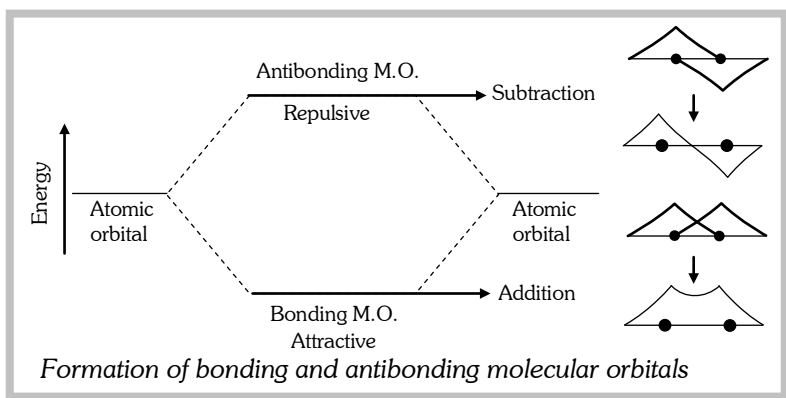


Chemical Bonding and Molecular Structure Part 2

Formation of bonding and antibonding molecular orbitals

(Linear combination of atomic orbitals – LCAO)

When two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase, constructive interaction occurs in the region between two nuclei and a bonding orbital is produced. The energy of the bonding orbitals is always lower (more stable) than the energies of the combining atomic orbitals. When they overlap out of phase, destructive interference reduces the probability of finding an electron in the region between the nuclei and antibonding orbital is produced. The energy of an antibonding orbital is higher (less stable) than the energies of the combining atomic orbitals. Thus, the number of molecular orbitals formed from atomic orbitals is equal to the number of atomic orbitals responsible for their formation.



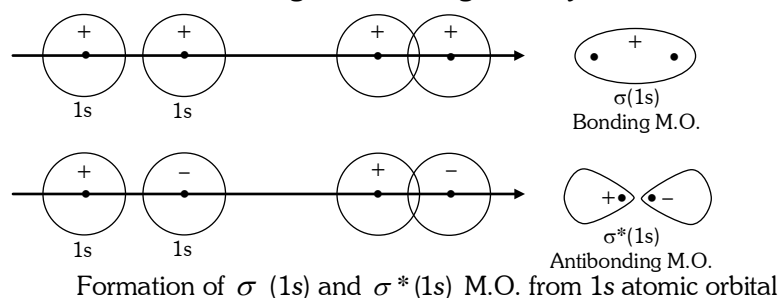
According to LCAO method, the following combination is not allowed. [consider the z-axis as the molecular axis). $np_x + np_y$, $np_x + np_z$ or $np_y + np_z$.

Table : Difference in Bonding molecular orbitals and Antibonding molecular orbitals.

Bonding molecular orbitals	Antibonding molecular orbitals
It is formed by linear combination of two atomic orbitals when their wave functions are added.	It is formed by linear combination of two atomic orbitals when their wave functions are subtracted.
i.e., $\Psi_b = \Psi_A + \Psi_B$	i.e., $\Psi_a = \Psi_A - \Psi_B$
Its energy is less than the combining atomic orbitals.	Its energy is more than the combining atomic orbitals.
It increases the electron density between the nuclei. It therefore stabilises the molecule.	It decreases the electron density between the nuclei. It therefore destabilises the molecule.
It has no nodal plane (plane where electron density is zero).	It has nodal plane.
It is symmetrical about internuclear axis.	It is symmetrical about internuclear axis and about a line perpendicular to it.

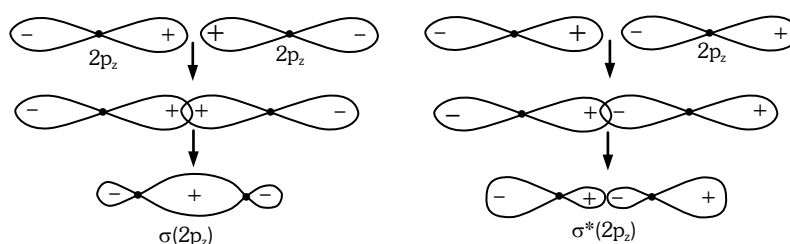
σ and π – Molecular orbitals

A sigma (σ) M.O. is one that has cylindrical symmetry around the internuclear axis. It does not show any change of sign or rotation through 180° about the axis. Sigma M.O. has no nodal plane (in which electron density is zero) along the internuclear axis. The bonding M.O. is designated by σ and antibonding by σ^* .



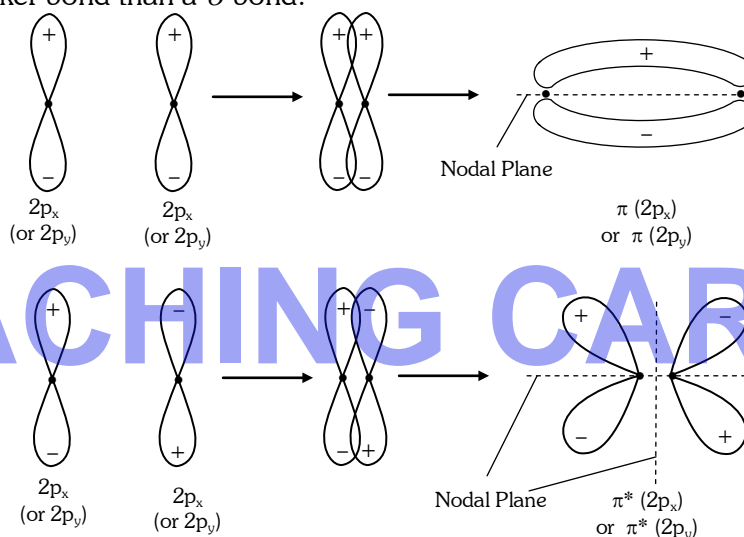
Chemical Bonding and Molecular Structure Part 2

Sigma (σ) M.O. is also formed when two p -atomic orbitals overlap in head on (along their axes) position.



Formation of $\sigma(2p_z)$ and $\sigma^*(2p_z)$ molecular orbitals.

π -molecular orbital is formed by the sideways overlapping of the p -atomic orbitals. It consists of two electron clouds, one lying above and the other lying below a plane passing through the nuclei. It has nodal planes. Since the energy of a M.O. is directly related to the nuclei of nodal planes. The π -MO is more energetic than the σ -MO. This explains why a π -bond is a weaker bond than a σ -bond.



Formation of $\pi(2p_x)$ or $\pi(2p_y)$ and $\pi^*(2p_x)$ or $\pi^*(2p_y)$ molecular orbitals.

Relative energies of Molecular orbitals : Initial energy of the atomic orbitals and the extent of their overlap is the criteria which determines the energy of the M.O.

(1) It is obvious that molecular orbitals formed from lower energy atomic orbitals have lower energy than the molecular orbitals formed from higher energy atomic orbitals.

(2) As the σ overlap is much more effective than π -overlap, σ p -molecular orbital is of lowest energy, even though originally all the three p -orbitals are of equal energy.

(3) The relative energies of the M.O. are obtained experimentally from spectroscopic data.

(4) The sequence in the order of increasing energy for O_2 , F_2 and Ne_2

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

(5) It may be noted that $\pi 2p_y$ and $\pi 2p_x$ bonding molecular orbitals are degenerate (*i.e.* have same energy).

Similarly $\pi^* 2p_y$ and $\pi^* 2p_x$ antibonding molecular orbitals are also degenerate (have the same energy).

(6) The main difference between the two types of sequences in energy level is that for molecules O_2 , F_2 and Ne_2 (Hypothetical) the $\sigma 2p_z$ M.O. is lower in energy than $\pi 2p_x$ and $\pi 2p_y$.

Chemical Bonding and Molecular Structure Part 2

(7) It has been found experimentally that in some of the diatomic molecules such as Li_2 , B_2 , C_2 and N_2 $\sigma 2p_z$ M.O. is higher in energy than $\pi 2p_y$ and $\pi 2p_x$ M.O.'s. Therefore, the order of increasing energy of these M.O.s changes to $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$.

Cause of exceptional behaviour of MO's in B_2 , C_2 and N_2

In atoms with Z upto 7, energy of $2s$ and $2p$ atomic orbitals lie fairly close. As a result the interaction between $2s$ and $2p$ orbitals is quite large. Thus $\sigma 2s$ and $\sigma^* 2s$ MO's become more stable with less energy at the cost of $\sigma 2p_x$ and $\sigma^* 2p_x$ which gets unstabilised (higher energy).

Stability of the molecules : Stability of the molecules can be explain in following ways.

(1) Stability of molecules in terms of bonding and antibonding electrons

Since electrons in bonding orbitals (N_b) increase the stability of the molecule, on the whole, depends on their relative numbers. Thus

- (i) If $N_b > N_a$, the molecule is stable.
- (ii) If $N_b < N_a$, the molecule is unstable.
- (iii) Even if $N_b = N_a$, the molecule is unstable. This is due to the fact the anti bonding effect is some what stronger than the bonding effect.

(2) Stability of molecules in terms of bond order

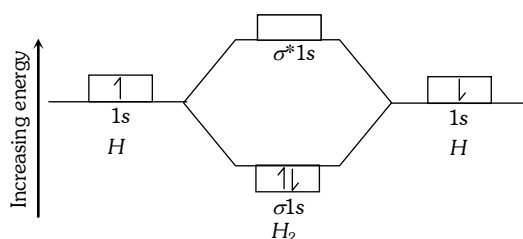
- (i) The relative stability of a molecule is further evaluated by a parameter known as bond order.
- (ii) It can be defined as number of covalent bonds present between two atoms in a molecule.
- (iii) It is given by one half of the differences between the number of electrons in bonding molecular orbitals and those in antibonding molecular orbitals.
- (iv) Bond order = $\frac{1}{2}$ [No. of electrons in bonding molecular orbitals – No. of electrons in antibonding molecular orbitals].
- (v) The bond order of 1, 2 and 3 corresponds to single, double and triple bonds respectively. It may be mentioned that according to M.O theory, even a fractional bond order is possible, but cannot be negative.

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

- (vii) 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.

MO energy level diagrams of some molecules : Energy level diagrams of some molecules are given below.

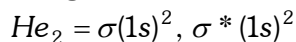
H_2 Molecule : H_2 molecule is formed from $1s^1$ atomic orbitals of two H - atoms. The atomic orbitals ($1s^1$) will combine to form two molecular orbitals $\sigma(1s)$ and $\sigma^*(1s)$. Two electrons are accommodated in $\sigma(1s)$ and $\sigma^*(1s)$ remains vacant. Thus bond order for $H_2 = \frac{1}{2}(2 - 0) = 1$. It is stable and diamagnetic in nature.



Chemical Bonding and Molecular Structure Part 2

He₂ molecule : If two atoms of He ($1s^2$) combine to form *He₂*, the probability of the formation of molecular orbitals is as shown in the figure.

Filling of electrons is as follows

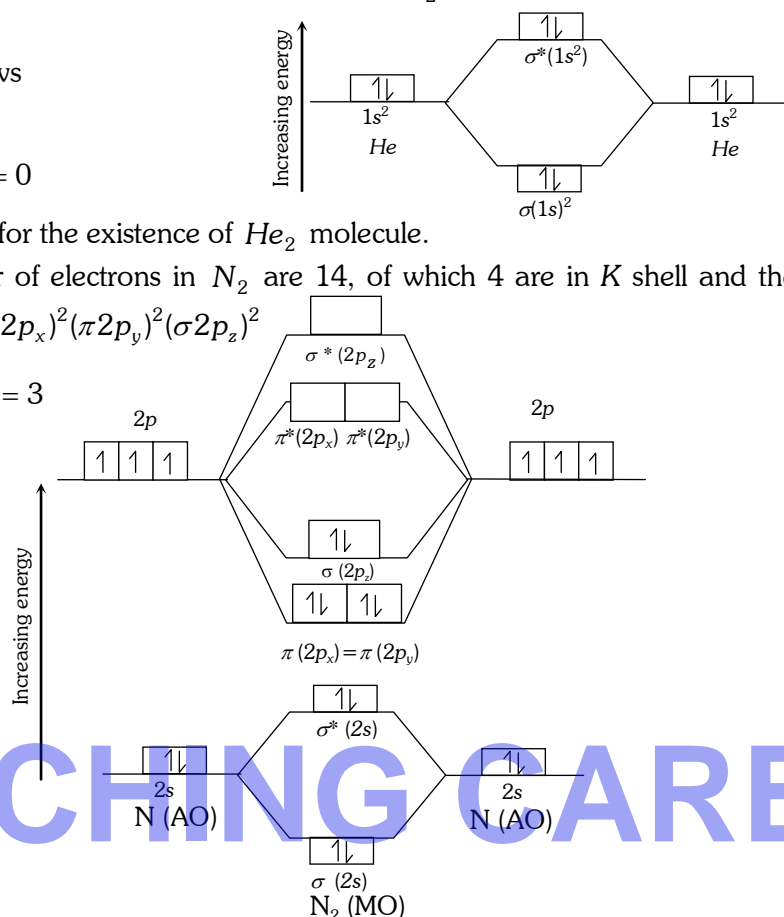


Thus bond order = $\frac{1}{2}(2 - 2) = 0$

Hence there is no possibility for the existence of *He₂* molecule.

N₂ molecule : Total number of electrons in *N₂* are 14, of which 4 are in K shell and the 10 electrons are arranged as, $KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

Bond order = $\frac{1}{2}(10 - 4) = 3$

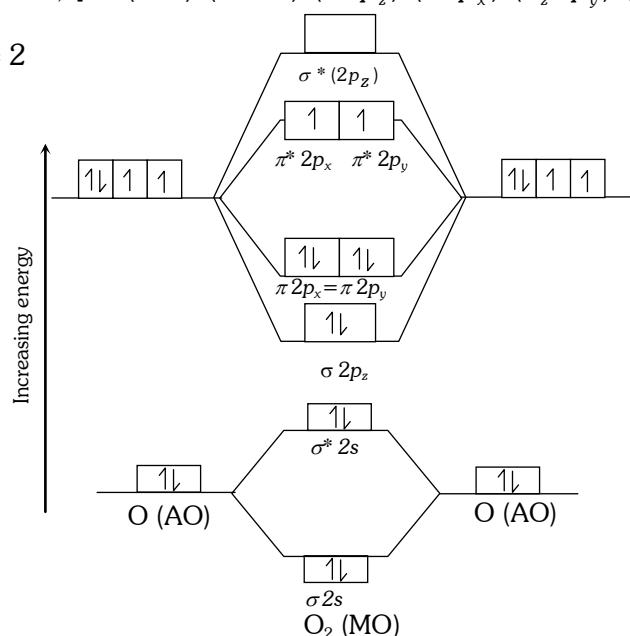


M.O. energy level diagram for *N₂* molecule.

O₂ molecule : Total number of electrons in *O₂* = 16

Electronic arrangement in M.O.'s, $[KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1]$

Bond order = $\frac{1}{2}(8 - 4) = 2$



M.O. Energy level diagram for *O₂* molecule

Chemical Bonding and Molecular Structure Part 2

Table : Bond order and magnetic nature of some molecules & ions

Molecule	Molecular Orbital Configuration	Valence electrons	N_b	N_a	Magnetic Nature	B.O.
H_2	$(\sigma 1s)^2$	2	2	0	Diamagnetic	1
H_2^+	$(\sigma 1s)^1$	1	1	0	Paramagnetic	0.5
H_2^-	$(\sigma 1s)^2(\sigma^* 1s)^1$	3	2	1	Paramagnetic	0.5
He_2	$(\sigma 1s)^2(\sigma^* 1s)^2$	4	2	2	Molecule does not exist	0
He_2^+	$(\sigma 1s)^2(\sigma^* 1s)^1$	3	2	1	Paramagnetic	0.5
He_2^-	$KK' (\sigma 2s)^1$	1	1	0	Paramagnetic	0.5
Be_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2$	4	2	2	Diamagnetic	0
B_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$	6	4	2	Paramagnetic	1
C_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2$	8	6	2	Diamagnetic	2
N_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$	10	8	2	Diamagnetic	3
N_2^+	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^1$	9	7	2	Paramagnetic	2.5
N_2^-	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2(\pi^* 2p_x)^1$	11	8	3	Paramagnetic	2.5
O_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1$	12	8	4	Paramagnetic	2
O_2^+	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^0$	11	8	3	Paramagnetic	2.5
O_2^{2+}	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$	10	8	2	Diamagnetic	3
O_2^-	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$	13	8	5	Paramagnetic	1.5
O_2^{2-}	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$	14	8	6	Diamagnetic	1
F_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$	14	8	6	Diamagnetic	1
Ne_2	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$	16	8	8	Molecule does not exist	0
CO	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$	10	8	2	Diamagnetic	3
NO	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$	11	8	3	Paramagnetic	2.5
NO⁺	$KK' (\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$	10	8	2	Diamagnetic	3

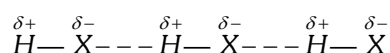
Chemical Bonding and Molecular Structure Part 2

Hydrogen bonding.

In 1920, **Latimer** and **Rodebush** introduced the idea of “**hydrogen bond**” to explain the nature of association of substances in liquid state like water, hydrogen fluoride, ammonia, formic acid, etc.

(1) Conditions for the formation of hydrogen bonding

- (i) *High electronegativity of atom bonded to hydrogen* : The molecule should contain an atom of high electronegativity such as *F, O* or *N* bonded to hydrogen atom. The common examples are H_2O , NH_3 and HF .



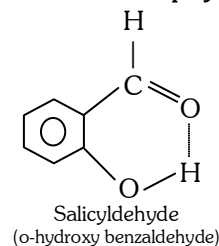
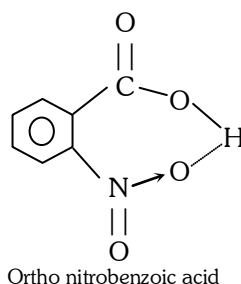
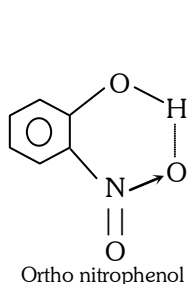
- (ii) *Small size of the electronegative atom* : The size of the electronegative atom should be quite small. This is due to the fact that the smaller the size of electronegative atom, the greater will be its attraction for the bonded electron pair. This will cause greater polarity in the bond between *H* and electronegative atom, which results in stronger hydrogen bond.

(2) Types of hydrogen bonding

- (i) *Intermolecular hydrogen bond* : Intermolecular hydrogen bond is formed between two different molecules of the same or different substances. For example:

- (a) Hydrogen bond between the molecules of hydrogen fluoride.
(b) Hydrogen bond in alcohol and water molecules

- (ii) *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.

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

(3) 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:

- (i) **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 . On the other hand, the molecules of HCl , HBr , HI do not have H-bonding (because *Cl, Br, I* are not so highly electronegative). This explains the non-existence of compounds like $KHCl_2$, $KHBr_2$ or

Chemical Bonding and Molecular Structure Part 2

KHI_2 . H -bond formed is usually longer than the covalent bond present in the molecule (e.g. in H_2O , $O-H$ bond = 0.99 \AA but H -bond = 1.77 \AA).

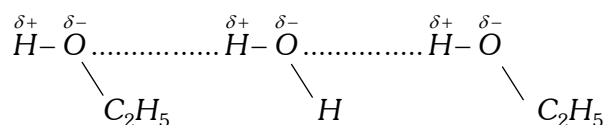
- (ii) **Association** : The molecules of carboxylic acids exist as dimers because of the hydrogen bonding. The molecular masses of such compounds are found to be double than those calculated from their simple formulae. For example, molecular mass of acetic acid is found to be 120.
- (iii) **High melting 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. A few examples are given below:

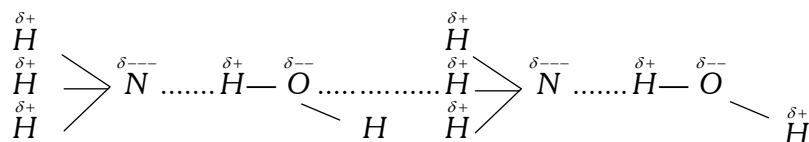
- (a) H_2O is a liquid whereas H_2S , H_2Se and H_2Te are all gases at ordinary temperature. The reason for this is that in case of water, hydrogen bonding causes association of the H_2O molecules with the result that the boiling point of water is more than that of the other compounds. On the other hand, there is no such hydrogen bonding in H_2S , H_2Se and H_2Te .
- (b) NH_3 has higher boiling point than PH_3 . This is again because there is hydrogen bonding in NH_3 but not in PH_3 .
- (c) Ethanol has higher boiling point than diethyl ether because there is hydrogen bonding in the former but there is no hydrogen bonding in the later.

Intramolecular hydrogen bonding is not possible in case of m - and p -isomers because of the size of the ring which would be formed. Thus, here the intermolecular hydrogen bonding takes place which causes some degree of association with the result the m - and p -isomers melt and boil at higher temperatures.

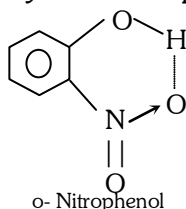
- (iv) **Solubility** : The compound which can form hydrogen bonds with the covalent molecules are soluble in such solvents. For example, lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecules as shown below :



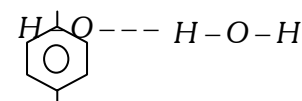
Similarly, ammonia (NH_3) is soluble in water because of hydrogen bonding as represented below:



The intermolecular hydrogen bonding increases solubility of the compound in water while, the intramolecular hydrogen bonding decreases. This is due to the fact that the formation of internal hydrogen bond prevents hydrogen bonding between the compound and water which thus reduced solubility of the compound in water.



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



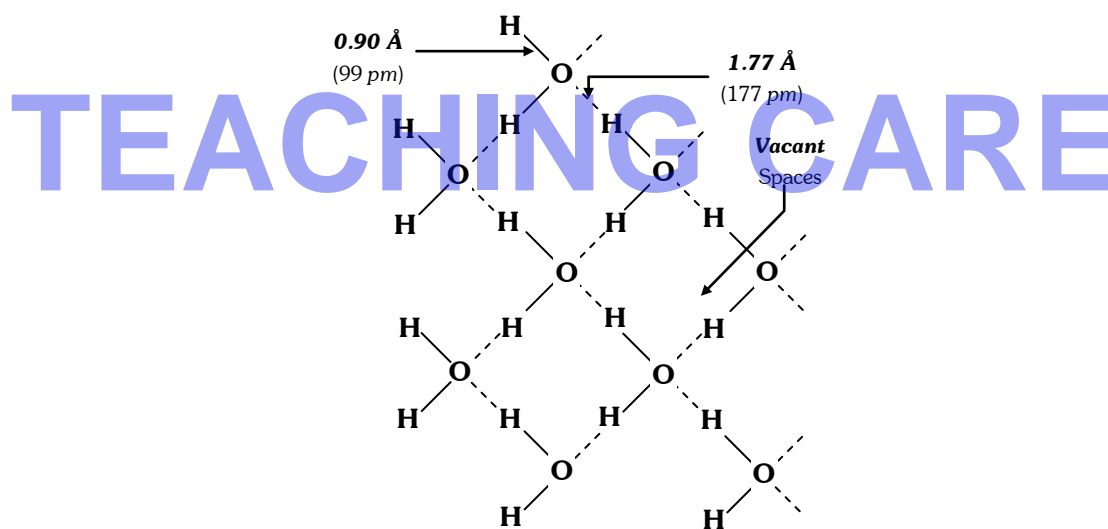
p -Nitrophenol

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

Chemical Bonding and Molecular Structure Part 2

- (v) **Volatility** : As the compounds involving hydrogen bonding between different molecules (intermolecular hydrogen bonding) have higher boiling points, so they are less volatile.
- (vi) **Viscosity and surface tension** : The substances which contain hydrogen bonding exist as associated molecules. So their flow becomes comparatively difficult. In other words, they have higher viscosity and high surface tension.
- (vii) **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 277 K, 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

Important Tips

- Hydrogen bonding is strongest when the bonded structure is stabilised by resonance.
- The bond length of hydrogen bond is the order of 250 to 275 pm.
- The bond that determines the secondary structure of protein is hydrogen bond.
- Pairs of DNA are held together by hydrogen bonds.
- Chlorine has the same electronegativity as nitrogen but does not form strong hydrogen bonds. This is because of the larger size than that of nitrogen.

Chemical Bonding and Molecular Structure Part 2

Types of bonding and forces in solids.

(1) Ionic bonding : Solid containing ionic bonds consists of any array or a net work of positive and negative ions arranged systematically in a characteristic pattern. The binding forces are strong electrostatic bonds between positive and negative ions. *e.g.*, Compounds of elements of group 1 and 2 with elements of group 16 and 17 *e.g.*, *NaCl*, *CaS* etc.

(2) Covalent bonding : The solid containing covalent bonding consists of an array of atoms that share electrons with their neighbouring atoms. The atoms are linked together by strong covalent bonds extending into three dimensional structure. *e.g.*, Diamond, Silicon carbide, Silicon dioxide etc.

(3) Molecular bonding : The solid containing molecular bonding consists of symmetrical aggregates of discrete molecules. However, these molecules are further bound to other molecules by relatively weak force such as dipole-dipole forces (Vander Waal forces), dispersion forces or *H*-bonds depending upon the nature of molecules. The existence of weak attractive forces among the non polar molecules was first proposed by **S.D. Vander waal**. Vander waal's forces are non-directional, non valence force of attraction. *Vander Waal force* \propto *molecular mass* \propto *Boiling point* \propto *Size of atom or molecule*. The forces present in the crystals of naphthalene, Iodine and dry ices solid CH_4 , solid hydrogen are Vander Waals forces. SiO_2 Possesses giant covalent molecular structure due to tetravalency and catenation nature of Si.

(4) Metallic Bond

The constituent particles in metallic solids are metal atoms which are held together by metallic bond. **Lorentz** proposed a simple theory of metallic bond. This theory is known as electron gas model or electron sea model.

A metal atom consists of two parts, valence electrons and the remaining part (the nucleus and the inner shell electrons) called kernel. The kernels of metal atoms occupy the lattice sites while the space in-between is occupied by valence electrons. These electrons are not localized but are mobile. The attraction between the kernels and the mobile electrons, which hold the kernel together, is known as metallic bond. Low ionisation energy and sufficient number of vacant orbital in the valency shell are essential conditions for metallic bonding. Metallic bond is electrostatic in nature. The strength of the metallic bond depends on the number of valency electron and the charge on the nucleus. As the number of valency electron and the charge increase, the metallic bond becomes strong. Due to this fact alkali metals are soft and have low melting and boiling points while transition metals are hard and have high melting and boiling points. Strong metallic bonding is also favoured by smaller size of kernel. Ge, Cu, Zn has metallic bonding while brass etc does not have metallic bonding.

Metals have properties like metallic lustre, thermal and electrical conductivity due to delocalized mobile electrons. Thermal conductivity of metal decreases with increase in temperature because the kernels start vibrating.

Since the metallic bond is non-directional; metals can be twisted, drawn into wires or beaten into sheets. This is because the kernels can slip over each other when a deforming force is applied.

The relative strength of various bonds is **Ionic > Covalent > Metallic > H-bond > vander waal forces**.