CHEMICAL BONDING

The attractive force which holds various constituents (atom, ions etc) together in different chemical species is called a chemical bond.

Introduction

Every element in universe has tendency to accquire stability (minimum energy). That is done by combining one atom which another leading to the formation of a compound. This can be happens in three ways:

1. Electron transfer giving rise to an ionic bond via formation of cation and anion force of attraction are electrostatic intraction.

2. By sharing of electrons gives rise to a chemical bond while the formation of chemical bond more than 40 kj/mole of energy released.

3. Coordinate bond or dative bond (special type of covalent bond).

The Octed Rule

- Each atom shares electrons with neighbouring atoms to achieve a total of eight valence electrons (octet).

- One exception is Hydrogen atom (1s orbital duplet)

- The octet Rule provides a simple way of constructing a lewis strucutre, a diagram that shows the patterns of bonds and lone pair in a molecule.

**Problem:** Write the lewis dot structure of CO, NO_2^-, C_2H_2, C_2H_4

Soln. (i)

or $:C\equiv O:$

(ii)

(iii)

or $H-C\equiv C-H$

$8e^-$ $8e^-$
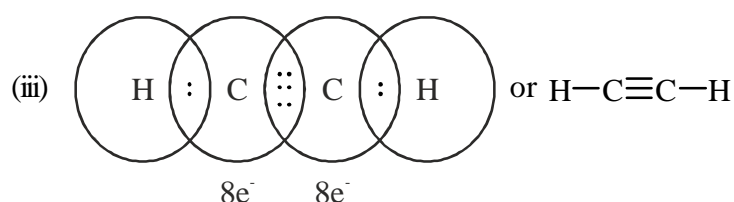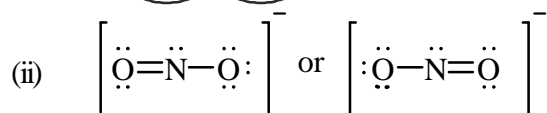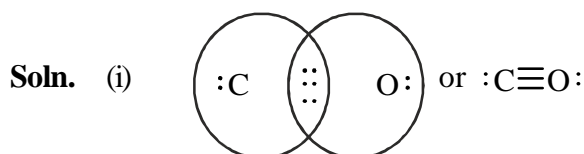
C_2H_2 molecule.

(iv) C_2H_4

C_2H_4 molecule
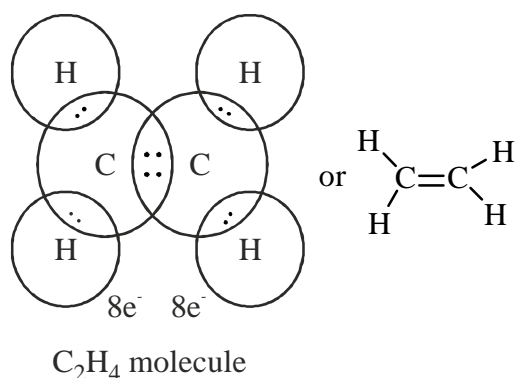
Formal Charge

$$\begin{bmatrix} \text{Formal charge (F.C.)} \\ \text{on an atom in a lewis} \\ \text{structure} \end{bmatrix} = \begin{bmatrix} \text{Total Number of} \\ \text{valence electrons} \\ \text{in the free atom} \end{bmatrix} - \begin{bmatrix} \text{Total number of} \\ \text{non-bonding} \\ \text{electrons} \end{bmatrix}$$
$$- \frac{1}{2}\begin{bmatrix} \text{Total number of bonding} \\ \text{(shared) electrons} \end{bmatrix}$$

Eq. O_3
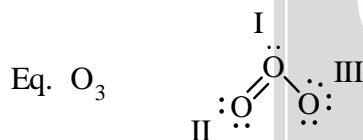
The formal charge on:

$$I = 6 - 2 - \frac{1}{2}(6) = +1, \quad II = 6 - 4 - \frac{1}{2}(4) = 0, \quad III = 6 - 6 - \frac{1}{2}(2) = -1$$

Hence O_3 with formal charger as follows
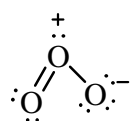
Limitation of the Octet Rule

•   Octet Rule is not universal

•   Octet Rule based upon inertness but some noble gases form various compounds eg XeF_2, $KrF_2 XeoF_2$ etc.

•   it is quite useful to understand the structure of most of the organic compounds.

•   there are three types of exceptions to the octet rule.

(1) **Incomplete octet of the central atom:**

    •   the elements having less than four valenec electrons form incomplete octet.

    •   these compounds are very often referred as electron defficient compounds.

       Eg. LiCl, BeH_2, BCl_3, $AlCl_3$, $BeCl_2$

(2) **Odd-electrons molecules:** in molecules with an odd number of electrons.

    Eg. $\ddot{N}=\ddot{O}$, $\ddot{O}=\overset{+}{\ddot{N}}-\ddot{O}\colon^-$
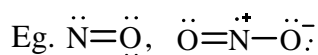
(3) **The Expanded Octet:**

- the compounds having more than eight valence electrons around the centeralatom.

- the elements in and beyond the third period of the periodic table (3d orbital also available for bonding) form expanded octet.

Eg. PCl_5, ClF_3, SF_6, SiF_6^{2-}, H_2SO_4

Bond Parameters:

(a) Bond length: "Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule."

Note: Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques.
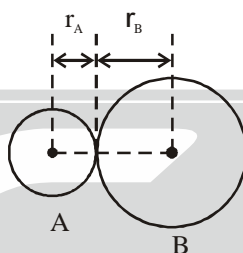
The bond length in a covalent molecule AB.

$$\boxed{\text{Bond length } (R) = r_A + r_B}$$

r_A = covalent radius of A atom; r_B = covalent radius of B atom.

Covalent radius: The covalent radius is measured approximately as the radius of an atom is core which is contact with the core of an adjacent atom in a bonded situation.

The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule.
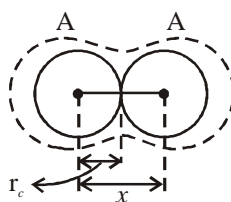
$$\boxed{r_C = \frac{x}{2}}$$

x = Bond length of a homodiatomic molecule

(e.g. H_2, O_2, N_2 etc)

r_C = Covalent radius of atom in a molecule.

e.g. AA type molecule:

Vander waals radius: The van der waals radius represents the overall size of the atom which included its valence shell in a non-bonded situation. Further, "The vander waals radius is half of the distance between two similar atoms in separate molecules in a solid.
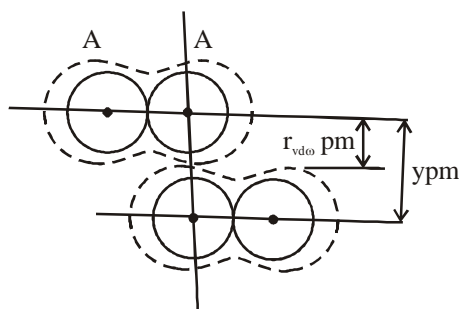


Van der waals radius $(r_{vd\omega}) = \dfrac{y}{2}$ pm .

y = Internuclear distance between two atoms of different molcules, when they are nearest to each other.

(b) **Bond angle** (θ)**:** It is defined as " the angle between the hybrid orbitals containing bonding electron pairs around the central atom in a molecule/complex ion."
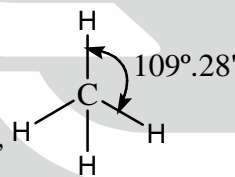
Note: Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods.

• It gives idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape.
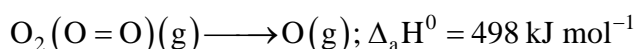
e.g. (i) H_2O bond angle $\theta = 104.5°$,
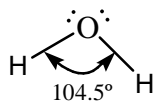
 (ii) CH_4, $\theta = 109°.28'$,

(c) **Bond enthalpy:** (ΔH)**:** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

• The unit of bond enthalpy is kJ mol^{-1}.

   e.g.: H — H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

$$H_2(g) \longrightarrow H(g); \quad \Delta_a H^0 = 435.8 \text{ kJ / mol}$$

$$O_2(O=O)(g) \longrightarrow O(g); \Delta_a H^0 = 498 \text{ kJ mol}^{-1}$$

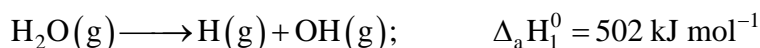**Note:** Larger the bond dissociation enthalpy, stronger will be the bond in the molecule.

• $HCl(g) \longrightarrow H(g) + Cl(g); \quad \Delta_0 H^0 = 431.0 \text{ kJ / mol}$.

Note: In case of polyatomic molecule, the measurement of bond strength is more complicated.

For example in case of H_2O molecule, the enthalpy needed to break the two O—H bonds is not same

$$H_2O(g) \longrightarrow H(g) + OH(g); \quad \Delta_a H_1^0 = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g); \quad \Delta_a H_2^0 = 427 \text{ kJ mol}^{-1}$$

The difference in the ΔH^0 value shows that the second O—H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O—H bond in different molecule like C_2H_5OH (ethanol) and H_2O. Therefore in polyatomic molecules the term mean or aveage bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken. e.g. H_2O

Average bond enthalpy $\left(\Delta H\right) = \dfrac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$

Factors on Which Bond Energy Depends

(a) Bond Length : Shorther the bond length, greater is the bond energy. For example,

	C—C	C = C	C ≡ C
Bond length (pm)	154	134	120
Bond energy (kJ mol⁻¹)	347.2	615.0	811.6

(b) Size of Bonded Atoms : Shorter the size of bonded atoms, greater is the bond energy. Thus, bond energy

values decrease down the group. For example,

	Li—Li	Na—Na	K—K
Bond energy (kJ mol⁻¹)	108.7	75.3	54.3

(c) Bond Order : Bond energy increases as the bond order. This is evident from above where $C \equiv C$ bond has greater bond energy than $C = C$ bond which has greater bond energy than C—C bond.

(d) Electronegativity: The greater the electronegativity difference between the bonded atoms, greater is the bond energy. For example

	HF	HCl	HBr	HI
Electronegativity difference	1.9	0.9	0.7	0.3
Bond energy (kJ mol⁻¹)	568.1	431.7	366.1	298.3

(e) Number of Lone Pair: The greater the number of lone pairs on the bonded atoms, the greater is the repulsion between them. This results in a weaker bond. Hence bond energy decreases.

(f) Hybridization: The extent of overlapping in case of hybridised orbitals is greater than that of unhybridised orbitals. Therefore, hybridised orbitals from stronger bonds and have higher bond energy than the unhybridised orbitals. As the percentage of p-character in the hybridised orbitals increases, the bond energy increases.

(g) Bond Angle : The greater the bond angle, the greater is the bond energy. For example, order of bond energies is as follows:

	BeF_2	>	BF_3	>	CCl_4
Bond angle	180°		120°		109° 28′

1.7 Resonance

Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bondig cannot be expressed by one lewis structure.

- the Experimental Evidence shows that all the C–O bonds are identical, with bond lengths (129 pm) between double-bond and single bond distances (116 and 143 pm) (Because of Resonance).

- the Resonance signifies that there is more than one possible way in which the valence electrons can be placed in a lewis structure.

- When a molecule has several Resonance structure, its overall Electronic Energy is lowered, making it more stable.