

## CHEMICAL BONDING

KEY CONCEPTS

## INTRODUCTION

A molecule will be formed if it is more stable and has a lower energy than the individual atom. Normally only electrons in the outermost shell of an atom are involved in forming bonds, and in this process each atom attains a stable electronic configuration of an inert gas.

## Types of Bonds :

| Atoms involved  | Bonding    |
|---|------------|
| (I) Metal + Nonmetal  | Ionic      |
| (II) Nonmetal + Nonmetal  | Covalent   |
| (III) Metal + Metal   | Metallic   |
| (IV) Electron deficient molecule or ion (Lewis acid) and electron rich molecule or ion (Lewis base) | Coordinate |
| (V) H and electronegative elements (N, O, F some times with Cl)                                     | Hydrogen   |

## Ionic, Covalent and coordinate bonding

## Ionic bonding

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



The oppositely charged ions get attracted through electrostatic force of attraction.

## Properties of ionic compounds :

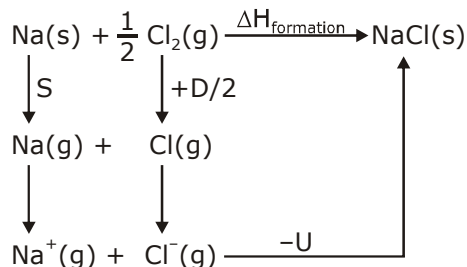
- In the solid state, each cation surrounds itself with anions and each anion with cations. These very large number of ions are arranged in an ordinary network called ionic crystals.
- They are good conductors of electricity in fused state or aqueous solution.
- They are generally soluble in polar solvents and insoluble in non-polar solvents.
- Have high melting point and boiling point than covalent compounds.
- Have strong force of attraction between cation and anion (Coulombic force)

$$F = \frac{Z_1 Z_2 e^2}{D r^2}$$

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Where  $Z_1$  and  $Z_2$  are charge on the ions,  $D$  is dielectric constant of the medium and  $r$  the inner-ionic distance (i.e., bond length).

**Born-Haber cycle** It is an indirect method to calculate the lattice energy of an ionic compound. For example, the lattice energy of sodium chloride can be calculated as follows.



Now, according to Hess's law,

$$\Delta H_{\text{formation}} = S + IE_1 + D/2 - EA_1 - U$$

Where S is the enthalpy of sublimation of metal (Na),  $IE_1$  is the first ionisation energy of sodium, D is the bond dissociation energy of  $Cl_2$  molecule,  $EA_1$  is the first electron affinity of Cl, U is the lattice energy of NaCl(s) and  $\Delta H_{\text{formation}}$  is the enthalpy of formation of NaCl.

### Covalent Bonding :

Whenever Chemical bond is formed by sharing of electrons then it is named as covalent bond.

### Coordinate Bonding or Dative Bond :

Whenever covalent bond is formed by unequal sharing of a pair of electrons between a Lewis base and Lewis acid is called coordinate bond.

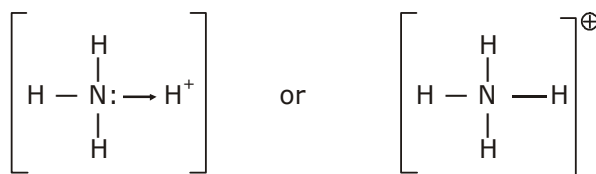
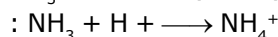
(I) It is represented as ( $\longrightarrow$ ) and considered as  $\sigma$  bond.

(II) Atom/ion/molecule donating electron pair is called donor or Lewis base.

(III) Atom/ion/molecule accepting electron pair is called acceptor or Lewis acid.

### Formation of $NH_4^+$ :

$NH_3$  has three (N – H) bonds and one lone pair. In  $NH_4^+$  formation. This lone pair is donated to  $H^+$  ion.



Note : In a multiple bond ( $\leftarrow$ ) sign is treated as a pi-covalent bond (Bock bond).

### Valence Bond (V.B) theory :

According to this theory, a covalent bond is formed by the overlapping of atomic orbitals. Important points of this theory are summarised below.

(I) Orbitals undergoing overlapping should be half-filled.

(II) Half-filled orbitals should contain the electron with opposite spin.

(III) Strength of a covalent bond depends upon the extent of overlapping, for example, axial or lateral overlapping.

(IV) If the atomic orbitals overlap axially, then the bond formed is called a sigma ( $\sigma$ ) bond.

(V) A sigma bond is always stronger than a pi-bond.

(VI) Covalent bonds formed by the overlap of s-s and s-p orbitals are always sigma.

(VII) By the overlap of p-p orbitals, one sigma and two pi bonds are formed.

(VIII) Increasing strength of  $\sigma$  covalent bonds is in the order  $s - s < s - p < p - p$  (when internuclear distance is constant)

(IX) A single covalent bond is always a sigma bond. In a double covalent bond, one is sigma and the other is pi-bond. In a triple covalent bond, one is sigma and two are pi-bonds.

### Hybridisation :

It is defined as the concept of intermixing of orbitals of same energy or of slightly different energy to produce entirely new orbitals of equivalent energy, identical shapes and which are symmetrically disposed is plane.

Important features of hybridisation are given below.

- (I) Only the orbitals generated are equal in number to that of pure atomic orbitals which are intermixed.
- (II) The hybrid orbitals generated are equal in number to that of pure atomic orbitals which are intermixed.
- (III) A hybrid orbital, like an atomic orbital, can have two electrons of opposite spins.
- (IV) Hybrid orbitals usually form sigma bonds. If there are pi-bonds, equal number of atomic orbitals must be left unhybridised for pi-bonding.

### Valence shell electron pair repulsion (VSEPR) Theory (Gillespie theory) :

- (I) The shape of a molecule is determined by repulsion between the electron pairs ( $\ell p$  and  $bp$ ) present in the valence shell of the central atom.
- (II) The order of repulsion is  $(\ell p-\ell p) > (\ell p-bp) > (bp-bp)$

### Determination of the Type of Hybridisation :

The number of electron pairs = Bond Pairs + lone pairs  
( $\sigma$  Bond)

**Table Shapes of molecules on the basis of VSEPR theory and hybridisation**

| Total electron pairs | Bond pairs | Lone pairs | Type of hybridization | Geometry due to repulsion | Bond angle                   | Example   |
|----------------------|------------|------------|-----------------------|---------------------------|------------------------------|-----------|
| 2                    | 2          | 0          | $sp$                  | Linear                    | $180^\circ$                  | $BeCl_2$  |
| 3                    | 3          | 0          | $sp^2$                | Trigonal Planar           | $120^\circ$                  | $BF_3$    |
| 3                    | 2          | 1          | $sp^2$                | Angular                   | $< 120^\circ$                | $SO_2$    |
| 4                    | 4          | 0          | $sp^3$ or $dsp^2$     | Tetrahedral               | $109^\circ 28'$              | $CH_4$    |
| 4                    | 3          | 1          | $sp^3$ or $dsp^2$     | Pyramidal                 | $< 109^\circ 28'$            | $NH_3$    |
| 4                    | 2          | 2          | $sp^3$ or $sp^2$      | Bent                      | $< 109^\circ 28'$            | $H_2O$    |
| 5                    | 5          | 0          | $sp^3d$               | Trigonal bipyramidal      | $120^\circ$ & $90^\circ$     | $PCl_5$   |
| 5                    | 4          | 1          | $sp^3d$               | See Saw                   | $< 120^\circ$ & $< 90^\circ$ | $SF_4$    |
| 5                    | 3          | 2          | $sp^3d$               | Bent T-shaped             | $< 90^\circ$                 | $ClF_3$   |
| 5                    | 2          | 3          | $sp^3d$               | Linear                    | $180^\circ$                  | $I_3^-$   |
| 6                    | 6          | 0          | $sp^3d^2$             | Octahedral                | $90^\circ$                   | $SF_6$    |
| 6                    | 5          | 1          | $sp^3d^2$             | Square pyramidal          | $< 90^\circ$                 | $BrF_5$   |
| 6                    | 4          | 2          | $sp^3d^2$             | Square planar             | $90^\circ$                   | $XeF_4$   |
| 7                    | 7          | 0          | $sp^3d^3$             | Pentagonal bipyramidal    | $90^\circ$ & $72^\circ$      | $IF_7$    |
| 7                    | 6          | 1          | $sp^3d^3$             | Pentagonal pyramidal      | $< 90^\circ$ & $< 72^\circ$  |           |
| 7                    | 5          | 2          | $sp^3d^3$             | Pentagonal planar         | $72^\circ$                   | $XeF_5^-$ |

### Molecular Orbitals (M.O.) Theory :

- (I) There is Linear combination of Atomic Orbitals (LCAO) to form molecular orbitals (M.O.)

(II) The number of molecular orbitals produced is equal to the number of atomic orbitals that are combined.

(III) Two types of molecular orbitals are formed.

(a) Bonding molecular orbitals at a lower energy than the combining atomic orbitals which favour bond formation.

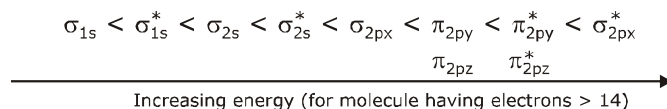
(b) Anti - bonding molecular orbitals at a higher energy than the combining atomic orbitals which opposes the bond formation.

Following molecular orbitals are formed when atomic orbitals overlap.

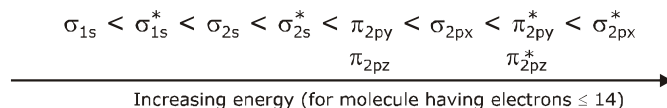
| Atomic orbitals | Bonding M. O.   | Anti-bonding M.O. |
|-----------------|-----------------|-------------------|
| 1s + 1s         | $\sigma$ 1s     | $\sigma^*$ 1s     |
| 2s + 2s         | $\sigma$ 2s     | $\sigma^*$ 2s     |
| $2p_x + 2p_x$   | $\sigma$ $2p_x$ | $\sigma^*$ $2p_x$ |
| $2p_y + 2p_y$   | $\pi$ $2p_y$    | $\pi^*$ $2p_y$    |
| $2p_z + 2p_z$   | $\pi$ $2p_z$    | $\pi^*$ $2p_z$    |

Electrons are filled in the increasing order of energy of the molecular orbitals which is in order of Aufbau rule

(a) When total electrons in the molecule or ions are more than 14 (simple order of energy level of M. O.).



(b) When total number of electrons in the molecule or ions are  $\leq 14$  (modified order of energy level of M.O.).



(I) The electrons are filled in molecular orbitals in the same way as in atomic orbitals, that is, as per the Hund's Rule, Pauli exclusion principle and Aufbau rule.

(II) Number of covalent bonds between two atoms is called Bond order and is given by

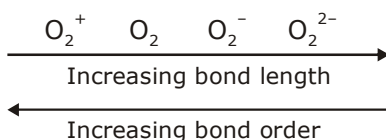
$$\text{Bond order (B.O.)} = \left( \frac{N_B - N_A}{2} \right)$$

Where,  $N_B$  = number of electrons in bonding molecular orbital and  $N_A$  = number of electrons in anti bonding molecular orbitals.

(III) For a stable molecule/ion,  $N_B > N_A$

(IV) A given molecule or ion is paramagnetic if it has unpaired electrons in the molecular orbital. Otherwise it is diamagnetic

(V) Greater the bond order, shorter the bond length and greater the bond energy. Thus for  $O_2$ ,  $O_2^+$ ,  $O_2^-$ ,  $O_2^{2-}$



**Fajan's Rule :**

This rule is used to decide relative ionic & covalent character in a molecule. A molecule is predominantly covalent if

(I) Smaller the size of cation.

(II) larger the size of anion.

(III) greater the charge on cation and anion.

(IV) ion does not have inert gas configuration but it possesses pseudo inert gas configuration (18 electrons in the ultimate shell).

(I)  $\xrightarrow{\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}}$   
decreasing covalent character due to increase in the size of cation

(II)  $\xrightarrow{\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}}$   
decreasing ionic character because of increase in anionic size

(III)  $\xrightarrow{\text{NaF} > \text{Na}_2\text{O} > \text{Na}_3\text{N}}$   
increasing covalent nature due to increase of charge on anion and increase in size of anion

(IV) CuCl and NaCl

$[\text{Cu}^+] = [\text{Ar}]3d^{10}$ ;  $[\text{Ne}^+] = [\text{Ne}]$

Cations with 18-electron shells (pseudo inert gas configuration) has greater polarising power than 8-electron shell (inert gas configuration) ion with the same charge and size. Thus, CuCl is more covalent than NaCl.

**Hydrogen Bonding :**

(I) The concept of H-bonding was introduced by Latimer and Rodebush.

(II) H-bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, O and N is held with weak electrostatic forces by the non-bonded pair of electron of another atom. That is, it is a dipole-dipole interaction.

(III) Of all the electronegative donor atoms, only F, O, and N enter into stable H-bond formation.

(IV) The weak electrostatic interaction leading to the H-bond formation is shown by dashed(.....) lines.

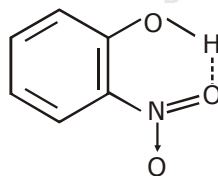
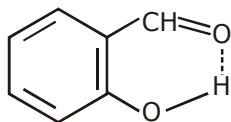
(V) Greater the electronegativity difference, stronger is the H-bond. For example,

**Intramolecular H-bonding ;**

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.

(a) o-hydroxy benzaldehyde

(b) o-nitrophenol

**Intermolecular H-bonding**

This type of H-bonding takes place between hydrogen and electronegative element (like F, O, N) present between molecules of the same substance ( $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ ) or different substances ( $\text{H}_2\text{O}$  and  $\text{NH}_3$ ).