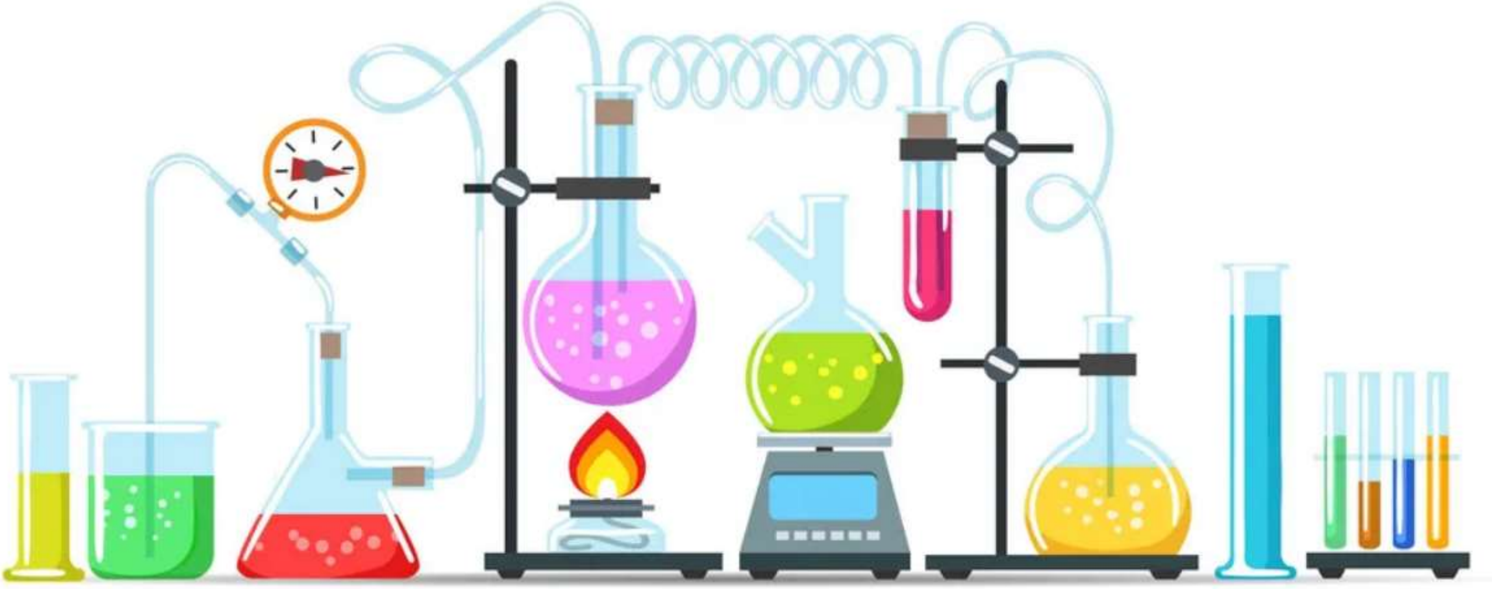
CHEMISTRY



CHEMICAL BONDING AND MOLECULAR STRUCTURE

Introduction:

Structure and Bonding is the heart of chemistry. Chemical bond is very important to explain the properties and structure of compound. The important aspect of each type of force is its relative strength, how rapidly it decreases with increasing distance and whether it is directional in nature or not.

Chemical Bond:

It is the force of attraction between two atoms which hold them together in a compound or molecule. Nature loves stability and bond formation is associated with stability. Every element has a tendency to occupy inert electronic configuration which is considered as very stable. Noble gas electronic configuration can be achieved by

1. Transference of electrons
2. Mutual sharing of electrons
3. Donation of lone pair of electrons

Types of Bond

In order to explain the formation of a chemical bond in terms of electrons, Lewis postulated that atoms achieve stable octet when they are linked by a chemical bond. On the basis of this chemical bonds are following type:

1. Ionic bond
2. Covalent bond
3. Co-ordinate bond
4. Metallic bond
5. Hydrogen bond
6. van der Waal's bond

Lewis Dot Structures

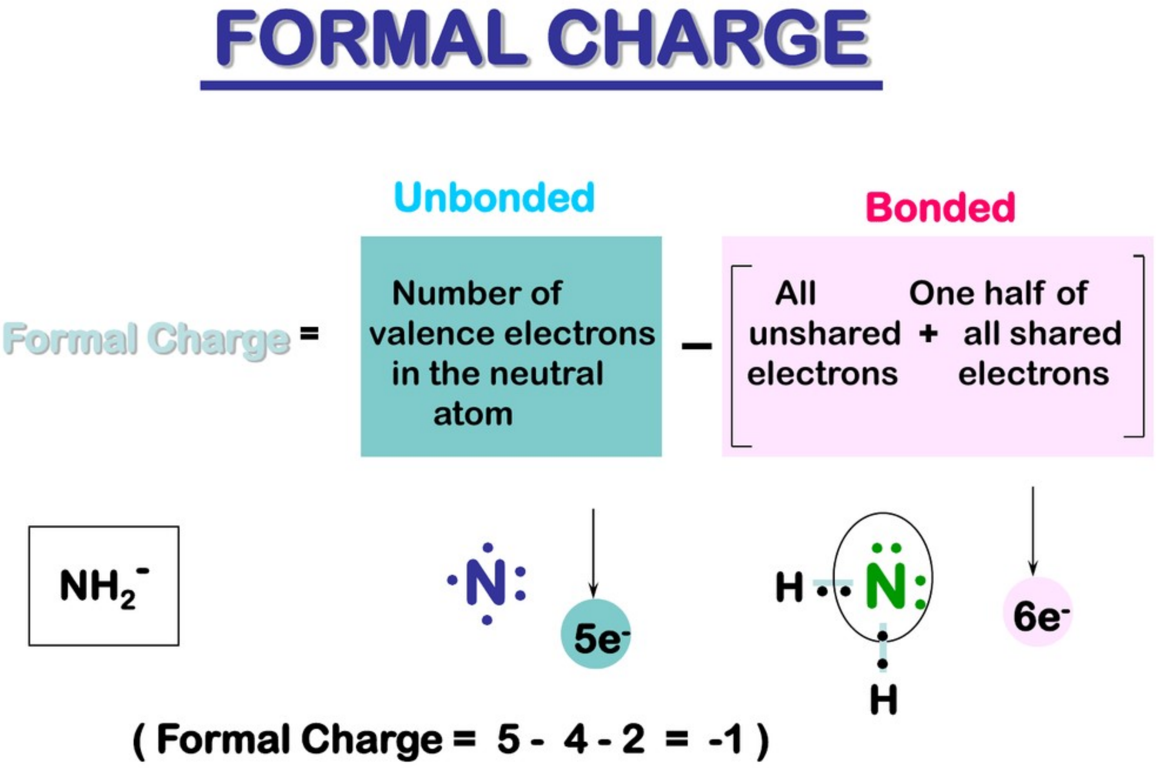
Valence Electrons: In the formation of a molecule only the outer shell electrons take part in chemical bond combination and they are known as valence electrons. In Lewis symbols, an element is shown with symbol and valence electrons.

Octet Rule

It is proposed by Kossel and Lewis and according to this, "Every atom has a tendency to attain Noble gas electronic configuration or to have 8 valence electrons". This is known as law of octet rule or if it has two valence electrons then this is known as law of duplet. According to Lewis, only those compounds will be stable which follow octet rule.

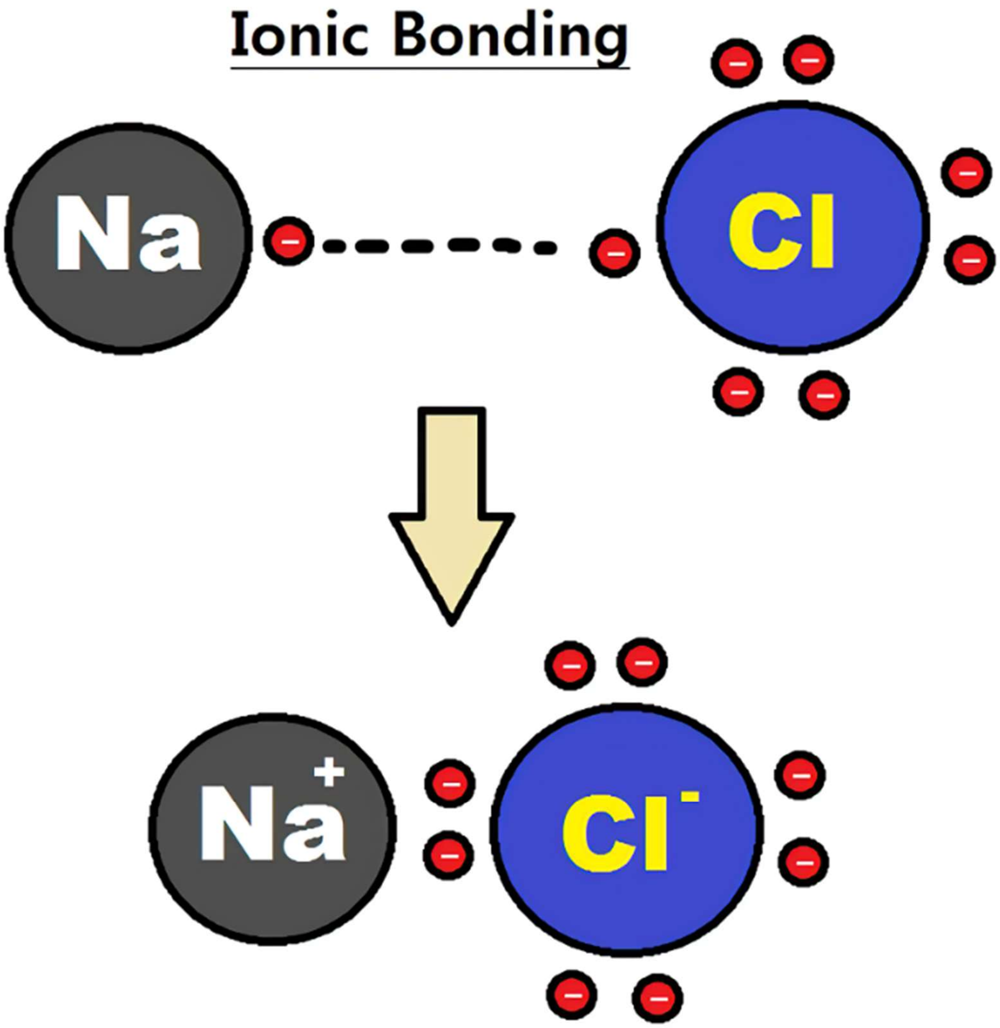
Formal Charge

Formal charge on an atom is the difference between the number of valence electrons is an isolated atom and the number of electrons assigned to that atom in a Lewis structure. It is expressed as:



Ionic Bond

An ionic bond is formed by complete transference of one or more electrons from the valence shell of one atom to the valence shell of another atom. In this way both the atoms acquire stable electronic configurations of noble gases. The atom which loses electron becomes a positive ion and the atom which gains electron becomes negative ion.



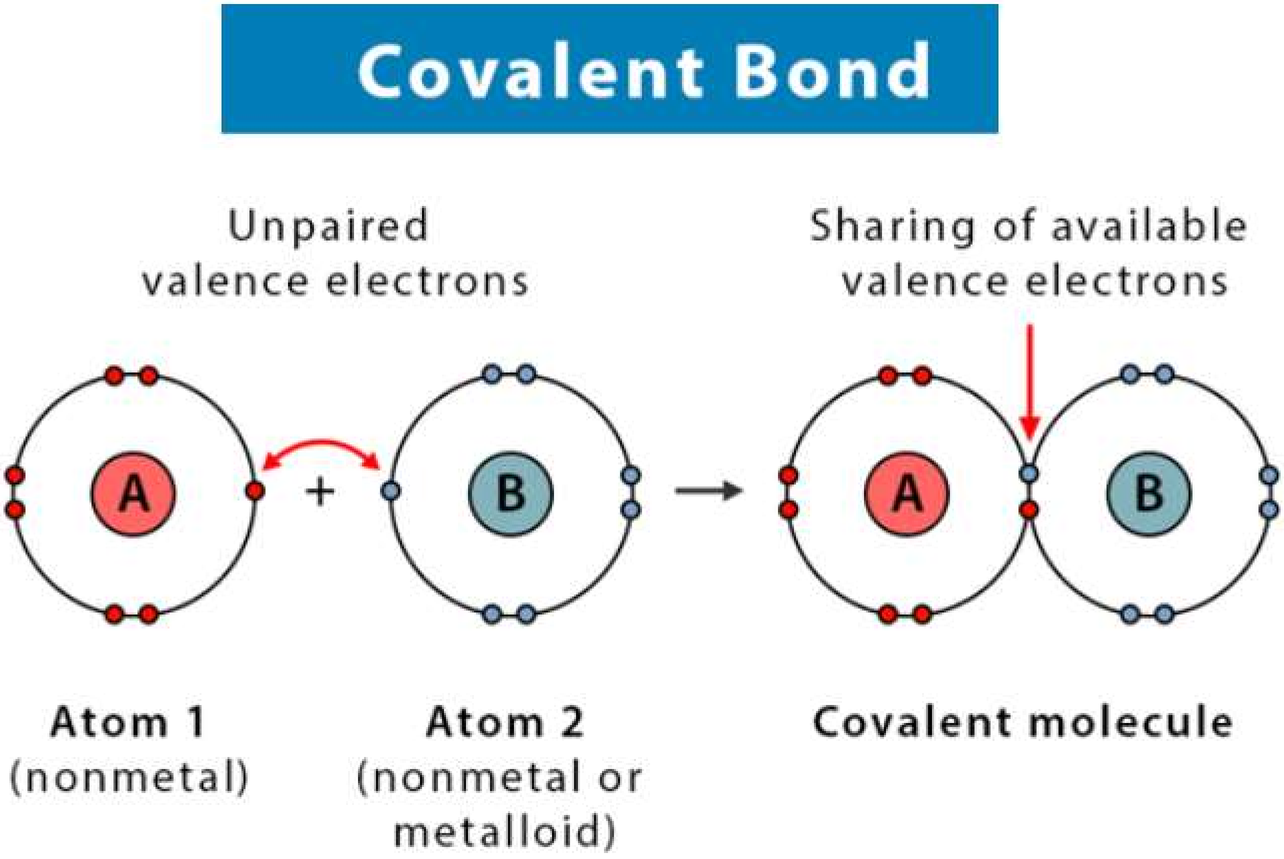
Note: Electrovalency is the number of electrons lost or gained during the formation of an ionic bond or electrovalent bond.

Characteristics of Ionic Compounds:

1. They are hard, brittle and crystalline.
2. They have high melting and boiling points.
3. They are polar in nature.
4. The linkage between oppositely charged ions is non rigid and non directional.
5. They are soluble in polar solvents such as water and insoluble in non polar solvents such as CCl_4, Benzene, ether etc.
6. They are good conductors of electricity in fused state and in solution due to mobility of the ions. They are bad conductors of electricity in solid state because ions are unable to move.

Covalent Bond

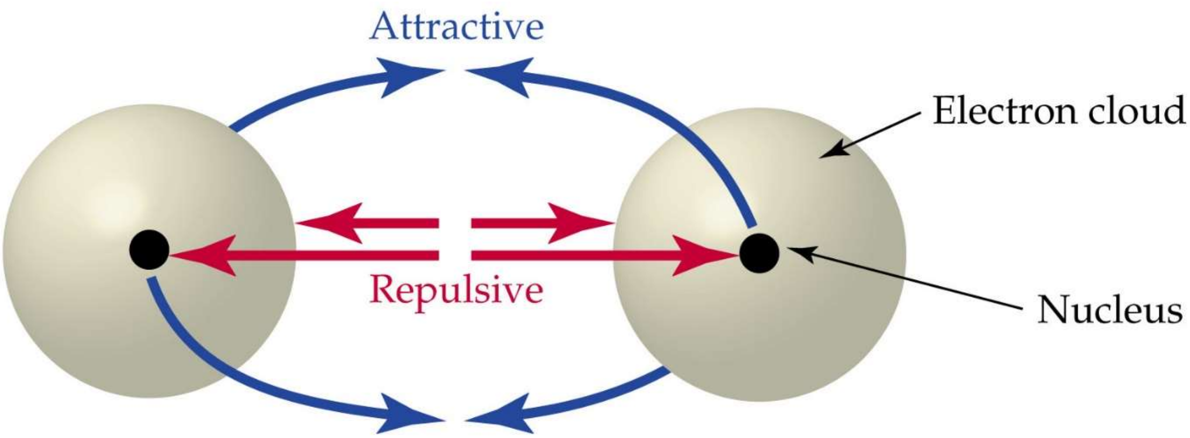
A force which binds atoms of same or different elements by mutual sharing of electrons is called a covalent bond. If the combining atoms are same the covalent molecule is known as homoatomic. If they are different, they are known as heteroatomic molecule.



Valence Bond Theory (VBT)

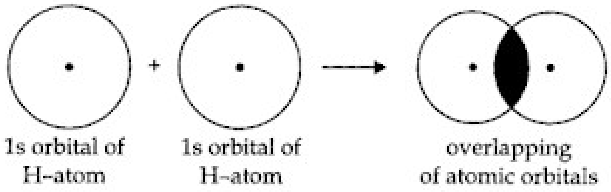
Valence bond theory was introduced by Heitler and London (1927) and developed by Pauling and others. It is based on the concept of atomic orbitals and the electronic configuration of the atoms. Let two hydrogen atoms A and B having their nuclei NA and NB and electrons present in them are eA and eB. As these two atoms come closer new attractive and repulsive forces begin to operate.

1. The nucleus of one atom is attracted towards its own electron and the electron of the other and vice versa.
2. Repulsive forces arise between the electrons of two atoms and nuclei of two atoms. Attractive forces tend to bring the two atoms closer whereas repulsive forces tend to push them apart.



Orbital overlap concept

If we refer to the minimum energy state in the formation of hydrogen molecule the two H-atoms are enough near so as to allow their atomic orbitals to undergo partial interpenetration. This partial interpenetration of atomic orbitals is called overlapping of atomic orbitals. The overlap between the atomic orbitals can be positive, negative or zero depending upon the characteristics of the orbitals participating to overlap.

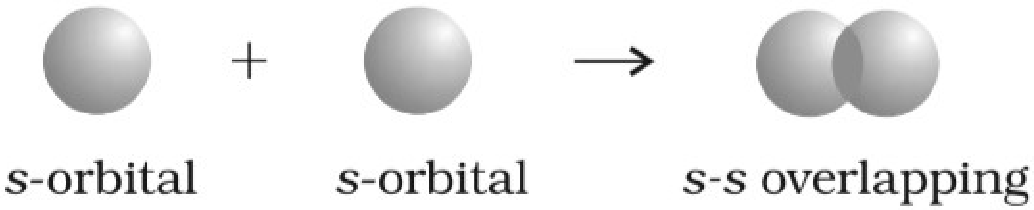


Types of overlapping

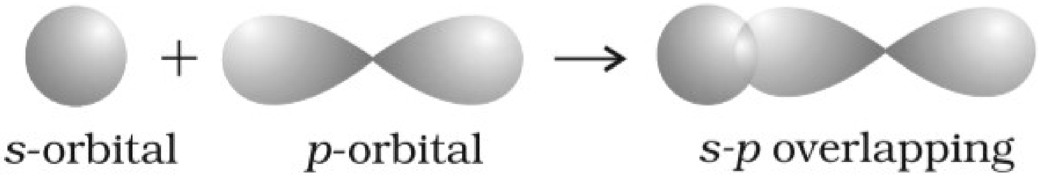
The covalent bonds can be classified into two different categories depending upon the type of overlapping. These are:

Sigma (σ) bond: This type of covalent bond is formed by the axial overlapping of half-filled atomic orbitals. The atomic orbitals overlap along the internuclear axis and involve end to end or head on overlap. There can be three type of axial overlap among s and p-orbitals as discussed below:

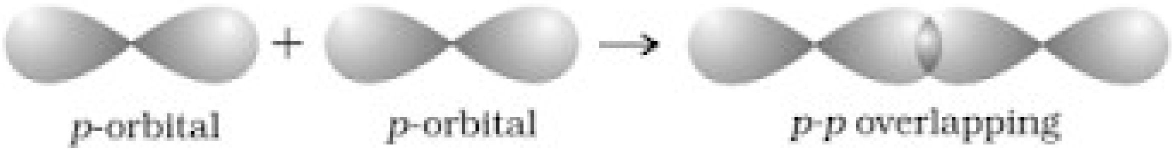
i. **s-s overlap:** In this case, there is overlap of two half-filled s-orbitals along the internuclear axis as shown below.



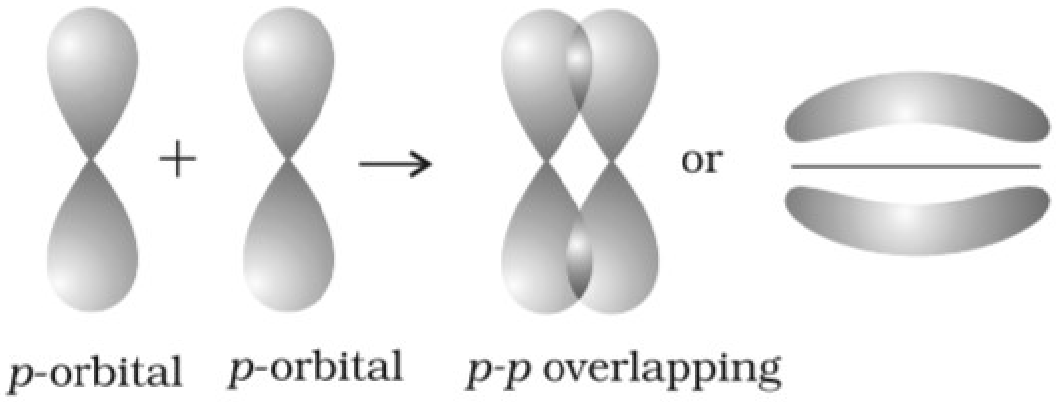
ii. **s-p overlapping:** It involves the overlapping of half filled s-orbitals of one atom with the half filled p-orbitals of the other atom. The bond thus formed is called s-p sigma bond.



iii. **p-p overlapping:** It involves the co-axial overlapping between half filled p-orbitals of one atom with half filled p-orbitals of the other atom. The bond as formed is called p-p sigma bond.



pi (π) bond: This type of covalent bond is formed when the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms. The electrons involved in the π bond formation are called pi-electrons.



Hybridisation: Hybridisation is 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. The atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals.

Salient Features of Hybridisation:

i. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
ii. The hybridised orbitals are always equivalent in energy and shape.
iii. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
iv. The type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation:

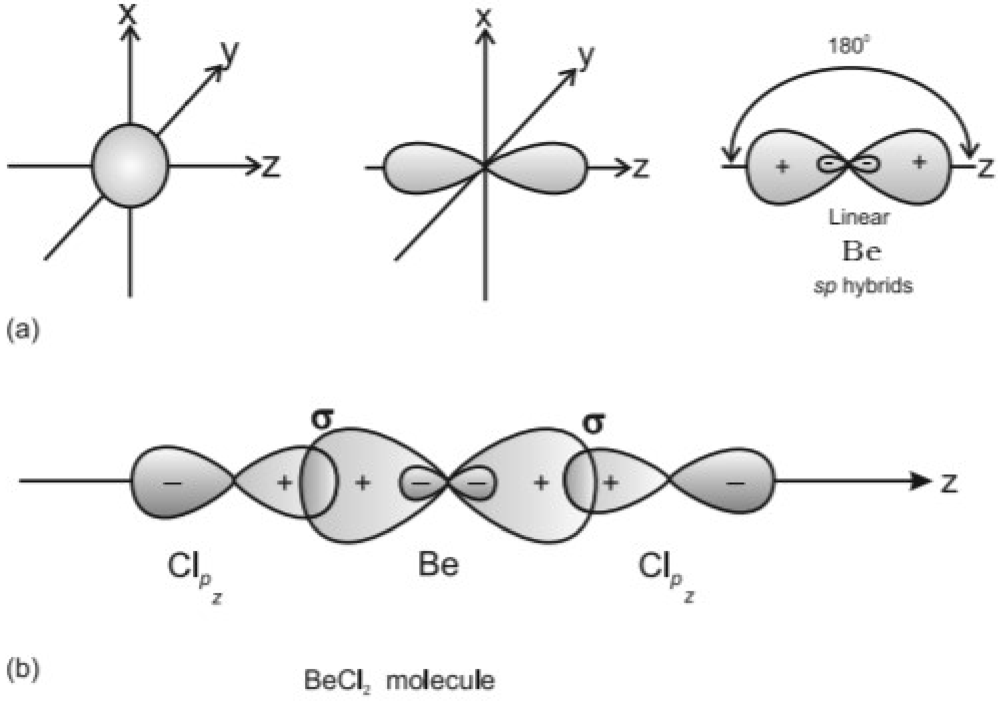
i. The orbitals present in the valence shell of the atom are hybridised.
ii. The orbitals taking part in hybridisation must have only a small difference of energies.
iii. Promotion of electron is not essential condition prior to hybridisation.
iv. It is not necessary that only half filled orbitals participate in hybridisation.

Types of hybridisation

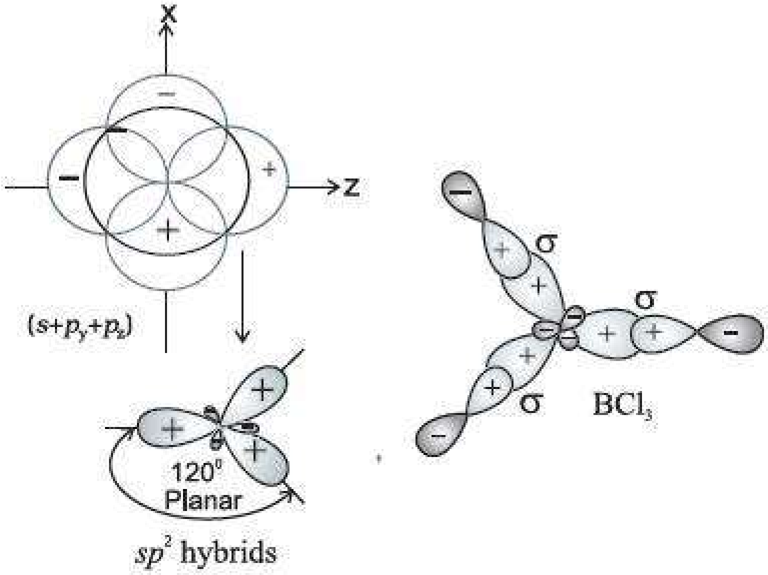
There are many different types of hybridisation depending upon the type of orbitals involved in mixing such as sp^3, sp^2, sp, sp^3d, sp^3d^2 etc.

i. **sp-hybridisation:** In this hybridisation one s and one p orbitals hybridise to produce two equivalent hybrid orbitals, known as sp hybrid orbitals. The two sp-hybrid orbitals are oriented in a straight line making an angle of 180° and therefore the molecule possesses linear geometry. Each of hybrid orbitals has 50% s-character and 50% p-character.

Example of molecules having sp-hybridisation are BeF_2, $BeCl_2$, BeH_2 etc.



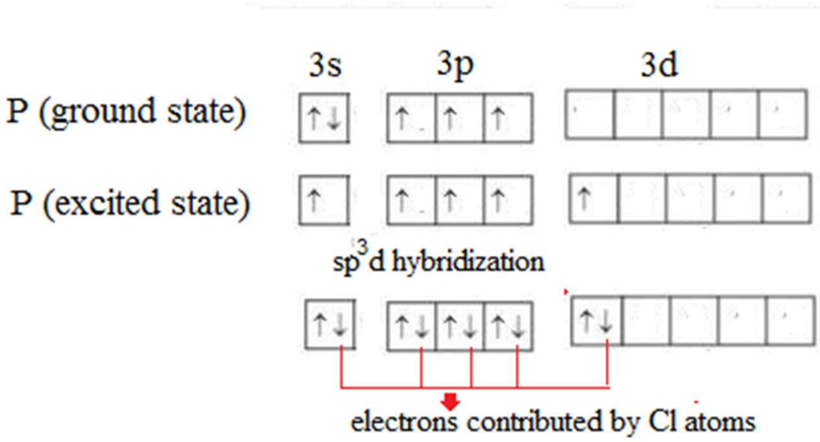
ii. **sp^2-hybridisation:** In this hybridisation one s and one 2p orbitals hybridise to produce three equivalent hybrid orbitals, known as sp^2 hybrid orbitals. sp^2 hybrid orbitals are larger in size than sp-hybrid orbitals but slightly smaller than that of sp^3 hybrid orbitals. Each sp^2 hybrid orbitals has 1/3 (or 33.33%) s-character and 2/3 (or 66.7%) p-character. Example, BF_3, BCl_3, BH_3 etc.

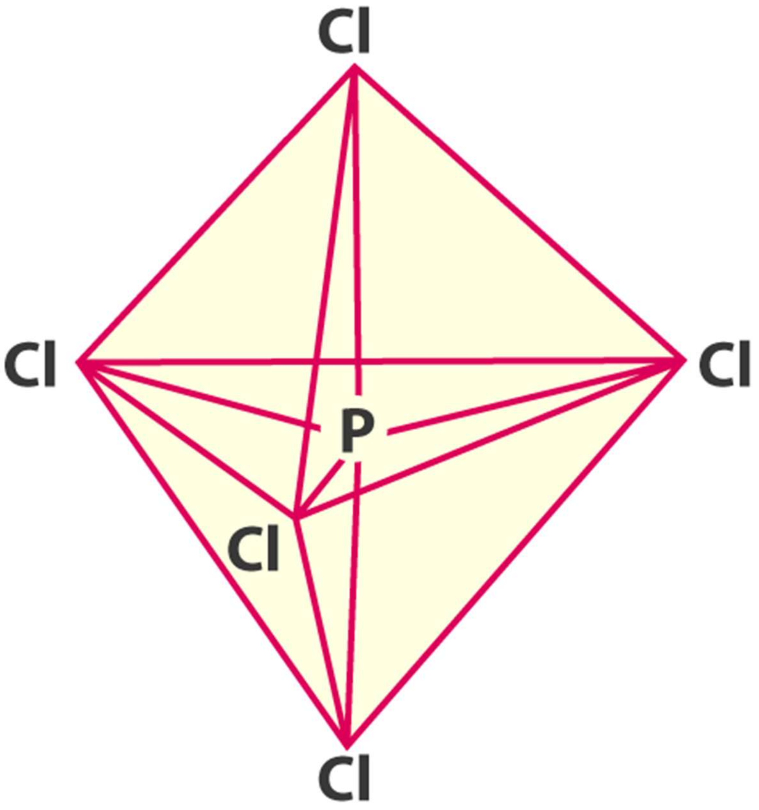


iii. **sp^{3}d-hybridisation:** This type of hybridisation involves mixing of one s, three p and one d-orbitals to form five sp^{3}d hybridised orbitals which adopt trigonal bipyramidal.

Formation of PCl_5: The ground state electronic configuration of phosphorus is $1s^2\ 2s^2\ 2p^6\ 3s^2$

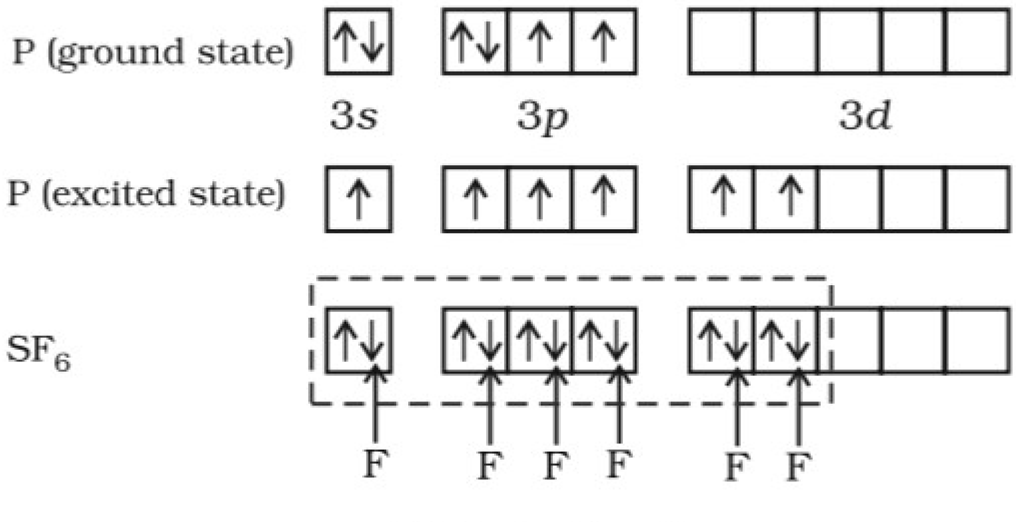
$3p^3$. Under the conditions of bond formation the 3s-electrons get unpaired and one of the electron is promoted to vacant $3d_{z^2}$ orbital. The ground state and excited state configurations of phosphorus are shown below:



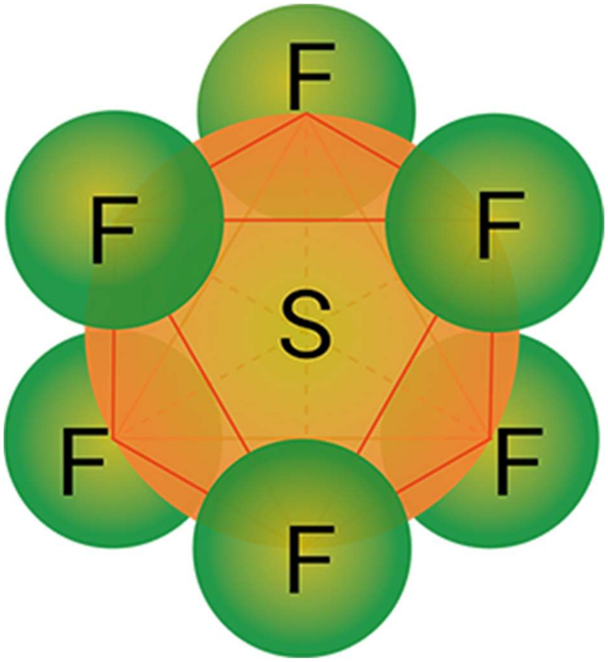


iv. **sp^3d^2-hybridisation:** In this type of hybridisation one s, three p and two d-orbitals undergo intermixing to form six identical sp^3d^2 hybrid orbitals. These six orbitals are directed towards the corners of an octahedron and lie in space at an angle of 90° to one another.

The ground state outer configuration of 16S is $3s^2\ 3p^4$. In the excited state the electron pairs in 3s and 3px orbitals get unpaired and one out of each pair is promoted to vacant $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. The ground state and excited state configuration of 16S are given as follows:



sp³d² hybridisation



Valence Shell Electron Pair Repulsion (VSEPR) Theory

Sidgwick and Powell in 1940, proposed a simple theory based on repulsive character of electron pairs in the valence shell of the atoms. It was further developed by Nyholm and Gillespie (1957). Main Postulates are the following:

i. The exact shape of molecule depends upon the number of electron pairs (bonded or non bonded) around the central atoms.

ii. The electron pairs have a tendency to repel each other since they exist around the central atom and the electron clouds are negatively charged.

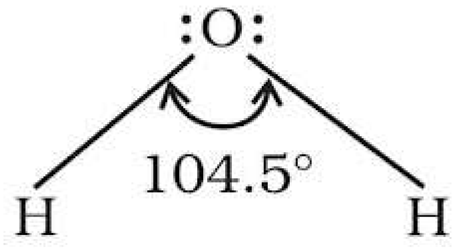
iii. Electron pairs try to take such position which can minimize the rupulsion between them.

iv. The valence shell is taken as a sphere with the electron pairs placed at maximum distance.

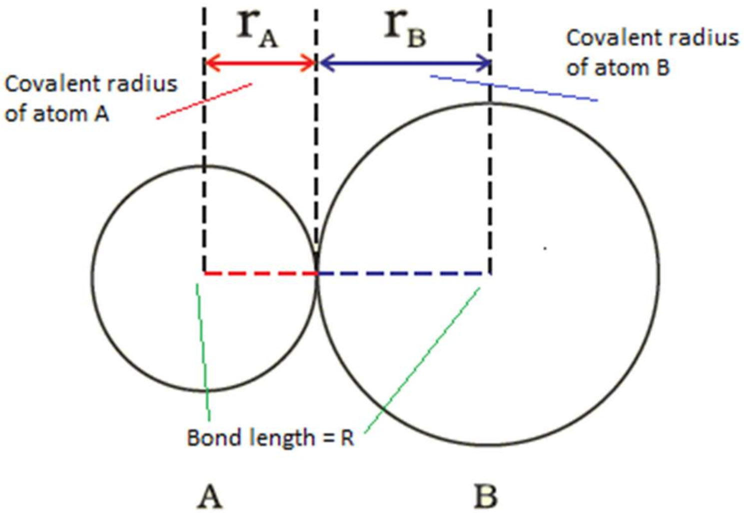
v. A multiple bond is treated as if it is a single electron pair and the electron pairs which constitute the bond as single pairs.

Bond Parameters:

i. **Bond Angle:** It is the distance between two consecutive crests or troughs and is denoted by λ. It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods.



ii. **Bond Length:** Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.



iii. **Lattice Enthalpy:** The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1}.

iv. **Bond Order:** Bond order is defined as half of the difference between the number of electrons present in bonding and antibonding molecular orbitals. The bond order may be a whole number, a fraction or even zero. It may also be positive or negative.

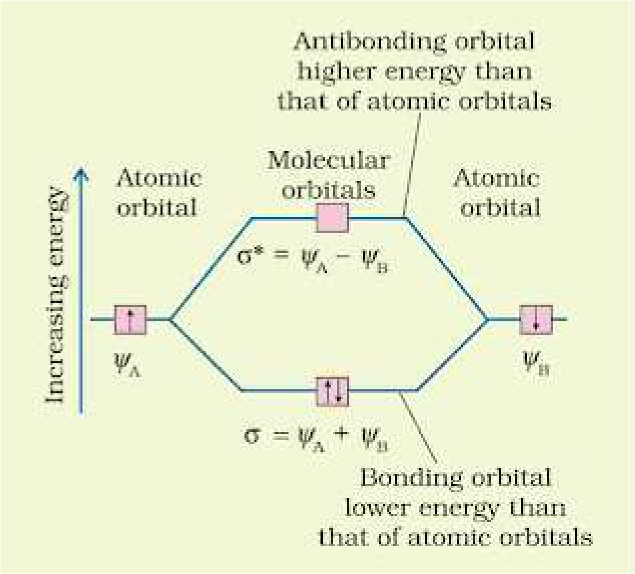
Bond order (B.O.) $= \frac{1}{2}\,[\mathbf{Nb} - \mathbf{Na}]$

v. **Bond Enthalpy:** 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. For example, the H – H bond enthalpy in hydrogen molecule is 435.8 kJ mol$^{-1.}$

Molecular Orbital Theory (MOT)

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. According to MOT, a molecule is considered to be quite different from the constituent atoms. All the electrons belonging to the atoms constituting a molecule are considered to be moving along the entire molecule under the influence of all the nuclei. Thus, a molecule is supposed to have orbitals of varying energy levels, in same way as an atom. These orbitals are called molecular orbitals.

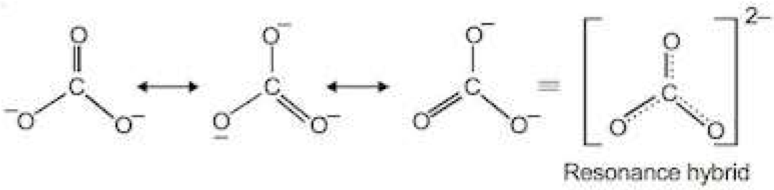
Energy Level Diagram for Molecular Orbitals:



Resonance

When light of a suitable frequency is allowed to incident on a metal, ejection of electrons take place. This phenomenon is known as photo electric effect.

When a compound has same molecular formula but different structural formulas and structures differ with respect to electrons only. These structures are known as resonating structures or canonical structures. None of these structures can explain all the properties of that compound. This phenomenon is known as resonance.



Hydrogen Bonding

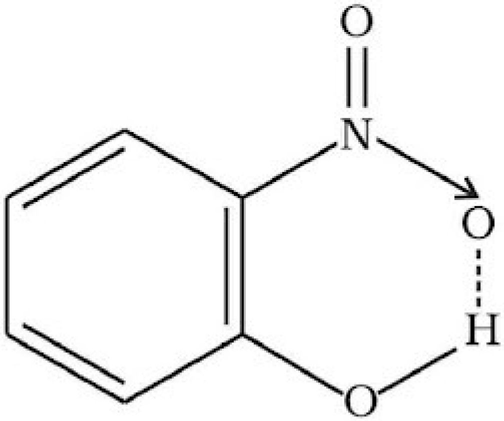
When highly electronegative elements like nitrogen, oxygen, flourine are attached to hydrogen to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. Thus, partial positive charge develops on hydrogen atom which forms a bond with the other electronegative atom. This bond is known as hydrogen bond and it is weaker than the covalent bond.

Types of Hydrogen Bonding:

i. **There are two types of hydrogen bonding:** It is a type of hydrogen bonding between two similar or dissimilar molecules. Example : H – F, HF and water, NH_3, NH_3 and water, alcohol, alcohol and water etc.

$$H^{\delta+} - X^{\delta-} --- H^{\delta+} - X^{\delta-} --- H^{\delta+} - X^{\delta-}$$

ii. **Intramolecular hydrogen bonding:** It is a type of hydrogen bonding within the molecule. Example : Salicylaldehyde, O-nitrophenol etc.



Applications of Hydrogen Bonding

i. **State:** Hydrogen bonding may affect the state of a compound. For example, H_2O is liquid at room temperature whereas H_2S is gas. It is due to presence of intermolecular hydrogen bonding between H_2O molecules, which is not present in H_2S molecules.

ii. **Solubility:** Only those covalent molecules are soluble in water which have tendency to form intermolecular hydrogen bonding with water molecules.

iii. **Boiling point:** Intermolecular hydrogen bonding increases the boiling point of compound. For example, NH_3 has higher boiling point than PH_3. This is because, there is intermolecular hydrogen bonding in NH_3 but not in PH_3.

iv. **Density of ice is lower than water:** In ice, hydrogen bonding gives rise to a cage like structure of H–O–H molecules, in which each H–O–H molecule is linked tetrahedrally to four other H–O–H molecule. In this structure, some vacant spaces are formed, which decrease the density of ice.

Metallic Bonding

The force that binds a metal atom to a number of electrons within its sphere of influence is known as metallic bond.

This model could easily explain the following properties of metals:

i. High electrical conductivity
ii. High thermal conductivity
iii. Bright metallic lustre
iv. Malleability
v. Ductility
vi. Tensile strength
vii. Elasticity

Summary

1. **Chemical Bond:** The force of attraction which holds various chemical entities in different species.
2. Electrovalent Bond : The attractive force between the oppositely charged ions which comes into existence by the transference of electrons.
3. **Electrovalency:** The number of electrons which an atom loses or gains while forming ionic or electrovalent bond.
4. **Covalent Bond:** The bond comes into existence by the mutual sharing of electrons by the atoms participating in bonding.
5. **Valence Bond Approach of Covalent Bond:** The bond is formed by the overlapping of halffilled atomic orbitals having electrons with opposite spins.
6. **Covalency:** The number of half-filled atomic orbitals which an atom provides for participation in overlapping at the time of bonding.
7. **Dative Bond or Co-ordinate Bond:** The bond is formed by sharing of electrons in which the shared pair of electrons is contributed by one of the atom called donor while the other atom is called acceptor.
8. **Hybridisation:** The process of mixing or merging of orbitals (of slightly different energies) of an atom to form another set of orbitals with equivalent shape and energy.

9. **Geometry of the Molecule:** The definite relative arrangement of the bonded atoms in a molecule.
10. **Regular and Irregular Geometry:** The molecule is said to possess regular geometry if the repulsive interactions among the electron pair around the central atom are of equal magnitude. If the repulsive interactions among the electron pairs are unequal, the geometry is referred to as irregular.
11. **Electronegativity:** The power of an atom to attract bonding pair of electrons towards itself.
12. **Dipole Moment (μ):** A vector quantity defined by the product of charge developed on any of the atom and distance between the atoms; creating a dipole.
13. **Polar and Non-Polar Molecules:** The molecules with dipole moment (μ) > 0 are called polar molecules while those with μ = 0 are non-polar molecules.
14. **Dipole-Dipole Interactions:** The attractive interactions among the opposite ends of polar molecules in liquid and solid state.
15. **Hydrogen Bond:** The electrostatic force of attraction between covalently bonded H-atom of one molecule and the electronegative atom (F or N or O) of the other molecule.
16. **Resonance:** When a molecule is represented by more than one electronic arrangement none of which is able to explain the observed characteristics of the molecule, then the actual structure is intermediate of various electronic arrangements and is known as resonance hybrid. The various electronic arrangements are called resonating structures or canonical structure.
17. **Molecular Orbital Theory (MOT):** According to this theory, in molecules the electrons are present in new orbitals called molecular orbitals. Molecular orbitals are not associated with a particular atom but belong to nuclei of all the atoms constituting the molecule.
18. **LCAO Method:** This is an approximate method, according to which the molecular orbitals are obtained by linear combination of atomic orbitals.

MIND MAP : LEARNING MADE SIMPLE CHAPTER - 4

Chemical Bonding and Molecular Structure

Chemical Bond:Attractive forces which hold the various chemical constituents together in different chemical species.

Types:

(i) Covalent Bond: A chemical bond formed between two atoms by mutual sharing of electrons between them to complete their octet.

(ii) Ionic Bond: A chemical bond formed by complete transference of electrons from one atom to another acquire the stable nearest noble gas configuration.

Lattice Enthalpy

Energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

Valence Shell Electron Pair Repulsion (VSEPR)

Postulates:

- Shape of molecule depends upon the number of valence shell electron pairs around central atom.
- Pairs of electrons in the valence shell repel one another.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion.
- The valence shell is taken as a sphere with electron pairs localising on spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- When one or more resonance structures can represent a molecule, VSEPR model is applicable:
- **Decreasing order of repulsive interaction:**

lp – lp > lp – bp > bp – bp

Valence Bond Theory: Given by L Pauling. It explains that a covalent bond is formed between two atoms by overlap of their half-filled valance orbitals, each of which contains one unpaired electron.

Orbital Overlap Concept: Formation of a covalent bond results by pairing of electrons in valence shell with opposite spins.

Types of Overlapping: (i) Sigma (σ) bond – end to end.
(ii) Pi (TT) bond – axis remain parallel to each other.

Hybridisation: Process of intermixing of orbitals of different energies resulting in formation of new set of orbitals of equivalent energies and shape.

Types of Hybridisation –(i) sp (ii) sp^2 (iii) sp^3

Bonding Molecular Orbitals: Addition of atomic orbitals.

Antibonding Molecular Orbitals: Substraction of atomic orbitals.

Bond Parameters

(I) Bond Length: Equilibrium distance between the nuclei of two bonded atoms in molecule.

(ii) Bond Angle: Angle between the orbitals containing bonding electron pairs around central atom in a molecule complex ion.

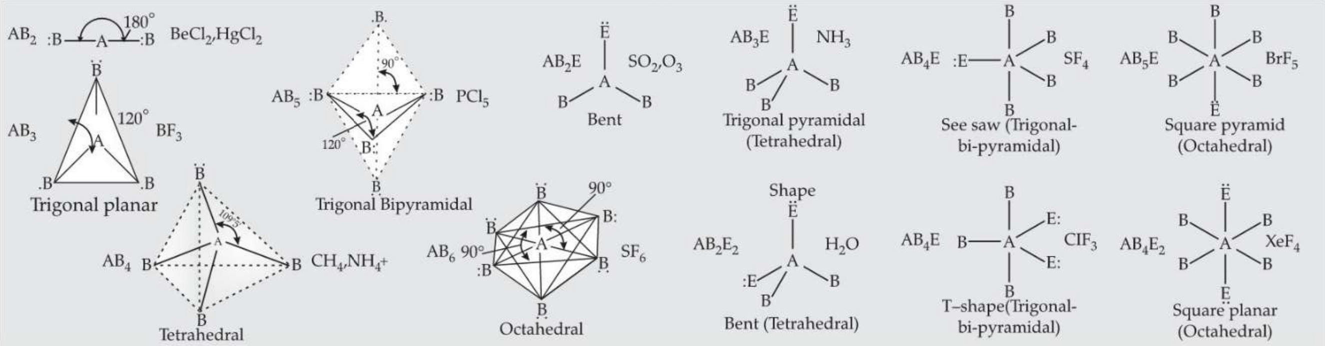
(iii) Bond Enthalpy: Amount of energy required to break one mole of bonds of particular type between 2 atoms.

(iv) Bond Order: Number of bonds between the two atoms of a molecule.

(v) Resonance Structures: Are a set of two or more Lewis structures that collectively describe the electronic bonding a single polyatomic species.

(vi) Dipole Moment: Product of the magnitude of the charge and distance between centres of positive and negative charge. u= Q x r

Hybridization



Chemical Bonding

Kossel Lewis approach to chemical bonding:

- * Lewis pictured the atom as a positively charged 'kernel' and the outer shell accommodates a maximum of eight electrons.
- Lewis postulated that atoms achieve the stable octet when linked by chemical bonds.
- Kossel gave following facts:
- * In the periodic table, highly electronegative halogens and highly electropositive alkali separated by noble gases.
- * Formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with gain and loss of electron by respective atoms.
- * Negative and positive ions formed attain noble gas electronic configurations.
- Negative and positive ions are stabilized by electrostatic attraction.

Octet Rule: Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons to complete octet in their valence shells.

Lewis Dot Structure provides a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule.

How To Write A Lewis Dot Structure:

Step 1: Add the valence electrons of the combining atoms to obtain total number of electrons.

Step 2: For anions, each negative charge means addition of one electron. For cations, each positive charge means subtraction of one electron from total number of valence electrons.

Step 3: Write chemical symbols of combining atoms.

Step 4: Least electronegative atom occupies central position.

Step 5: After accounting for shared pairs of electrons remaining are either utilized for multiple bonding or remain as lone pairs.

Formal Charge= (Total number of valence electrons in free atom) – (Total number of non-bonding electrons) – 1/2(Total number of bonding electrons)

Limitations Of Octet Rule:

- Shows three types of exceptions (ie) incomplete octet of central atom, odd-electron molecules and expanded octet.
- Does not account for the shape of molecules.
- Fails to explain stability of molecules.

Hydrogen Bond: Formed when the negative end of one molecule attracts the positive end of other.

Types:

(i) Intermolecular: Between two different molecules of same or different compounds.

(ii) Intramolecular : H atom is between two highly electronegative atoms.

Molecular orbital theory

Postulates:

- Electrons in a molecule are present in various molecular orbitals as electrons are present in atomic orbitals.
- Atomic orbitals of comparable energies and proper symmetry combine.
- Atomic orbitals is monocentric while a molecular orbital is polycentric.
- Number of molecular orbital formed is equal to number of combining molecular orbitals.
- Bonding molecular orbitals has low energy and high stability

Types of MO: σ(Sigma),ℼ (Pi), δ (Delta)

Important Questions

Multiple Choice questions-

Question 1. Based on VSEPR theory, the number of 90° F-Br-F angles in BrF_5 is

(a) 0

(b) 2

(c) 4

(d) 8

Question 2. The hybrid state of Sulphur in SO_2 molecule is:

(a) sp^2

(b) sp^3

(c) sp

(d) sp^3d

Question 3. In allene (C_3H_4), the type(s) of hybridization of the carbon atoms is (are)

(a) sp and sp^3

(b) sp and sp^2

(c) Only sp^2

(d) sp^2 and sp^3

Question 4. The state of hybridization of the central atom and the number of lone pairs over the central atom in POCl3 are

(a) sp, 0

(b) sp^2, 0

(c) sp^3, 0

(d) dsp^2, 1

Question 5. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?

(a) $Ca^{2+} < Mg^{2+} < Be^+ < K^+$

(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$

(c) $Be^{2+} < K+ < Ca^{2+} < Mg^{2+}$

(d) $K+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

Question 6. Which one of the following does not have sp^2 hybridized carbon?

(a) Acetone

(b) Acetic acid

(c) Acetonitrile

(d) Acetamide

Question 7. Which one of the following is paramagnetic?

(a) NO+

(b) CO

(c) O_2^-

(d) CN

Question 8. Which of the following structures will have a bond angle of 120° around the central atom?

(a) Linear

(b) Tetrahedral

(c) Triangular

(d) Square planar

Question 9. An atom of an element A has three electrons in its outermost orbit and that of B has six electrons in its outermost orbit. The formula of the compound between these two will be

(a) $A_3 B_6$

(b) $A_2 B_3$

(c) $A_3 B_2$

(d) $A_2 B$

Question 10. In which of the following, the angle around the central atom is largest?

(a) CS_2

(b) SF_4

(c) SO_2

(d) BBR_3

Question 11. Based on lattice enthalpy and other considerations which one the following alkali metals chlorides is expected to have the higher melting point?

(a) RbCl

(b) KCl

(c) NaCl

(d) LiCl

Question 12. In which of the following substances, the intermolecular forces are hydrogen bonds?

(a) Hydrogen Chloride

(b) Hydrogen Sulphide

(c) Dry Ice

(d) Ice

Question 13. Which one of the following pairs of species have the same bond order?

(a) CN^- and NO^+

(b) CN^- and CN^+

(c) O2$^-$ and CN^-

(d) NO^+ and CN^+

Question 14. Dipole-induced dipole interactions are present in which of the following pairs?

(a) H_2O and alcohol

(b) Cl_2 and CCl_4

(c) HCl and He atoms

(d) SiF_4 and He atoms

Question 15. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are)

(a) Sp and sp^3

(b) Sp and sp^2

(c) Only sp^2

(d) sp^2 and sp^3

Very Short:

1. What change in energy takes place when a molecule is formed from its atoms?
2. Arrange the following in order of increasing bond strengths.
3. Name the shapes of the following molecules: CH_4, C_2H_2, CO_2.
4. Arrange the following in order of increasing strengths of hydrogen bonding O, F, S, Cl, N
5. Identify the compound/compounds in the following in which S does not obey the Octet rule: SO_2, SF_2, SF_4, SF_6.
6. Name one compound each involving sp^3, sp^2, sp hybridization.

7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Questions:

1. Which out of CH_3F and CH_3Cl has a higher dipole moment and why?
2. Define the term chemical bond. What are its different types?
3. Why covalent bonds are called directional bonds whereas ionic bonds are called non-directional?
4. AlF_3 is a high melting solid whereas SiF4 is a gas. Explain why?
5. Using the VSEPR theory identifies the type of hybridization and draw the structure of OF_2 What are oxidation states of O and F?
6. Account for the following: The experimentally determined N-F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.

Long Questions:

1. State with reasons, which is more polar CO_2 or N_2O?
2. Out of peroxide ion (O_2) and superoxide ion (O_2) which has larger bond length and why?
3. Explain the formation of the following molecules according to the orbital concept, F2, HF, O_2, H_2O, N_2, NH_3 molecules.
4. What is a hydrogen bond, what are its causes, and give the conditions for hydrogen bonding? What is the strength of hydrogen bonding? Describe the two types of hydrogen bonding.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

   Reason (R) : This is because sodium and chloride ions acquire octet in sodium chloride formation.

   (i) A and R both are correct, and R is the correct explanation of A.

   (ii) A and R both are correct, but R is not the correct explanation of A.

   (iii) A is true but R is false.

(iv) A and R both are false.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : Though the central atom of both NH3 and H_2O molecules are

   sp3 hybridised, yet H–N–H bond angle is greater than that of

   H–O–H.

   Reason (R) : This is because nitrogen atom has one lone pair and oxygen

   atom has two lone pairs.

   (i) A and R both are correct, and R is the correct explanation of A.

   (ii) A and R both are correct, but R is not the correct explanation of A.

   (iii) A is true but R is false.

   (iv) A and R both are false.

Case Study Based Question:

1. Read the passage given below and answer the following questions:

   Chemical bonding, involve interactions that account for the association of atoms into molecules, ions, crystals, and other stable species that make up the familiar substances of the everyday world. When atoms approach one another, their nuclei and electrons interact and tend to distribute themselves in space in such a way that the total energy is lower than it would be in any alternative arrangement. If the total energy of a group of atoms is lower than the sum of the energies of the component atoms, then bond together and the energy lowering is the bonding energy.

   The ideas that helped to establish the nature of chemical bonding came to fruition during the early 20th century, after the electron had been discovered and quantum mechanics had provided a language for the description of the behaviour of electrons in atoms. However, even though chemists need quantum mechanics to attain a detailed quantitative understanding of bond formation, much of their pragmatic understanding of bonds is expressed in simple intuitive models. These models treat bonds as primarily of two kinds-namely, ionic and covalent.

   The type of bond that is most likely to occur between two atoms can be predicted on the basis of the location of the elements in the periodic table, and to some extent the properties of the substances so formed can be related to the type of bonding.

   A key concept in a discussion of chemical bonding is that of the molecule. Molecules are the smallest unit of compounds that can exist. One feature of molecules that can be predicted with reasonable success is their shape. Molecular shapes are of considerable importance for understanding the reactions that compounds can undergo, and so the link between chemical bonding and chemical reactivity is discussed briefly in this article.

(1) According to molecular orbital theory, which of the following will not be available molecule?

(a) He_2^{2+}

(b) He_2^{+}

(c) H_2^{-}

(d)) H_2^{2-}

(2) Which of the following compounds of chlorine contains both ionic as well as covalent bonds?

(a) NaCl

(b) $NaClO_4$

(c) PCl_3

(d) $POCl_3$

(3) In PO_4^{3-}, the formal charge on each oxygen atom and P – O bond order respectively are:

(a) - 0.75, 1.25

(b) - 0.75, 1.0

(c) - 0.75, 0.6

(d) - 3, 1.25

(4) On the basis of valence bond theory, the formation of H2 molecules from two H-atoms involves.

(a) The overlap of vacant is orbitals of two H-atom

(b) The lowering of potential energy of the system as the two H-atom come near to each other

(c) The maximum energy of the system at the equilibrium internuclear distance

(d) Stabilisation of the molecule; when the nuclei are brought still closer to each other from the equilibrium inter-nuclear distance.

2. Read the passage given below and answer the following questions:

In order to explain the shapes of molecules adequately, Sidgwick and Powell in 1940 proposed a theory based on the repulsive interaction of the electron pairs in the valence shell of the atoms.

Nyholm and Gillespie (1950) further developed and redefined the concept. The mai postulates of this theory are as follows:

The number of valence shell electron pairs (bonded or non-bonded) present around the central atom decides the shape of the molecules. The shared electron pairs are called bond pairs and unshared or non-bonding electrons are called lone pairs. Electron pairs of valence shell repel one another because their electron clouds are negatively charged.

These electron pairs arrange themselves in such a way so that there is minimum repulsion and maximum distance in between them. The valence shell is considered as a sphere in which the electron pairs are localised on the spherical surface at maximum distance from one another.

A lone pair occupies more space than a bonding pair, since it lies closer to the central atom. This means that the repulsion between the different electron pairs follow the order:

Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

$$(lp - lp) > (lp - bp) > (bp - bp)$$

(1) Which of the following molecule has net dipole moment zero?

(a) HF

(b) H_2O

(c) BF_3

(d) $CHCl_3$

(2) Which one of the following species contains three bond pairs and one lone pair around the central atom?

(a) H_2O

(b) BF_3

(c) NH_2^-

(d) PCl_3

(3) Why do the deviations occur from idealised shape of H_2O and NH_3 molecules?

(a) Same hybridisation

(b) Different hybridisation

(c) Repulsive effect

(d) None of the above

(4) The species, having bond angles of 120° is:

(a) PH_3

(b) ClF_3

(c) NCl_3

(d) BCl_3

Answer Key:

MCQ

1. (a) 0
2. (a) Sp^2
3. (b) Sp and sp^2
4. (c) sp^3, 0
5. (d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
6. (c) Acetonitrile
7. (c) O_2^-
8. (c) Triangular
9. (b) $A_2 B_3$
10. (b) SF_4
11. (c) NaCl
12. (d) Ice
13. (d) NO^+ and CN^+
14. (c) HCl and He atoms
15. (b) sp and sp^2

Very Short Answer:

1. There is a fall in energy.

2. $F_2 < Cl_2 < O_2 < N_2$

3. CH_4: Tetrahedral; C_2H_2: Cylindrical; CO_2: linear

4. Cl < S < N < O <F.

5. SF_4, SF_6.

6. sp^3: CH_4: sp^2: C_2H_4: sp: C_2H_2

7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Answer:

Ans: 1. The dipole moment of CH_3Cl is greater than that of CH_3F. The C-F bond length in CH_3F is smaller than the C-Cl bond length in CH_3Cl. The charge separation in the C-F bond is more than in the Cl-C bond- fluoride being more electronegative than chlorine. The bond length has a greater effect than the charge separation. Hence the dipole moment of CH_3C1 is greater than that of CH_3F.

Ans: 2. The attractive forces which hold the constituent atoms in molecules or species in lattices etc. are called a chemical bond.
They are of the following types:

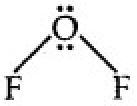
1. Electrovalent or ionic bond
2. Covalent bond
3. Coordinate or dative bond
4. metallic bond
5. hydrogen bond
6. van der Waals forces.

Ans: 3. A covalent bond is formed by the overlap of half-filled atomic orbitals which have definite directions. Hence covalent bond is directional. In ionic compounds, each ion is surrounded by a number of oppositely charged ions and hence there is no definite direction.

Ans: 4. AlF_3 is an ionic solid due to the large difference in electronegativities of Al and F whereas SiF_4 is a covalent compound and hence there are only weak van der Waal's forces among its molecules.

Ans: 5. The electron dot structure of OF_2 is

Or

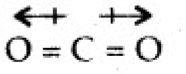


Thus, the central atom (O-atom) has 4 pairs of electrons (2 bond pairs and 2 lone pairs). Hence oxygen in OF_2 is sp^3 hybridized and the molecule is V-shaped oxidation state of F = – 1, oxidation state of O = + 2.

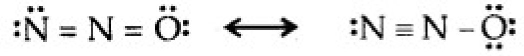
Ans: 6. This is because both N and F are small and hence have high-electron density. So they repel the bond pairs thereby making the N-F bond length larger.

Long Answer:

Ans: 1. N_2O is more polar than CO_2 which is a linear molecule and thus symmetrical. Its net dipole moment is zero.



N_2O is linear but unsymmetrical. It is a resonance hybrid of the following canonical structures:

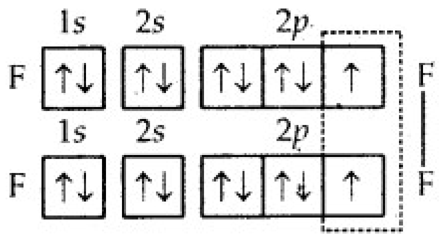


It has a net dipole moment of 0.116 D.

Ans: 2. The bond order of O_2^- is 1.5 while that of O_2^{2-} is 1.0.

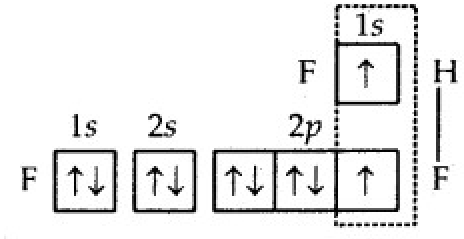
The lesser the bond order, the greater is the bond length as the bond order is inversely proportional to bond length. (Hence O_2^{2-} has a larger bond length than $O_2^{2-.}$

Ans: 3. 1. Formation of F2 molecule. Atomic number (Z) of fluorine is 9 and its orbital electronic configuration is $1s^2$ $2s^2$ $2p^2x$, $2p^2y$, $2p^1z$. Thus, a fluorine atom has one half-filled atomic orbital. Therefore, two atoms of fluorine combine to form the fluorine molecule as a result of the combination for their half-filled atomic orbitals shown in Fig. The two atoms get linked by a single covalent bond

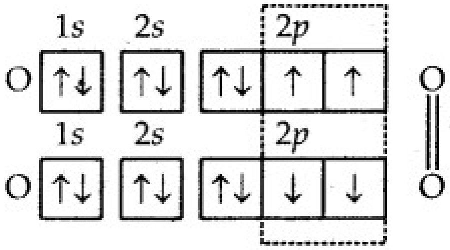


Formation of F_2 molecule

2. Formation of HF molecule. Fluorine atom, as stated above, has one half-filled atomic orbital. Hydrogen atom (Z = 1) has only one electron in Is orbital. Thus, the hydrogen fluoride (HF) molecule. is formed as a result of the combination (or overlap) of the half-filled orbitals belonging to the participating atoms.



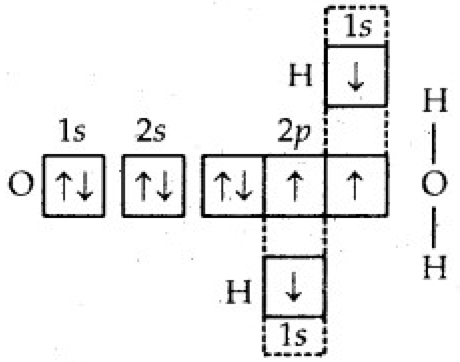
3. Formation of O_2 molecules. The atomic number (Z) of oxygen is 8 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^2x\ 2p^1x\ 2p^1z$. This means that an oxygen atom has two half-filled orbitals with one electron each. Two such atoms will combine to form a molecule of oxygen as a result of the overlap of the half-filled orbitals with opposite spins of electrons.



Formation of O_2 molecule

Thus, the two atoms of oxygen are bonded to each other by two covalent bonds or double bonds (O = O).

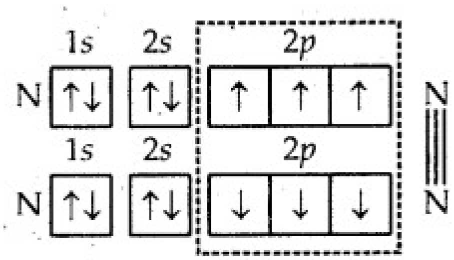
4. Formation of H_2O molecule. In the formation of the H_2O molecule, the two half-filled orbitals of the oxygen atom combine with the half-filled orbitals (1s) of the hydrogen atoms. Thus, the oxygen atom gets linked to the two hydrogen atoms by single covalent bonds as shown in



Formation of H_2O molecule

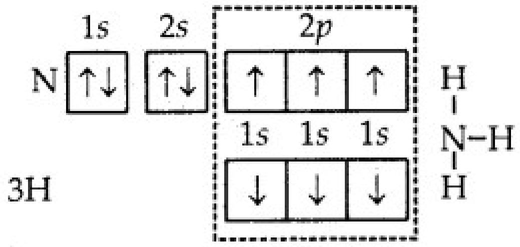
5. Formation of N_2 molecule. The atomic number of nitrogen is 7 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^1x\ 2p^1y\ 2p^1\ z$. This shows that the nitrogen atom has three

half-filled atomic orbitals. Two such atoms combine as a result of the overlap of the three half-filled orbitals and a triple bond gets formed (N = N)



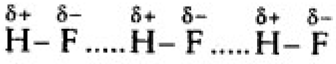
Formation of N_2 molecule

6. Formation of NH_3 molecule. In the formation of ammonia (NH_3) molecule, three half-filled orbitals present in the valence shell of nitrogen atom combine with 1s orbital of three hydrogen atoms with one electron each. As a result, the nitrogen atom completes its octet and a molecule of NH_3 is formed in which the nitrogen atom is linked to three hydrogen atoms by covalent bonds.



Formation of NH_3 molecule

Ans: 4. When hydrogen is connected to small highly electronegative atoms such as F, O, and N in such cases hydrogen forms an electrostatic weak bond with an electronegative atom of the second molecule, this type of bond binds the hydrogen atom of one molecule and the electronegative atom of the 2nd molecule is called as hydrogen bond. It is a weak bond and it is denoted by dotted lines e.g., in HF, hydrogen forms a weak bond with the electronegative F atom of the 2nd molecule neighboring HF.



$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

So it means hydrogen is acting as a bridge between two molecules by one covalent bond and the other by a hydrogen bond. Due to this hydrogen bonding, HF will not exist as a single molecule but it will exist as an associated molecule (HF)n. So hydrogen bond may be defined as a weak electrostatic bond that binds the hydrogen atom of one molecule and electronegative bond atoms (F, O, N) of the second neighboring molecule.

Cause of hydrogen bonding: When a hydrogen atom is bonded to an electronegative atom (say F, O, N) through a covalent bond, due to electronegativity difference, the electronegative atom attracts the shared pair of electrons towards its side with a great force as a result of which the shared pair of electrons will be displaced toward electronegative atom and away from a hydrogen atom.

Due to which hydrogen atom will acquire a slightly negative charge and if another molecule is brought nearer to it in such a way that electronegative atom of the second molecule faces hydrogen atom of the 1st molecule, due to opposite charges present on the atoms, an electrostatic bond will be formed between the hydrogen atom of one molecule and electronegative atom of 2nd molecule and this is called as hydrogen bond.

$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

Conditions for hydrogen bonding. The following two necessary conditions for hydrogen bonding are:

1. Hydrogen atom should be connected to highly electronegative atom say F, O, or N.
2. The electronegative atom of which the hydrogen atom is connected should be the same in size.

The smaller the size of the electronegative atom greater will be the attraction of that atom for shared pair of electrons and hence that pair will be displaced more nearer to that atom and hence that atom will develop greater negative charge and the hydrogen atom will develop a greater positive charge and hence hydrogen atom of this molecule will easily attract negative atom of the Ian molecule and hence a hydrogen bond will be easily formed.

As both these conditions are satisfied only by F, O, N atoms so only three atoms show hydrogen bond.

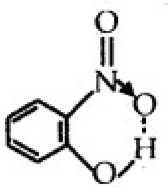
Strength of Hydrogen Bond: A hydrogen bond is a very weak bond. It is weaker than an ionic or a covalent bond. Its strength ranges from 13 kJ mol-1 to 42 kJ mol^{-1}. The strength of the hydrogen bond for some of the molecules is the order H-F H (40 kJ mol-1) > O-H…… O (28 kJ mol^{-1}) > H-N…… H (13 kJ mol^{-1}) whereas the strength of a covalent bond is quite high. For example, the bond strength of the H-H bond in H_2 is 433 kJ mol^{-1}

Types of H-bonding

There are two types of hydrogen-bonds

1. Intermolecular hydrogen bond. It is formed between two different molecules of the same or different compounds. For example H-bond in case of HF, alcohol, or water.

2. Intramolecular Hydrogen bond. It is formed when a hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol, hydrogen is in between the two oxygen atoms.



Assertion Reason Answer:

1. (i) A and R both are correct, and R is the correct explanation of A.
2. (i) A and R both are correct, and R is the correct explanation of A.

Case Study Answer:

1. Answer:

(1) (d)) H_2^{2-}

(2) (b)$NaClO_4$

(3) (a) - 0.75, 1.25

(4) (b) The lowering of potential energy of the system as the two H-atom come near to each other

2. Answer:

(1) (c) BF_3

(2) (d) PCl_3

(3) (c) Repulsive effect

(4) (d) BCl_3