

Crash Course for NEET 2020

KEY NOTES ON Chemical Bonding and Molecular structure

Biomentors Classes Online, Mumbai

NCERT Based - Very Important Points

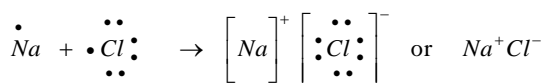
The force which holds the atoms or ions together within the molecule is called a chemical bond. (अणु के भीतर परमाणुओं या आयनों को एक साथ रखने वाले बल को रासायनिक बंध कहते हैं।)

Bonds are of following types. (बंध निम्न प्रकार के होते हैं।)

Electrovalent bond (विद्युत संयोजी आबंध)

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

जब एक धातु परमाणु एक या अधिक इलेक्ट्रॉनों को अ-धातु परमाणु में स्थानांतरित करता है, तो एक विद्युत संयोजी आबंध बनता है।



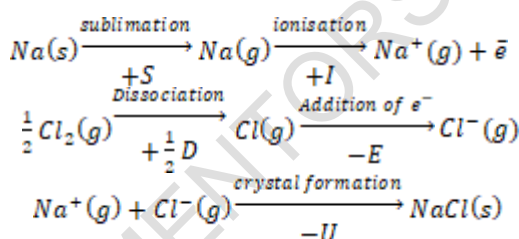
Some other examples are: MgCl_2 , CaCl_2 , AlF_3 , NaCl .

Conditions for formation of electrovalent bond

A high difference of electronegativity between two atoms is necessary for the formation of an electrovalent bond. (एक विद्युत संयोजी आबंध के गठन के लिए दो परमाणुओं के बीच विद्युत्-ऋणात्मकता का एक उच्च अंतर आवश्यक है।)

Born Haber cycle: - (बोर्न हैबर चक्रण)

Born Haber cycle for the formation of sodium chloride is given below.



Where
S = Heat of sublimation of Na Metal
I = Ionisation energy of Na
D = Heat of dissociation of molecular chlorine
E = Electron affinity of chlorine atom
U = Lattice energy of NaCl

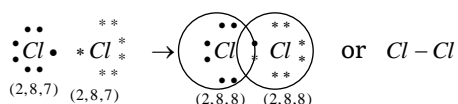
The amount of heat liberated (Q) in the overall reaction is the heat of formation of NaCl.
Thus $Q = S + I + \frac{1}{2} D - E - U$

Covalent bond (सहसंयोजी आबंध)

when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have multiple bonds

एक इलेक्ट्रॉन युग्म द्वारा संयुग्मित दो परमाणु सहसंयोजी आबंध द्वारा आबंधित कहलाते हैं। कई यौगिकों के परमाणुओं के बीच बहु आबंध उपस्थित होते हैं

A covalent bond between two similar atoms is non-polar covalent bond while it is polar between two different atoms having different electro negativities. (दो समान परमाणुओं के बीच एक सहसंयोजक बंधन अ-ध्रुवीय सहसंयोजक बंध जब की दो अलग-अलग परमाणुओं के बीच ध्रुवीय बंध है जो विभिन्न विद्युत्-ऋणात्मकता वाले हैं)



Some other examples are : $\text{H}_2\text{S}, \text{NH}_3, \text{HCN}, \text{PCl}_3, \text{PH}_3$,

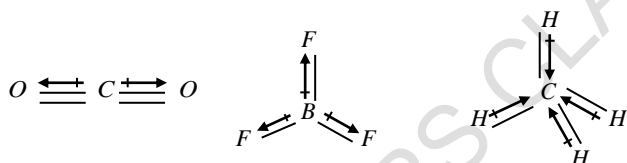
Dipole moment (द्विध्रुव आघूर्ण)

It is defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. (द्विध्रुव आवेश का मान तथा धनात्मक और ऋणात्मक आवेशों के बीच की दूरी की गुणफल के रूप में परिभाषित किया जाता है)

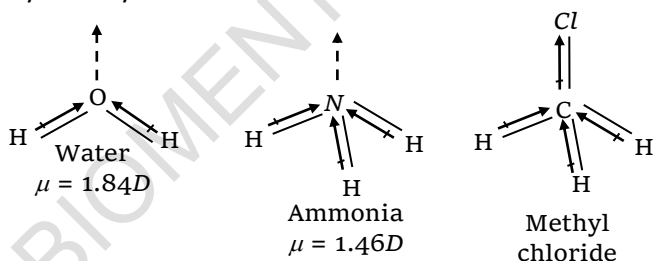
$$\mu = \text{Electric charge} \times \text{bond length}$$

Dipole moment is indicated by an arrow pointing towards the negative end. Dipole moment has both magnitude and direction and therefore it is a vector quantity.

Symmetrical polyatomic molecules are not polar so they do not have any value of dipole moment. $\mu = 0$ due to symmetry



Unsymmetrical polyatomic molecules always have net value of dipole moment; thus such molecules are polar in nature. $\text{H}_2\text{O}, \text{CH}_3\text{Cl}, \text{NH}_3$, etc are polar molecules as they have some positive values of dipole moments. $\mu \neq 0$ due to asymmetry



Dipole moment is an important factor in determining the geometry of molecules. 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. (अणुओं की ज्यामिति के निर्धारण में द्विध्रुव आघूर्ण

एक महत्वपूर्ण कारक है। हर आयनिक यौगिक में फैजान के शासन के अनुसार सहसंयोजक चरित्र का कुछ प्रतिशत होता है। यौगिक में कुछ सहसंयोजी चरित्र वाले आयनिक वर्ण की गणना निम्नलिखित समीकरण द्वारा की जा सकती है।)

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

Molecular geometry and dipole moment (आणविक ज्यामिति और द्विध्रुवीय आघूर्ण)

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 Square planar See saw	Zero Zero Non zero	CH_4, CCl_4 XeF_4 $SF_4, TeCl_4$
AX_5	Trigonal bipyramidal Square pyramidal	Zero Non zero	PCl_5 $BrCl_5$
AX_6	Octahedral Distorted octahedral	Zero Non zero	SF_6 XeF_6
AX_7	Pentagonal bipyramidal	Zero	IF_7

Fajan's rule (फाजान्स नियम)

The magnitude of polarization or increased covalent character depends upon a number of factors. These factors are, (ध्रुवीकरण या बढ़े हुए सहसंयोजक गुण का परिमाण कई कारकों पर निर्भर करता है। ये कारक हैं,)

(1) **Small size of cation (धनायन का छोटा आकार):** Smaller size of cation means greater will be the polarizing power which means greater will be the covalent nature of the bond.

(2) **Large size of anion (ऋणायन का बड़ा आकार):** Larger the size of anion means greater will be polarizing power which means greater will be the covalent nature of the bond.

(3) **Large charge on either of the two ions (दोनों आयनों में से किसी पर भी बड़ा आवेश):** As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases which increases the ability of forming the covalent bond.

Types of covalent bonds (सहसंयोजन के प्रकार)

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
More stable	Less stable
Less reactive	More reactive
Can exist independently	Always exist along with a σ -bond

Hybridization (संकरण)

It is defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape (लगभग समान ऊर्जा वाले कक्षकों के आपस में मिलकर ऊर्जा के पुनर्वितरण द्वारा समान ऊर्जा तथा आकार वाले कक्षकों को बनाने की प्रक्रिया को संकरण कहलाते है)

Identification 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^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3 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(अनुनाद)

When one or more electrons contribute to more than one bond in a molecule and are localized to any of the bond in which they contribute, the phenomenon is called as resonance. In resonance a single structure is not sufficient to explain all the properties of molecule. So such all contributing structures are called as resonating structures or resonance hybrid.

Resonance is shown by ozone, benzene etc.

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.

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

Bond characteristics (बंध के गुण)

(1) Bond length (बंध की लम्बाई)

“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 ($1 \text{ \AA} = 10^{-10} \text{ m}$)

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 (बंध की लंबाई को प्रभावित करने वाले कारक)

(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, $sp^3 > sp^2 > sp$

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

(2) Bond energy (बंध ऊर्जा)

“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 (बंध ऊर्जा को प्रभावित करने वाले कारक)

(i) As the size of the atom increases the bond length also increases and causes the decrement in bond energy.

(ii) As the no of lone pairs increases, repulsion between the atoms increases and it causes in low bond energy.

(iv) The bond energy decreases as the contribution of %s characteristic decreases. It means the bond energy will be in 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 the order of bond energy is as follows. $Cl-Cl > F-F > Br-Br > I-I$,

(3) Bond angle (बंध कोण)

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 (बंध कोण को प्रभावित करने वाले कारक)

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

(iii) By increasing lone pair of electron, bond angle decreases

	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 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 non 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 : $lp - lp > lp - bp > bp - bp$.

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

Type of molecule	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	$SO_2, SnCl_2, NO_2^-$
AX_4	2	2	sp^3	$< 109^\circ 28'$	Tetrahedral	V-shape, Angular	$H_2O, H_2S, SCl_2, OF_2, NH_2^-, ClO_2^-$
AX_4	3	1	sp^3	$< 109^\circ 28'$	Tetrahedral	Pyramidal	$NH_3, NF_3, PCl_3, PH_3, AsH_3, ClO_3^-, H_3O^+$
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_3^-, 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_7	6	1	sp^3d^3	-	Pentagonal pyramidal	Distorted octahedral	XeF_6

Hydrogen bonding (हाइड्रोजन आबंधन)

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.

(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.

Effects of hydrogen bonding (हाइड्रोजन आबंधन को प्रभावित करने वाले कारक)

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^-).

(2) **Association** : The molecules of carboxylic acids exist as dimers because of the hydrogen bonding.

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

(4) **Solubility** : The compound which can form hydrogen bonds with the covalent molecules are soluble in such solvents.