The need for Chemical Bonding

Why a particular shape?

Why some atoms combine while some don't?

How exactly are these atoms combining?

How much energy is released/gained?

Valence Electrons : Outer shell electrons that take part in chemical combination are known as valence electrons.

Octet Rule

Atoms can combine either by transfer of electrons(Ionic bond) or by sharing of valence electron(covalent or co-ordinate bond) in order to have 8 electrons in their valence shell. This is known as octet rule.

Why Bonds are formed?

Type of Bonds?

Octet theory to understand that atoms bond to attain the noble gas configuration, which is particularly stable

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electons from one atom to another is called as Ionic or electrovalent bond.

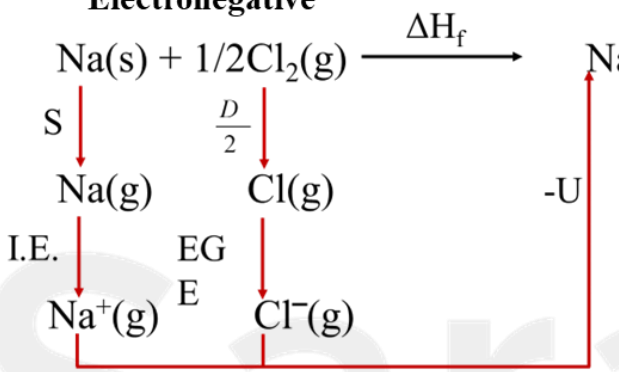
1. **Electropositive atom loses electron**
2. **Electronegative atom gains electron**

MIND MAP

Chemical Bonding

Cl^- ------- Na^+

Electronegative



Conditions for formation of Ionic Bond

1. **Ionisation Enthalpy**
2. **Electron Gain Enthalpy**
3. **Lattice Enthalpy**

1 + 2 + 3 negative

3.a) Ionization Enthalpy

Low I.E.

3.b) Electron Affinity

High EA

3.c) Lattice Energy

High LE

Factors Affecting Lattice Energy

$$U \propto \frac{Z^+Z^-}{r}$$

(a) L.E. $\propto Z^+, Z^-$

Z^+ = charge on cation

Z^- = charge on anion

Ex MgO > NaCl

(b) Lattice energy (L.E.) $\propto \frac{1}{r}$

$r = r_+ + r_-$ = interionic distance

Ex: NaCl > KCl

Electrovalency

The valence of an ion, equal to the number of positive or negative charges acquired by an atom through a loss or gain of electrons.

General Characteristics of Electrovalent Compounds

(1) Crystalline Nature: Due to non-directional force of attraction between ions, normally electrovalent compounds form solid crystals.

(2) M.P. & B.P.: Due to network of electrostatic force of attraction, usually M.P. & B.P. of ionic compounds are high. Boiling point of NaCl = 1413°C

General Characteristics of Electrovalent Compounds

(3) Hard & Brittle: Electrovalent compounds are hard due to strong forces of attraction between oppositely charged ion which keeps them in allotted position.

(4) Electrical Conductivity: Ionic compounds in solid form do not conduct electricity. Ions remain intact on account of electrostatic forces of attraction. But when ionic compounds are melted or dissolved in a polar solvent, the ions become mobile & move towards the respective electrode & act as carriers of electric current.

(5) Solubility : Ionic compounds are more soluble in polar solvents and less soluble in non polar solvents.

$$NaCl(s) \xrightarrow{\Delta H_f} Na^+(aq) + Cl^-(aq)$$

$$NaCl(s) \xrightarrow{+U} Na^+(g), Cl^-(g) \xrightarrow{-\Delta H_{hydration}} Na^+(aq) + Cl^-(aq)$$

Condition for Solvation

$$\Delta H_{hydration} > \Delta H_{Lattice\ energy}$$

MIND MAP

Chemical Bonding

Factors affecting Hydration energy

(1) Hydration energy (H) $\propto \{\frac{1}{r^+}$ & $\frac{1}{r^-}$ are radius of cation and anion$\}$

Hydration energy mainly depends on the cation radius because the value of $\frac{1}{r^-}$ is negligible in comparision to $\frac{1}{r^+}$

Size of Na^+ = 102 pm

Size of Cl^- = 181 pm

(2) Dielectric constant of solvent The capacity of solvent to neutralise the charge of ionic compounds is given by it's Dielectric constant. It is represented by ε.

Ex. 1) LiF < NaF < KF < RbF < CsF

Exceptions

1) $BeF_2 > BaF_2 > SrF_2 > MgF_2 > CaF_2$

Above happens because BeX_2 forms a soluble complex in water, leading to increased solubility.

2) $MgC_2O_4 < CaC_2O_4 < SrC_2O_4 < BaC_2O_4 < BeC_2O_4$

Polarizing power of a cation is usually called Ionic Potential or Charge Density

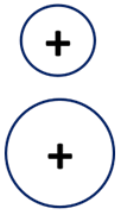
$$\text{Ionic Potential } \phi \text{ (phi)} \propto \frac{\text{Charge on cation}}{\text{Size of Cation}}$$

Fajan's Rules

$$\text{Ionic Potential } \phi \text{ (phi)} \propto \frac{\text{Charge on cation}}{\text{Size of Cation}}$$

Fajan's Rules

Rule 1 : A small positive ion favors covalency



$BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$

Size of cation ↑ ϕ ↓ Covalent character ↓

Rule 2 : A large anion favors covalency

Size of anion ↑ ϕ ↑ Covalent character ↑

LiF < LiCl < LiBr < LiI

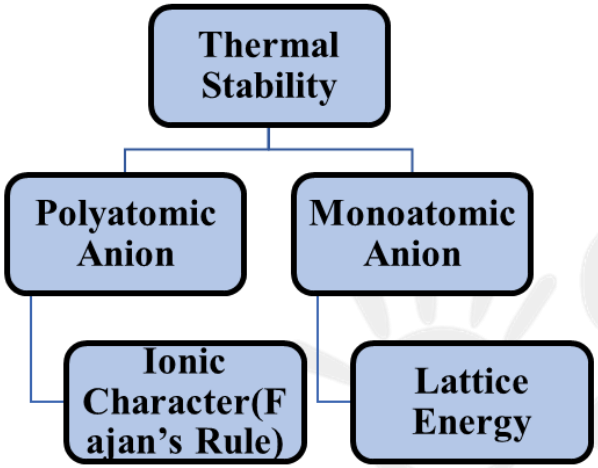
Predominantly Ionic AlF_3 → Predominantly Covalent $AlBr_3$

Size of cation ↑ ϕ ↓ Size of anion ↑ ϕ ↑

Charge on ion ↑ ϕ ↑ Pseudo inert > Inert

Application of Fajan's Rule

1. Colour in Ionic compounds
2. Thermal Stability
3. Melting point
4. Solubility
5. Ionic Mobility



For compounds having monoatomic anions, thermal stability is decided by the Lattice Energy.

$$TS \propto LE \propto \frac{1}{\text{Interionic distance}}$$

Ag_2S is less soluble than Ag_2O in H_2O

$Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water $\phi \uparrow$ solubility $\downarrow$

Variation of M.P.

M.P. of covalent < M.P. of ionic

$BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ →

MIND MAP

Chemical Bonding

ionic charater ↑ MP ↑ ϕ ↑ MP ↓

Ionic Mobility

$$\text{Ionic Mobility} \propto \frac{1}{\text{Hydrated Size}}$$

$$\text{Conductivity} \propto \frac{1}{\text{Hydrated Size}}$$

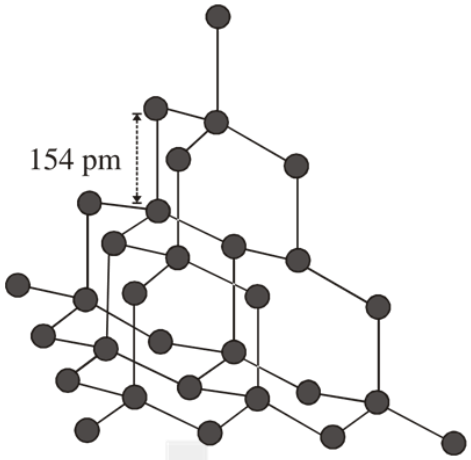
Covalent Bond

It is the electrostatic force of attraction between the nucleus of one atom and electron cloud of another atom when electron pairs are shared equally between two atoms.

Properties of Covalent compounds

Physical state: F_2, Cl_2(gases) Br_2(liquid), I_2(solid)

Melting and Boiling Points : With the exception of few which have giant 3-D structures such as diamond, carborundum (SiC), silica (SiO) ,others have realtively low melting and boiling points.



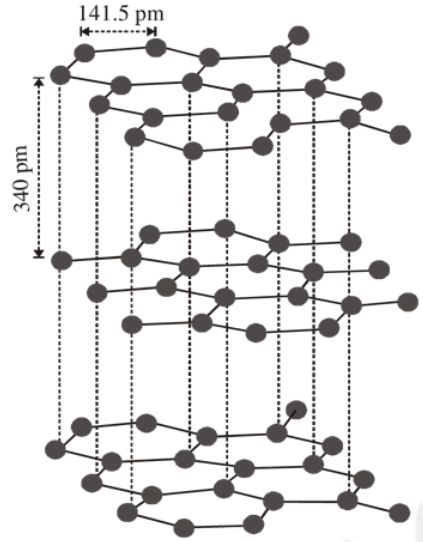
Electrical conductivity :

(a) In general covalent substances are bad conductors of electricity.

(b) Substances which have polar character like HCI in solution, can conduct electricity.

(c) Covalent solids having giant molecules, are bad conductors since they do not contain charged particles or free elelctrons.

(d) The graphite can conduct electricity since electrons can pass through one layer.



MIND MAP

Chemical Bonding

- Covalent Bond
  - Lewis & Kössel
    - Lewis ,Kössel &Langmuir
  - VSEPR
    - Gillespie
  - VBT
    - Heitler & London
  - MOT
    - R.S. Mulliken

Solubility :

(a) In general, covalent substances are insoluble in polar solvent like water but soluble in non polar solvents like benzene, CCI4, ether etc .. This is based on the principle" like dissolves like."

Isomerism:

The covalent bond is rigid & directional. On account of this, there is a possibility of different arrangements of atoms in space. Covalent compounds can thus show isomerism.

Covalency :

Capacity to form covalent bond is known as covalency.

Lewis Concept

How to draw the Lewis structure

1) Identify the central atom
a) least electronegative atom
b) less in number
c) atom which can form maximum number of bonds
d) Sometimes can't be decided on the basis of EN or number of atoms (less). In such cases, that atom is central atom which appears in central position of given formula of molecule/ion.

Maximum number of bonds that a central atom can form depends upon which period it belongs to. If it belongs to second period or below then it can only have less than or equal to 8 electrons. If it belongs to third period or above it can have more than 8 electrons.

Lewis Structure for Ions

For elements other than halogens, where the octet is completed in case of a uninegative charge, distribute the charge in such a way that octet of none of the surrounding atom is complete before it forms a bond with central atom.

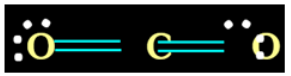
For halogens, it attaches itself with central atom by forming a co-ordinate or dative bond.

Formal Charge

Formal Charge (F.C.) on an atom in Lewis Structure = Total number of valence electrons in the free atom − Total number of non bonding (lone pair) electrons − ½[Total number of bonding (shared) electrons]

Bond Parameters

1) Bond Length: The equilibrium distance between the nuclei of two bonded atoms in a molecule.
2) Bond Angle: Angle between the orbitals containing bonding electron pairs around the central atom.



3) Bond Enthalpy: Energy required to break one mole of bond in gaseous state

4) Bond Enthalpy: Energy required to break one mole of bond in gaseous state

5) Bond Order: Number of bonds between two atoms in a molecule

Limitations of octet rule

Incomplete octet of central atom

BF_3

Expanded octet

SF_6

Odd electron molecules

NO_2

Noble gases also react

XeO_2

VSEPR

Valence Shell Electron Pair Repulsion Theory

Main Postulates of VSEPR

1. The shape of the molecules is determined by repulsions between all of the electron pairs present in the valence shell of central atom.
2. It follows that repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair, which is greater than the repulsion between two bond pairs.

lp – lp > lp – bp > bp – bp

MIND MAP

Chemical Bonding

Main Postulates of VSEPR

3. The magnitude of repulsions between bonding pair of electrons depends on the electronegativity difference between the central atom and the other atoms.

4. Double bond causes more repulsion than single bond, and triple bond causes more repulsion than a double bond.

VBT Valence Bond Theory

The Origins

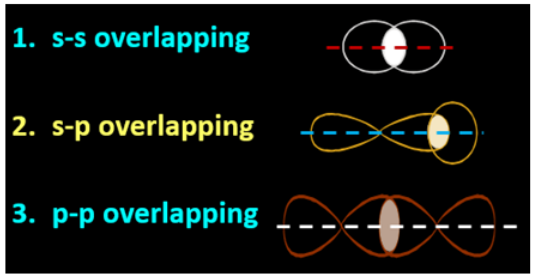
- It is based on quantum mechanical principles
- As science was progressing, scientists felt that Wave-mechanical treatement can help in solving the way bonding happens.
- A theory was proposed by Heitler and London in 1927, further developed by Pauling and others

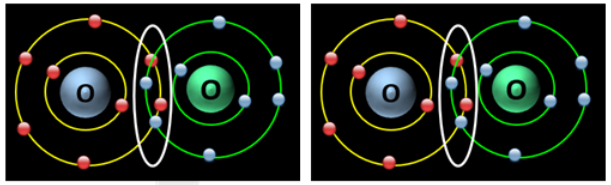
The formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

Overlapping

More the extent of overlapping, stronger is the bond.

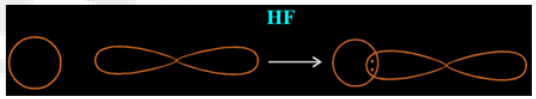
Types of σ overlapping





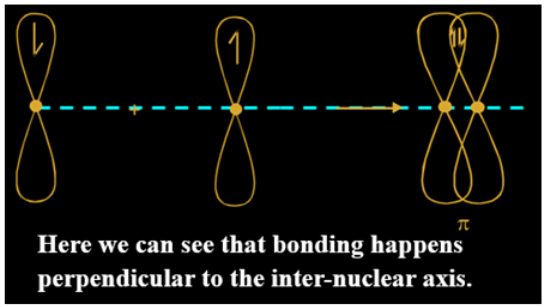
Sigma (σ) bond

A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called sigma (σ) bond.



Pi (π) bond

π bonds are those which are formed by the sidewise or lateral overlapping of p and d - orbitals.



The Overlapping takes place at the side of two lobes and hence, the extent of overlapping is smaller.
Thus π bond is weaker than σ bond

Summary

1. VBT explains bonding by taking wave-mechanical approach.
2. Orbitals having electrons with opposite spins overlap to form bonds.
3. S orbitals are non directional. p,d and f orbitals are directional.
4. Bond Strength is proportional to directional character and and inversely proportional to size. Size is the dominat factor.
5. Sigma bonds are formed when orbitals overlap along the internuclear axis, pi bonds form when orbitals overlap perpendicular to internuclear axis.

Hybridisation

Definition : Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

MIND MAP

Chemical Bonding

C_2H_2	sp	Linear
SO_2	sp^2	V-shape
NH_3	sp^3	Pyramidal
IF_3	sp^3d	T-shape
IF_5	sp^3d^2	Sqaure Pyramidal
IF_7	sp^3d^3	PBP

Hybridisation of following species in specified state

Species	Cationic part	Anionic part
PCl_5	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5	PBr_4^+ (sp^3)	Br^-
XeF_6	XeF_5^+ (sp^3d^2)	F^-
N_2O_5	NO_2^+ (sp)	NO_3^- (sp^2)
I_2Cl_6(liquid)	ICl_2^+ (sp^3)	ICl_4^- (sp^3d^2)
Cl_2O_6	ClO_2^+ (sp^2)	ClO_4^- (sp^3)

In sp hybridisation, s = 0.5, p=0.5
In sp^2 hybridisation s = 1/3, p = 2/3.
In pd_z^2 , s = 0

Bent's Rule

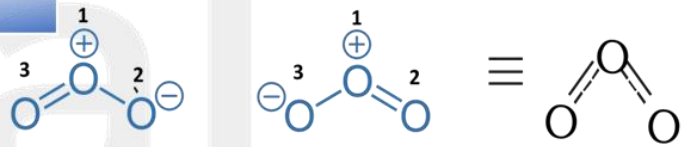
% s-character ∝ BDE ∝ BA ∝ 1/BL

Drago's Generalisation

Element of 3rd period (p-Block) and lower than 3rd period do not allow hybridisation in molecule when they form compound with less electronegative elements such as hydrogen
eg : PH_3, SiH_4, AsH_3 , H_2S do not undergo hybridisation

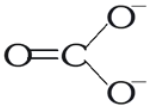
Resonance

$$\text{Bond order} = \frac{\text{Total number of bonds in all canonical forms}}{\text{Total canonical Structures}}$$

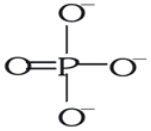


O— O Bond order = 3/2 = 1.5

$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$



C— O Bond order = 1.33



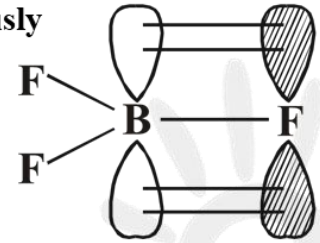
P — O Bond order = 1.25

Back Bonding

Back bonding generally takes place when

1) Out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period)
2) The other bonded atom is having some non-bonded electron pair(generally this atom is from the second period)

Both the conditions must be satisfied simultaneously



Vacant 2p-orbital — Filled 2p-orbital

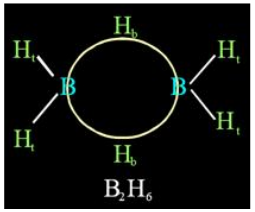
So back bonding can be of two types.

1. pπ–pπ (as in BF_3)
2. pπ–dπ (as in silyl isocyanate)

Type of Bridge Bond

3 centered-4 electron
When lone pair involved.
Example Al_2Cl_6

3 centered- 2 electron
When lone pair not involved.
Example B_2H_6



MIND MAP

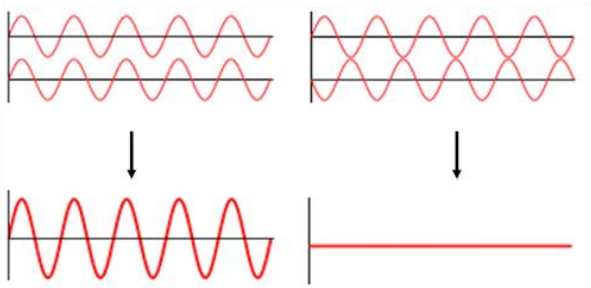
Chemical Bonding

Failures of VBT

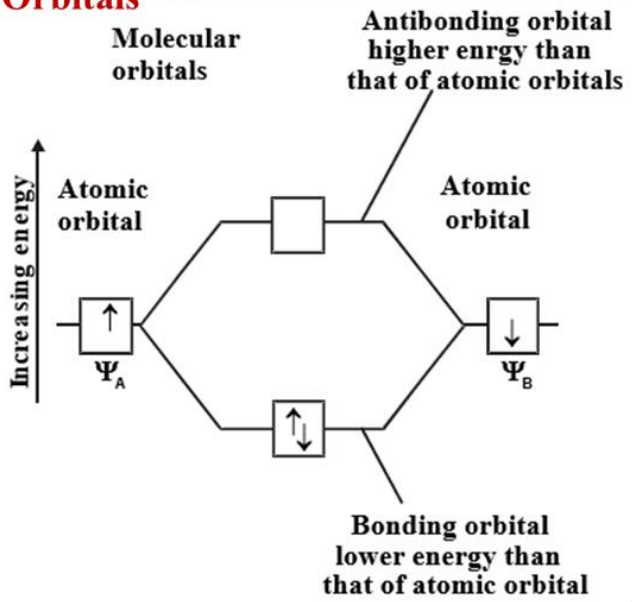
- It cannot explain the paramagnetic nature of O_2
- It cannot explain the formation of odd electron bond.
- It cannot explain fractional bond order in diatomic molecule.

Molecular Orbital Theory

1. In principle, Schrodinger equation can be written for any molecule.
2. However, since it can not be solved exactly for any system containing more than one electron, molecular orbitals which are more than one electron wave functions are difficult to obtain directly from the solution of the Schrodinger equation.
3. This difficulty is overcome by resorting to an approximation method called the Linear Combination of Atomic Orbitals(LCAO) method to form molecular orbitals.



Bonding and Anti-Bonding Molecular Orbitals



MIND MAP

Chemical Bonding

Conditions for the Combination of Atomic Orbitals

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, greater will be the electron-density between the nuclei of a molecular orbital.

Dipole Moment

$\mu = q \times d$

q = magnitude of charge on any one of the atom of the bond.

d = distance between two atoms of the bond.

Application Of Dipole Moment

To Determine Polarity and Geometry Of Molecule

If $\mu = 0$ compound is non polar and symmetrical

Example: CO_2, BF_3, CCl_4, CH_4. BeF_2 etc.

If $\mu \neq 0$ compound will be polar and unsymmetrical.

H_2O, SO_2, NH_3, Cl_2O, CH_3Cl, $CHCl_3$ etc.

Caution

In chemistry dipole moment direction is from positive to negative, whereas it's opposite is true in Physics!!

Weak Bonds

(a) Ion-dipole attraction
(b) Dipole-dipole attraction
(c) Ion-induced dipole attraction
(d) Dipole-induced dipole attraction
(e) Instantaneous dipole-Induced dipole (Dispersion force or London forces)

strength of Weak bonds a > b > c > d > e

Intermolecular Forces

Van der Waal's Forces

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

(a) Dipole-dipole attraction
(b) Ion-induced dipole attraction
(c) Dipole-induced dipole attraction
(d) Instantaneous dipole-Induced dipole (Dispersion force or London forces)

H-Bonding

1) Happens in the case of high EN elements. Such as F, O and N.
2) The electron pair is attracted towards electronegative atom so strongly that a dipole results.
3) The positive end of one molecule and negative end of other molecule will attract each other and weak electro-static force will develop. Thus, these molecules will associate together to form a cluster of molecules.

Applications of H-bonding

1) High B.P. & M.P. : NH_3, H_2O and HF have higher boiling and melting points in comparison to hydrides of other elements of V, VI and VII groups to which N, O and F belong respectively.
2) Physical State : H_2O exists as liquid under normal conditions whereas H_2S exists as a gas.
3) Solubility in water: Compounds which form hydrogen bonding with water will dissolve in water. For example, lower alcohol are soluble in water because their molecules can form H - bonds with water.