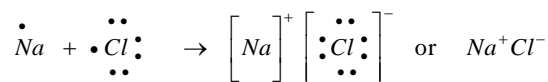




Chemical Bonding and Molecular Structure

Electrovalent bond

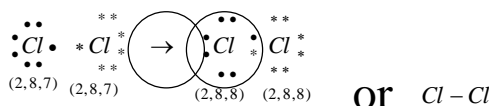
An electrovalent bond is formed when a metal atom transfers one or more electrons to a non-metal atom.



Some other examples are:, Na₂S, CaH₂, AlF₃, MgCl₂, CaCl₂, MgO etc.

Covalent bond

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.



Some other examples are: HCN, PCl₃, PH₃, H₂S, NH₃



Characteristics of covalent compounds

In general covalent substances are bad conductor of electricity.

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.

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

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

Dipole moment

“The product of magnitude of negative or positive charge (q) and the distance (d) between the centres of positive and negative charges is called dipole moment”.

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

As q is in the order of 10^{-10} esu and d is in the order of 10^{-8} cm, μ is in the order of 10^{-18} esu cm. Dipole moment is measured in “Debye” (D) unit. $1D = 10^{-18}$ esu cm = 3.33×10^{-30} coulomb metre (In S.I. unit).



(1) Dipole moment is an important factor in determining the geometry of molecules.

Molecular geometry and dipole moment

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 ₂ O, 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



			$\text{SF}_4, \text{TeCl}_4$
AX5	Trigonal bipyramidal	Zero	PCl_5
	Square pyramidal	Non zero	BrCl_5
AX6	Octahedral	Zero	SF_6
	Distorted octahedral	Non zero	XeF_6
AX7	Pentagonal bipyramidal	Zero	IF_7

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

(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 kcals	Bond energy 65 kcals
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

It 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 and 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.

Resonance

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.



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.

Bond characteristics

(1) Bond length

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

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

Bond energy is the amount of energy that is needed to break a mole of molecule bonds into its component atoms. It is also known as bond dissociation energy. It is the measure of strength of chemical bond hence greater is the bond energy, stronger is the bond. It is usually expressed in $kJ mol^{-1}$.

(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 ³	sp ²	sp
Bond angle	109°28'	120°	180°

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

	CH ₄	NH ₃	H ₂ O
Bond angle	109°	107°	105°

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

	<i>H₂O</i>	> <i>H₂S</i>	> <i>H₂Se</i>	> <i>H₂Te</i>
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.

	<i>PCl₃</i>	<i>PBr₃</i>	<i>PI₃</i>	<i>AsCl₃</i>	<i>AsBr₃</i>	<i>AsI₃</i>
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.



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

Type of mole-cule	No. of lone pairs of electrons	Hybridization	Bond angle	Expected geometry	Actual geometry	Examples
AX ₃	1	Sp ²	< 120°	Trigonal planar	V-shape, Bent, Angular	SO ₂ , SnCl ₂ , NO ₂ ⁻
AX ₄	2	Sp ³	< 109° 28'	Tetrahedral	V-shape, Angular	H ₂ O, H ₂ S, SCl ₂ , OF ₂ , NH ₂ ⁻ , ClO ₂ ⁻
AX ₄	1	Sp ³	< 109° 28'	Tetrahedral	Pyramidal	NH ₃ , NF ₃ , PCl ₃ , PH ₃ , AsH ₃ , ClO ₃ ⁻ , H ₃ O ⁺
AX ₅	1	Sp ³ d	< 109° 28'	Trigonal bipyramidal	Irregular tetrahedron	SF ₄ , SCl ₄ , TeCl ₄
AX ₅	2	Sp ³ d	90°	Trigonal bipyramidal	T-shaped	ICl ₃ , IF ₃ , ClF ₃
AX ₅	3	Sp ³ d	180°	Trigonal bipyramidal	Linear	XeF ₂ , I ₃ ⁻ , ICl ₂ ⁻
AX ₆	1	Sp ³ d ²	< 90°	Octahedral	Square pyramidal	ICl ₅ , BrF ₅ , IF ₅
AX ₆	2	Sp ³ d ²	–	Octahedral	Square planar	XeF ₄ , ICl ₄ ⁻
AX ₇	1	Sp ³ d ³	–	Pentagonal pyramidal	Distorted octahedral	XeF ₆

Molecular orbital theory or MOT

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



The main ideas of this theory are,

(a) When two atomic orbitals of comparable energy and proper symmetry combine or overlap, they lose their identity and form new orbitals. These new orbitals are known as molecular orbitals.

(b) Number of molecular orbitals formed is equal to the total number of combining atomic orbitals, thus these are also the energy states of a molecule in which the electrons are filled just as atomic orbitals.

(c) 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.

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

The bonding molecular orbital has lower energy than the atomic orbitals and the antibonding molecular orbital has greater energy than the atomic orbitals. Thus, bonding



molecular orbital has greater stability than the corresponding antibonding molecular orbital.

(e) The shapes of forming molecular orbitals based on the type of combining atomic orbitals.

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

Hydrogen bonding

Hydrogen bonding is not a covalent bond. It is a special type of dipole-dipole attraction between the molecules and a **hydrogen** atom. For the formation of H-bonding the molecule should have the attraction force between a **hydrogen** atom and an atom of high electro negativity such as F, O or N.

Types of hydrogen bond:

(a) Intermolecular hydrogen bond :



Two different molecules of the same or different compounds form intermolecular hydrogen bonds.

(b) Intramolecular hydrogen bond (Chelation)

The bond formed between the hydrogen atom and the strongly electronegative atom (F, O or N) present in the same molecule is known as intramolecular hydrogen.

Types of hydrogen bonding

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

(b) 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.