-1} .

Factors affecting bond energy

(i) Greater the size of the atom, greater is the bond length and less is the bond dissociation energy i.e. less is the bond strength.

(ii) For the bond between the two similar atoms, greater is the multiplicity of the bond, greater is the bond dissociation energy.

(iii) Greater the number of lone pairs of electrons present on the bonded atoms, greater is the repulsion between the atoms and hence less is the bond dissociation energy.

(iv) The bond energy increases as the hybrid orbitals have greater amount of s orbital contribution. Thus, bond energy decreases in the following order, $sp > sp^2 > sp^3$

(v) Greater the electronegativity difference, greater is the bond polarity and hence greater will be the bond strength i.e., bond energy, $H-F > H-Cl > H-Br > H-I$,

(vi) Among halogens $Cl - Cl > F - F > Br - Br > I - I$, (Decreasing order of bond energy) Resonance increases bond energy.

(3) Bond angle

In case of molecules made up of three or more atoms, the average angle between the bonded orbitals (i.e., between the two covalent bonds) is known as bond angle θ .

Factors affecting bond angle

(i) Repulsion between atoms or groups attached to the central atom may increase or decrease the bond angle.

(ii) In hybridisation as the s character of the s hybrid bond increases, the bond angle increases.

Bond type	sp	sp^2	sp^3
Bond angle	$109^\circ 28'$	120°	180°

(iii) By increasing lone pair of electron, bond angle decreases approximately by 2.5%.

	CH_4	NH_3	H_2O
Bond angle	109°	107°	105°

(iv) If the electronegativity of the central atom decreases, bond angle decreases.

	H_2O	H_2S	H_2Se	H_2Te
Bond angle	104.5°	92.2°	91.2°	89.5°

In case the central atom remains the same, bond angle increases with the decrease in electronegativity of the surrounding atom.

	PCl_3	PBr_3	PI_3	$AsCl_3$	$AsBr_3$	AsI_3
Bond angle	100°	101.5°	102°	98.4°	100.5°	101°

Valence shell electron pair repulsion theory (VSEPR)

The basic concept of the theory was suggested by Sidgwick and Powell (1940). It provides useful idea for predicting shapes and geometries of molecules. The concept tells that, the arrangement of bonds around the central atom depends upon the repulsion's operating between electron pairs (bonded or non bonded) around the central atom. Gillespie and Nyholm developed this concept as VSEPR theory.

The main postulates of VSEPR theory are

(1) For polyatomic molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.

(2) The geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or not bonded) present around the central atom and their repulsion due to relative sizes and shapes.

(3) If the central atom is surrounded by bond pairs only. It gives the symmetrical shape to the molecule.

(4) If the central atom is surrounded by lone pairs (lp) as well as bond pairs (bp) of e^- then the molecule has a distorted geometry.

(5) The relative order of repulsion between electron pairs is as follows: $lp - lp > lp - bp > bp - bp$.

A lone pair is concentrated around the central atom while a bond pair is pulled out between two bonded atoms. As such repulsion becomes greater when a lone pair is involved.

Table : 3.2 Geometry of Molecules/Ions having bond pair as well as lone pair of electrons

Type of mole-cule	No. of bond pairs of electron	No. of lone pairs of electrons	Hybridization	Bond angle	Expected geometry	Actual geometry	Examples
AX_3	2	1	sp^2	$< 120^\circ$	Trigonal planar	V-shape, Bent, Angular	$SO_2, SnCl, NO$
AX_4	2	2	sp^3	$< 109^\circ 28'$	Tetrahedral	V-shape, Angular	$H_2O, H_2S, SCl_2, OF_2, NH_3, ClO_2$
AX_4	3	1	sp^3	$< 109^\circ 28'$	Tetrahedral	Pyramidal	$NH_3, NF_3, PCl_3, PH_3, AsH_3, ClO_2, H_2O$
AX_5	4	1	sp^3d	$< 109^\circ 28'$	Trigonal bipyramidal	Irregular tetrahedron	$SF_4, SCl_4, TeCl_4$
AX_5	3	2	sp^3d	90°	Trigonal bipyramidal	T-shaped	ICl_3, IF_3, ClF_3
AX_5	2	3	sp^3d	180°	Trigonal bipyramidal	Linear	XeF_2, I_2, ICl_2
AX_6	5	1	sp^3d^2	$< 90^\circ$	Octahedral	Square pyramidal	ICl_5, BrF_5, IF_5
AX_6	4	2	sp^3d^2	—	Octahedral	Square planar	XeF_4, ICl_4
AX_6	6	1	sp^3d^3	—	Pentagonal pyramidal	Distorted octahedral	XeF_6

Molecular orbital theory or MOT

Molecular orbital theory was given by Hund and Mulliken in 1932.

The main ideas of this theory are,

(1) When two atomic orbitals combine or overlap, they lose their identity and form new orbitals. The new orbitals thus formed are called molecular orbitals.

(2) Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled just as atomic orbitals are the energy states of an atom in which the electrons of the atom are filled.

(3) In terms of probability distribution, a molecular orbital gives the electron probability distribution around a group of nuclei just as an atomic orbital gives the electron probability distribution around the single nucleus.

(4) Only those atomic orbitals can combine to form molecular orbitals which have comparable energies and proper orientation.

(5) The number of molecular orbitals formed is equal to the number of combining atomic orbitals.

(6) When two atomic orbitals combine, they form two new orbitals called bonding molecular orbital and antibonding molecular orbital.

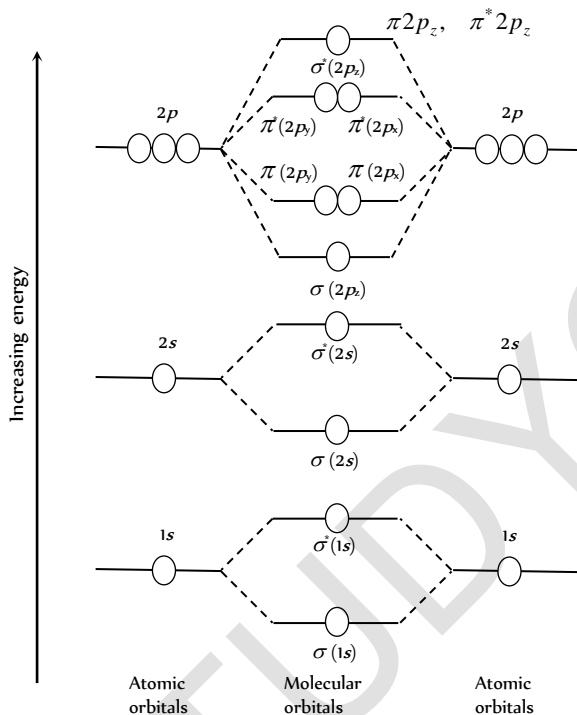
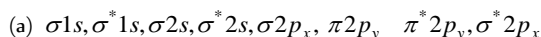
(7) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(8) The bonding molecular orbitals are represented by σ, π etc, whereas the corresponding antibonding molecular orbitals are represented by σ^*, π^* etc.

(9) The shapes of the molecular orbitals formed depend upon the type of combining atomic orbitals.

(10) The filling of molecular orbitals in a molecule takes place in accordance with **Aufbau principle**, **Pauli's exclusion principle** and **Hund's rule**. The general order of increasing energy among the molecular orbitals formed by the elements of second period and hydrogen and their general electronic configurations are given below.

(11) Electrons are filled in the increasing energy of the MO which is in order



Molecular orbital energy level diagram
(Applicable for elements with $Z > 7$)

Hydrogen bonding

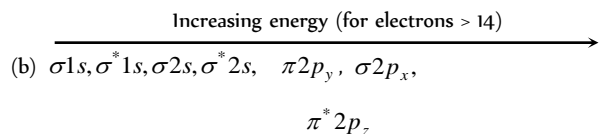
In 1920, **Latimer** and **Rodebush** introduced the idea of "hydrogen bond".

For the formation of H-bonding the molecule should contain an atom of high electronegativity such as *F, O* or *N* bonded to hydrogen atom and the size of the electronegative atom should be quite small.

Types of hydrogen bonding

(1) **Intermolecular hydrogen bond** : Intermolecular hydrogen bond is formed between two different molecules of the same or different substances.

(i) Hydrogen bond between the molecules of hydrogen fluoride.



Increasing energy (for electrons ≤ 14)
(12) Number of bonds between two atoms is called **bond order** and is given by

$$\text{Bond order} = \left(\frac{N_B - N_A}{2} \right)$$

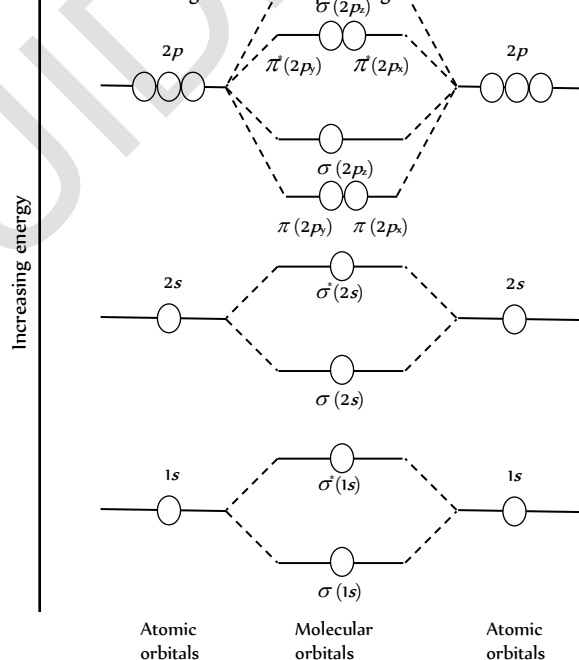
where N_B = number of electrons in bonding MO.

N_A = number of electrons in antibonding MO.

For a stable molecule/ion, $N_B > N_A$

(13) $\text{Bond order} \propto \text{Stability of molecule} \propto \text{Dissociation energy} \propto \frac{1}{\text{Bond length}}$

(14) If all the electrons in a molecule are paired then the substance is a diamagnetic on the other hand if there are unpaired electrons in the molecule, then the substance is paramagnetic. More the number of unpaired electron in the molecule greater is the paramagnetism of the substance.



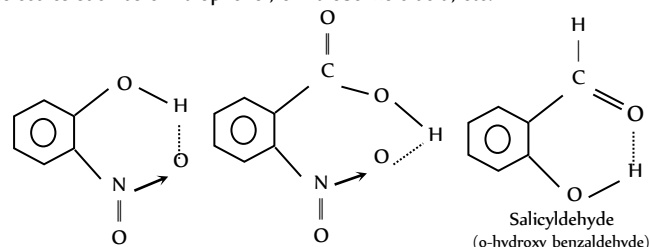
Molecular orbital energy level diagram obtained by the overlap of 2s and 2p_x atomic orbitals after mixing
(Applicable for elements with $Z < 7$)

(ii) Hydrogen bond in alcohol and water molecules

(2) **Intramolecular hydrogen bond** (Chelation)

Intramolecular hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (*F, O* or *N*) present in the same molecule. Intramolecular hydrogen bond results in the cyclisation of the molecules and prevents their association. Consequently, the effect of intramolecular hydrogen bond on the physical properties is negligible.

For example : Intramolecular hydrogen bonds are present in molecules such as *o*-nitrophenol, *o*-nitrobenzoic acid, etc.



Ortho nitrophenol

Ortho nitrobenzoic acid

Salicylaldehyde
(*o*-hydroxy benzaldehyde)

The extent of both intramolecular and intermolecular hydrogen bonding depends on temperature.

Effects of hydrogen bonding

Hydrogen bond helps in explaining the abnormal physical properties in several cases. Some of the properties affected by H-bond are given below,

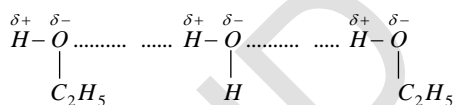
(1) **Dissociation** : In aqueous solution, hydrogen fluoride dissociates and gives the difluoride ion (HF_2^-) instead of fluoride ion (F^-). This is due to H-bonding in HF. This explains the existence of KHF_2 . H-bond formed is usually longer than the covalent bond present in the molecule (e.g. in H_2O , $\text{O}-\text{H}$ bond = 0.99 \AA but H-bond = 1.77 \AA).

(2) **Association** : The molecules of carboxylic acids exist as dimers because of the hydrogen bonding. The molecular masses of such compounds are found to be double than those calculated from their simple formulae. For example, molecular mass of acetic acid is found to be 120.

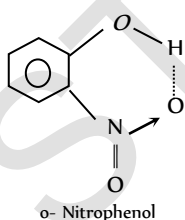
(3) **High melting and boiling point** : The compounds having hydrogen bonding show abnormally high melting and boiling points.

The high melting points and boiling points of the compounds (H_2O , HF and NH_3) containing hydrogen bonds is due to the fact that some extra energy is needed to break these bonds.

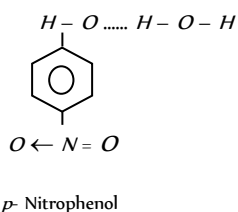
(4) **Solubility** : The compound which can form hydrogen bonds with the covalent molecules are soluble in such solvents. For example, lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecules as shown below,



The intermolecular hydrogen bonding increases solubility of the compound in water while, the intramolecular hydrogen bonding decreases.



Due to chelation, $-\text{OH}$ group is not available to form hydrogen bond with water hence it is sparingly soluble in water.

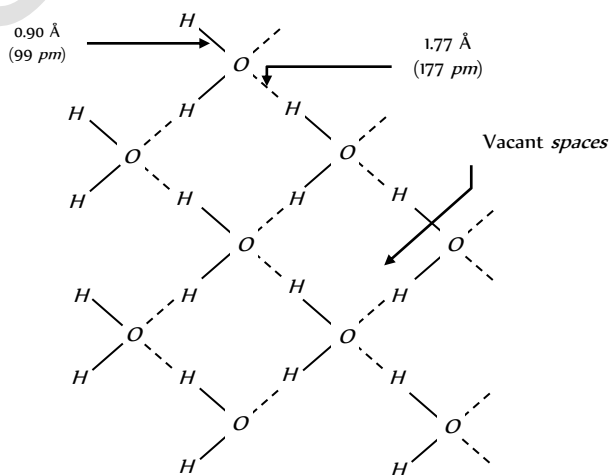


$-\text{OH}$ group available to form hydrogen bond with water, hence it is completely soluble in water.

(5) As the compounds involving hydrogen bonding between different molecules (intermolecular hydrogen bonding) have higher boiling points, so they are less volatile.

(6) The substances which contain hydrogen bonding have higher viscosity and high surface tension.

(7) **Explanation of lower density of ice than water and maximum density of water at 277K** : In case of solid ice, the hydrogen bonding gives rise to a cage like structure of water molecules as shown in following figure. As a matter of fact, each water molecule is linked tetrahedrally to four other water molecules. Due to this structure ice has lower density than water at 273K . That is why ice floats on water. On heating, the hydrogen bonds start collapsing, obviously the molecules are not so closely packed as they are in the liquid state and thus the molecules start coming together resulting in the decrease of volume and hence increase of density. This goes on upto 277K . After 277K , the increase in volume due to expansion of the liquid water becomes much more than the decrease in volume due to breaking of H-bonds. Thus, after 277K , there is net increase of volume on heating which means decrease in density. Hence density of water is maximum 277K .



Cage like structure of H_2O in the ice

Tips & Tricks

- ✍ A chemical bond is expected to be formed when the energy of the aggregate formed is about 40 kJ mole^{-1} lower than the separate particles.
- ✍ Formation of a chemical bond is always an exothermic process.
- ✍ Lattice energies of bi-bivalent solids > bi-univalent solids > uni-univalent solids. For example, lattice energy of $\text{Mg}^{2+}\text{O}^{2-}$ ($3932 \text{ kJ mole}^{-1}$) > $\text{Ca}^{2+}(\text{F}^-)_2$ ($2581 \text{ kJ mole}^{-1}$) > Li^+F^- ($1034 \text{ kJ mole}^{-1}$).
- ✍ When co-ordination number increases, the coulombic forces of attraction increases and hence stability increases.
- ✍ Ionic solids have negative vapour pressure.
- ✍ As a general rule, atomic crystals are formed by the lighter elements of the middle columns of the periodic table.
- ✍ FeCl_3 is more covalent than FeCl_2 because polarising power of Fe^{3+} is more than that of Fe^{2+} . Similarly SnCl_4 is more covalent than SnCl_2 .
- ✍ Boron forms the maximum number of electron deficient compounds than any other elements in the periodic table.
- ✍ Roughly each lone pair decreases the bond angle by 2.5° .
- ✍ Greater the number of the lone pairs at the two bonding atoms, greater is the repulsion between them and weaker is the bond.
- ✍ The actual number of *s*- and *p*-electrons present in the outermost shell of the element is called maximum covalency of that atom.
- ✍ The hydrogen bonds are tetrahedral in their directions and not planar.
- ✍ The hydrogen bond is stronger in HF and persists even in vapour state. Such bonds account for the fact that gaseous hydrogen fluoride is largely polymerised into the molecular species $\text{H}_2\text{F}_2, \text{H}_3\text{F}_3, \text{H}_4\text{F}_4, \text{H}_5\text{F}_5$ and H_6F_6 .
- ✍ Hydrogen bonding is strongest when the bonded structure is stabilised by resonance.
- ✍ Critical temperature of water is higher than that of O_2 because H_2O molecule has dipole moment.