14.

CHEMICAL BONDING

1. INTRODUCTION

A chemical bond consists of an attraction between atoms that allows the formation of chemical substances which contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction.

There are many approaches to understand the bonding in molecules as explained in the following topics.

2. LEWIS DOT DIAGRAM

Lewis postulated that atoms achieve the stable octet (i.e. 8 electrons in their outer most shells), when they are linked by chemical bonds. This can happen (i) by the transfer of electrons(s) from one atom to another, and (ii) by the sharing of a pair of electrons between the atoms. In Lewis Diagrams we represent the outer shell electrons by dots around atom represented by its symbol.

For many common electrons, the number of dots corresponds to the element's group number.

For e.g:

Lewis Diagrams for Molecules: Molecules can be depicted by Lewis Diagrams by placing dots or lines around the constituent elemental symbols. Once again, only valence electrons are shown. Lines denote bonded electron pairs, whereas dots are reserved for only unbound electrons. The following algorithm can be used to construct Lewis diagrams of most molecules.

(a) **Find the total number of electrons:** Determine the total number of valence electrons by reading the group number for each element.

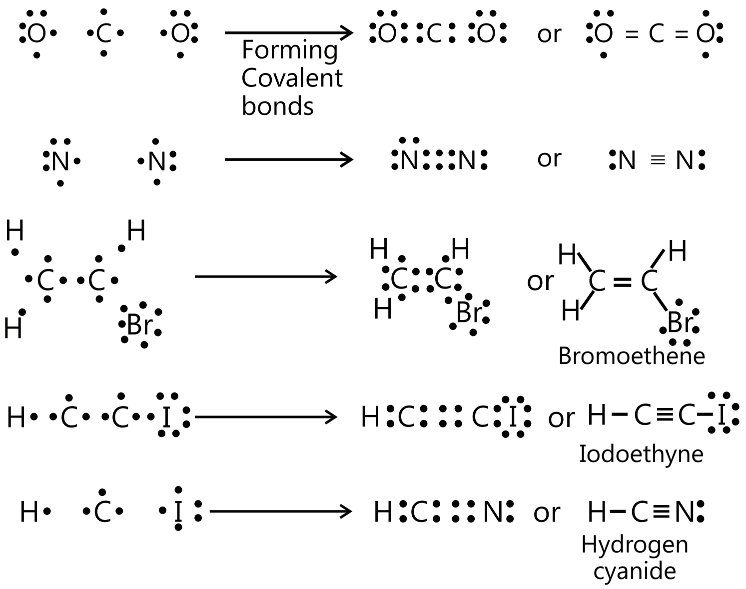
(b) **Draw a first tentative structure:** Frequently the central element is the one with least atoms in the molecule. In your first draft, attach the atoms with single bonds.

(c) **Add electrons as dots to get octets around atoms:** Each atom must have its valence shell completely filled. Remember to count bonds and lone electrons.

(d) **Count the total number of electrons:** Ensure the number of electrons displayed in the symbol agree with the calculation from step 1.

(e) **Cycle through steps 3 and 4:** By way of trial and error, repeat the steps above until a conclusion is reached.

For e.g.



3. BOND PARAMETERS

3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques, about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (figure). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms that are joined by a covalent bond.

(R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively.

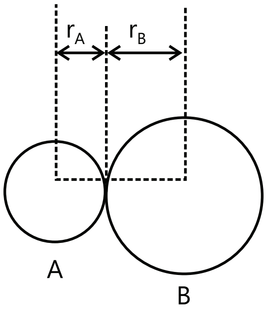
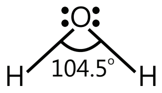


Figure 14.1: Bond length in covalent molecule AB.
$R = r_A + r_B$

3.2 Bond Angle

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 and can be experimentally determined by spectroscopic methods. It gives an idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example $H-O-H$ bond angle in water can be represented as under:



Covalent bond in the same molecule. The van der Waals radius represents the overall size of the atom which includes its valence shell in a non-bonded situation. Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in figure.

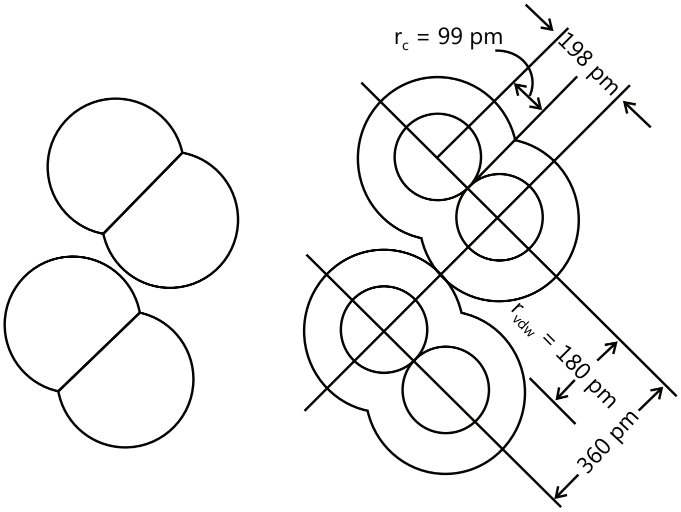


Figure 14.2: Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively)

3.3 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}.

$$H_2(g) \rightarrow H(g) + H(g);\ \Delta_a H^\Theta = 435.8 \text{ kJ mol}^{-1}$$

Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under:

$$O_2(O{=}O)\ (g) \rightarrow 2O(g);\ \Delta_n H^\Theta = 498 \text{ kJ mol}^{-1}$$

$$N_2(N \equiv N)(g) \rightarrow N(g) + N(g);\ \Delta_a H^\Theta = 946.0 \text{ kJ mol}^{-1}$$

It is important to note, that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a hetero-nuclear diatomic molecules like HCl, we have

$$HCl(g) \rightarrow H(g) + Cl(g);\ \Delta_n H^\Theta = 431.0 \text{ kJ mol}^{-1}$$

In case of polyatomic molecules, 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 the same.

3.4 Bond Order

In the Lewis description of a covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1, 2, 3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H^\Theta$ is 946 kJ mol^{-1}; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O^{2-}_2 have bond order 1. N_2, CO and NO^+ have bond order 3.

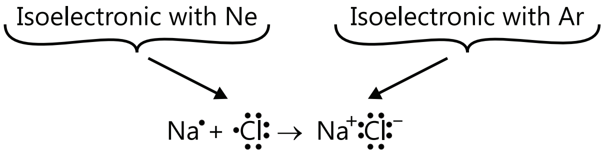
A general correlation useful for understanding the stabilities of molecules is that: with increase in the bond order, the bond enthalpy increases and the bond length decreases.

4. TYPES OF BONDING

4.1 Ionic Bond

The transfer of electrons from one atom to another results in an ionic bond.

An electron transfer that results in an ionic bond is more likely to occur when an atom with a low ionization energy reacts with an atom that has a large electron affinity.



Lewis electron dot formula for the ionic compound NaCl

Figure 14.3 Lewis electron dot formula for the ionic compound NaCl

CONCEPTS

- An ionic bond forms when electrons are transferred from one atom to another. During ionic bonding, the atoms become oppositely charged ions.
- Ionic bonding usually occurs between atoms of metals and atoms of non-metals.
- Energy is needed to remove electrons from metal atoms. Energy is released when most Non- metal atoms gain electrons.
- Ionic compounds form solids by building up a three-dimensional repeating pattern called a crystal lattice.
- Ionic compounds are brittle and highly soluble, with high melting and boiling points.

Vaibhav Krishnan (JEE 2009 AIR 22)

Lattice Energy: How much energy is released when the gaseous ions Na^+ and Cl^- form the ionic solid NaCl ?

$$Na^+(g) + Cl^+(g) \rightarrow NaCl(g) \qquad \Delta H_{1\ at} = ?$$

Where ΔH_{lat} is called the lattice energy:

$Cl^-(g) \rightarrow Cl(g) + e\text{-}$ $\quad \Delta H = -(-EA) = 349\ kJ$

$Cl(g) \rightarrow 1/2\ Cl_2(g)$ $\quad \Delta H = 1/2(-BE) = -121\ kJ$

$Na^+(g) + e^- \rightarrow Na(g)$ $\quad \Delta H = -IE_1 = -494\ kJ$

$Na(g) \rightarrow Na(s)$ $\quad \Delta H = -\Delta H_{sub} = -109\ kJ$

$Na(s) + 1/2Cl_2(g) \rightarrow NaCl(s)$ $\quad \Delta H_f = -411\ kJ$

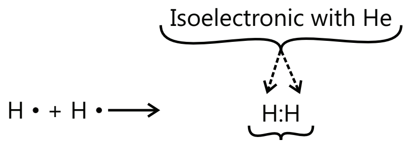
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ $\quad \Delta H_{lat} = -786\ kJ$

Where, EA is the electron affinity for Cl(g), BE is the bond energy for the Cl–Cl bond, IE_1 is the first ionization for Na(g), and ΔH_{sub} is the enthalpy of sublimation.

4.2 Covalent Bond

The sharing of an electron pair results in a covalent bond.

The covalency of an atom is the number of covalent bonds formed by the atom.



Lewis electron dot formula for the covalent compound H_2

Figure 14.4: Covalent bonding in hydrogen molecule

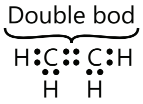
Table 14.1: Valencies of some elements

Element	Common Covalency
H	1
F, Cl, Br, I	1
O, S, Se	2
N, P, As	3
C, Si, Ge	4

4.3 Multiple Bonds

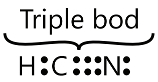
Multiple bonds result from the sharing of more than one pair of electrons by two atoms. Sharing of two pairs of electrons results in a double bond.

Example:



Sol: Each atom satisfies the octet rule and is consistent with the common covalency of the element.

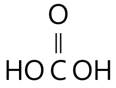
Example:



Generally, only elements in the second period and sulphur form multiple bonds and maintain an octet of electrons.

Illustration 1: Write the Lewis electron dot formula for carbonic acid, $OC(OH)_2$.

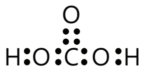
Sol: In these notes the formula $OC(OH)_2$ indicates that the atoms are arranged in the following sequence



$$\overset{\overset{\displaystyle O}{\|}}{HOCOH}$$

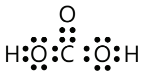
- Number of bonding electrons

$$\sum_{f}^{\text{all atoms}}(\text{octet of electron})S_1-\sum_{f}^{\text{all atoms}}(\text{valence electron})S_1$$



$$= [8_C + 3(8_O) + 2(2_H)] - [4_C + 3(6_O) + 2(1_H)]$$

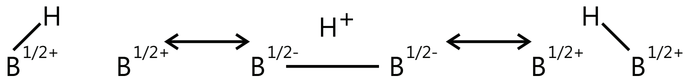
$$= 36 \text{ electrons} - 24 \text{ electrons} = 12 \text{ bonding electrons}$$



- Number of remaining electrons=Total number of valence electrons - number of bonding electrons =24 – 12 = 12 electrons

4.4 Bridge Bonding

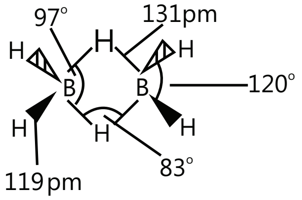
Boron compounds



Resonance structures of 3c-2e bond in diborane.

Three-centre-two-electron bonds are seen in many boron compounds, such as diborane (B_2H_6). The monomer BH_3 is unstable, since the boron atom is only surrounded by six valence electrons, and thus, to form a stable electron configuration closer to an octet, shares electrons with a B−H bond on another boron atom, forming a B−H−B 3-center-2-electron bond. In diborane, there are two such bonds: two H atoms bridge the two B atoms, leaving two additional H atoms in ordinary B−H bonds on each B.

The two electrons (corresponding to one bond) in a B−H−B bonding molecular orbital are spread out across three internuclear spaces. The reported bond order for each B−H interaction is 0.5, so that the bridging B−H bonds are weaker and longer than the terminal B−H bonds, as shown by the bond lengths in the structural diagram.



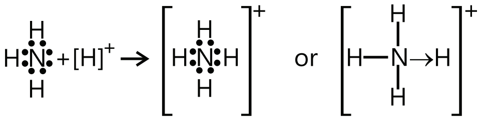
This bonding pattern is also seen in tri methyl aluminium, which forms a dimer $Al_2(CH_3)_6$ with the carbon atoms of two of the methyl groups in bridging positions. This type of bond also occurs in carbon compounds, where it is sometimes referred to as a hyper conjugation; another name for asymmetrical three-centre two-electron bonds.

Subdivision of covalent bonds: There are three types of covalent substances: individual molecules, molecular structures, and macromolecular structures. Individual molecules have strong bonds that hold the atoms together, but there are negligible forces of attraction between molecules. Such covalent substances are usually gases, for example, HCl, SO_2, CO_2, and CH_4. In molecular structures, there are weak forces of attraction. Such covalent substances are low-boiling-temperature liquids (such as ethanol), and low-melting-temperature solids (such as iodine and solid CO_2). Macromolecular structures have a large number of atoms linked in chains or sheets (such as graphite), or in 3-dimensional structures (such as diamond and quartz). These substances have high melting and boiling points, are frequently brittle, and tend to have high electrical resistivity. Elements that have high electronegativity, and the ability to form three or four electron pair bonds, often form such large macromolecular structures.

4.5 Coordinate Bonding

A covalent bond results from the sharing of a pair of electrons between two atoms, where each atom contributes one electron to the bond. It is also possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called coordinate bonds or dative bonds. Since, in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds only in the way they are formed, and once formed they are identical to normal covalent bonds.

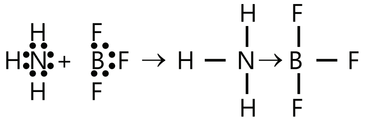
Even though the ammonia molecule has a stable electron configuration, it can react with a hydrogen ion H^+ by donating a share in the lone pair of electrons, forming the ammonium ion NH_4^+ :



$$H:\overset{H}{\underset{H}{\ddot{N}}}: + [H]^+ \rightarrow \left[H:\overset{H}{\underset{H}{\ddot{N}}}:H\right]^+ \text{ or } \left[H-\overset{H}{\underset{H}{N}}\rightarrow H\right]^+$$

Covalent bonds are usually shown as straight lines joining the two atoms, and coordinate bond as arrows indicating which atom is donating the electrons. Similarly, ammonia may donate its lone pair to boron trifluoride, and through this means the boron atom attains a share in eight electrons:

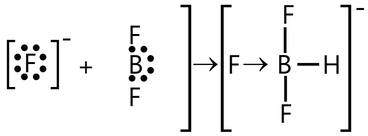
In a similar way, a molecule of BF_3 can form a coordinate bond by accepting a share in a lone pair from a F^- ion.



There are many other examples, including:

$PCl_5 + Cl^- \rightarrow [PCl_6]^-$

$SbF_5 + F^- \rightarrow [SbF_6]^-$



4.6 Metallic Bond

Metals are made up of positive ions packed together, usually in one of the three following arrangements:

1. Cubic close-packed (also called cafe-centered cubic).
2. Hexagonal close-packed.
3. Body-centered cubic.

Negatively charged electrons hold the ions together. The number of positive and negative charges is exactly balanced, as the electrons originated from the neutral metal atoms. The outstanding feature of metals is their extremely high electrical conductivity and thermal conductivity, both of which are because of the mobility of these electrons through the lattice.

5. POLAR COVALENT BONDS, ELECTRONEGATIVITY, AND OXIDATION NUMBERS

5.1 Polar Covalent Bonds

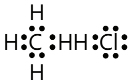
$$H:H \quad H_3C:CH_3 \quad \frac{\text{Bond Type}}{\text{Non polar Covalent}}$$

$H:\ddot{\underset{\cdot\cdot}{Cl}}:$ $\quad H^+{}_3C:CCl_3$ Polar Covalent

The fractional charge, d, is the charge that results from the unequal sharing of electrons. In heteronuclear bonds, one of the bonding atoms attracts the bonding pair of electrons more strongly than the other bonding atom. The numerical value of d is the fraction of the charge (4.80x 10^{-10} esu) on an electron.

The unequal sharing of an electron pair results in a polar covalent bond.

Table 14.2: Different types of bond and characteristics

Increasing Bond Polarity ⟶			
Type	**Nonpolar**	**Polar Covalent**	**Ionic**
Example	H : H	 $H:\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{C}}}}:H \quad H:\ddot{\underset{\cdot\cdot}{Cl}}:$	$Na^+,[:\ddot{\underset{\cdot\cdot}{Cl}}:]$
d	0	0.07 0.17	1.00
$\Delta\chi = \chi_B - \chi_A$	0	0.30 0.74	2.21

6. ELECTRONEGATIVITY

Electronegativity, χ, is a measure of the relative tendency of a bonded atom to attract electrons. The electronegativity of an atom is not experimentally measured, but calculated from bond energies, ionization energies, and electron affinities.

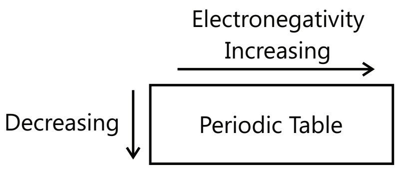


Figure 14.5: Trends of electronegativity in the periodic table

A rough approximation of Bond Type for AB Based on Δ_x

$\Delta_x = \chi_B - \chi_A$	Bond Type
≥ 1.7	Ionic
<1.7	Polar covalent
0	Nonpolar covalent

7. OXIDATION NUMBER

The oxidation number (oxid. No.) of an atom, is the number of valence electrons on the neutral atom minus the number of valence electrons assigned to the atom in the compound on the basis that the bonding electrons belong to the more electronegative atom.

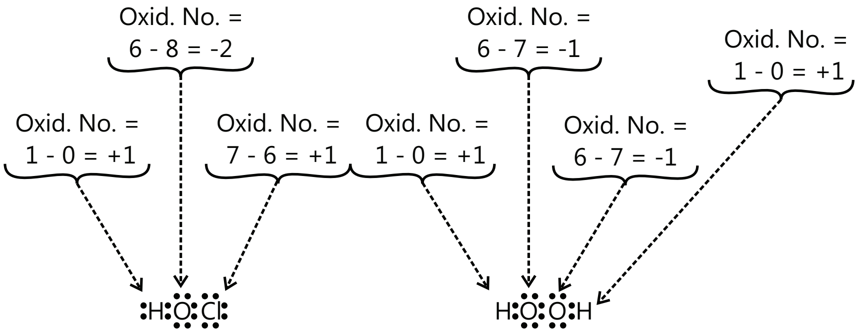


Figure 14.6: Illustration of oxidation number

8. DIPOLE MOMENTS AND POLARITY

8.1. Bond Dipole

An electric dipole is a positive charge, q, and a negative charge, q, of equal magnitude that are separated by a distance, r.

The dipole moment, μ, is $\mu = qr$

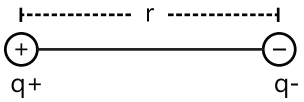


Figure 14.7: Electrical dipole

where, q is the magnitude of the charge in esu (electrostatic units) and r is the distance between the positive and negative charges in centimeter.

Note: A polar covalent bond is a dipole and has a dipole moment.

Illustration 2: Calculate the dipole moment, μ_{hu} for HCl. The magnitude of the fraction charge d, is 0.17 and the bond distance, r_{HCl}, is 1.27 Å.

Sol: $q = d(4.80.10^{-10}\text{esu}) = (0.17)\,(4.80\cdot 10^{-10}\ \text{esu}) = 8.\overline{16} \times 10^{-11}\text{esu}$

$$\mu_{HCl} = qr = (8.\overline{16}.10^{-11}\,\text{esu})\left(1.27\ \text{Å}\right)\left(1.10^{-8}\,\frac{\text{cm}}{\text{Å}}\right) = 1.\overline{03} \times 10^{-18}\text{esu} - \text{cm}$$

1D = 1Debye = 1.10^{-18} esu–cm

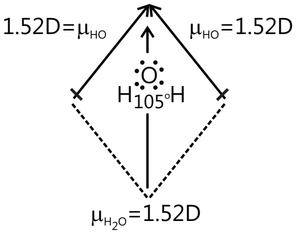
$$\mu_{HCl} = \left(1.\overline{03}.10^{-18}\,\text{esu}-\text{cm}\right)\left(\frac{1\text{D}}{10^{-18}\,\text{esu}-\text{cm}}\right) = \left(1.\overline{03}\text{D}\right)$$

The magnitude and direction of the dipole moment is represented by the vector, $+\!\!\rightarrow$

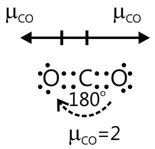
8.2. Molecular Dipole

The dipole moment for a molecule is the resultant dipole moment obtained from the vector sum of the individual bond dipole moments. Molecules that have a dipole moment are said to be polar. Molecules with μ= 0 are said to be nonpolar.

Example



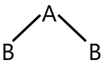
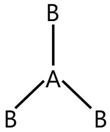
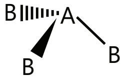
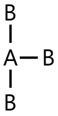
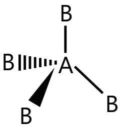
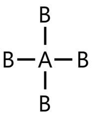
H_2O is polar molecule

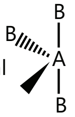
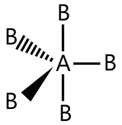
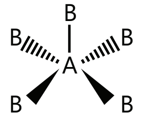
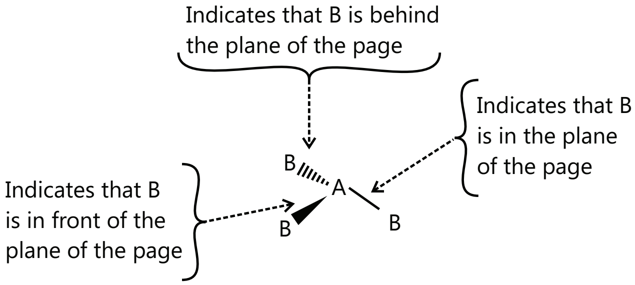
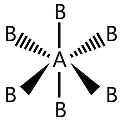


CO_2 is non polar molecule

The polarity of a molecule depends on its bond dipole moments and molecular geometry.

Table 14.3: Molecular Geometries and Polarities

Formula	Molecular Geometry	Polarity	Example (Exception)
AB	linear A — B	Polar	HCl
AB_2	Linear B—A—B	Nonpolar	CO_2(HCN)
AB_2	Bent 	Polar	H_2O
AB_3	Trigonal planar 	Nonpolar	$BF_3(FBCl_2)$
AB_3	Trigonal pyramidal 	Polar	NH_3
AB_3	T-shaped 	Polar	ClF_3
AB_4	Tetrahedral 	Nonpolar	$CH_4(HCCl_3)$
AB_4	Square planar 	Nonpolar	XeF_4

Formula	Molecular Geometry	Polarity	Example (Exception)
AB_4	Distorted tetrahedral 	Polar	SF_4
AB_5	Trigonal bipyramidal 	Polar	PF_5 (F_3PCl_2)
AB_5	Square pyramidal 	Polar	BrF_5
			
AB_6	Octahedral 	Nonpolar	SF_6

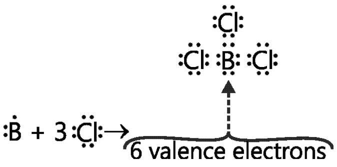
* Valid when the bonds are covalent, $\chi_B \neq \chi_A$ and all AB bonds in the nonpolar cases are identical in all respects, i.e. the same bond energies and bond lengths.

9. EXCEPTIONS TO THE OCTET RULE

9.1 Less than an Octet of Electrons

Atoms that have less than four valence electrons and form covalent bonds may not satisfy the octet rule.

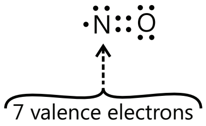
Example: BCl_3



9.2 Free Radicals

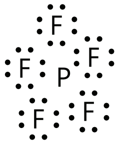
Free radicals are compounds with one or more unpaired electrons.

Example: NO.



9.3 More than an Octet of Electrons

Example: PF_5



The phosphorus atom in PF_5 has ten valence electrons.

Atoms in the second period never exceed on octet of electrons.

9.4 Ions of the Transition and Post-Transition Metals

Example: Cr^{3+} is not isoelectronic with Ar.

Cr^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$; Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$

9.5 Method for the Determination of Lewis Electron Dot Formula for Covalent Compounds

When the central atom is in the third, fourth, etc. period, determine the total number of valence electrons and distribute them as follows.

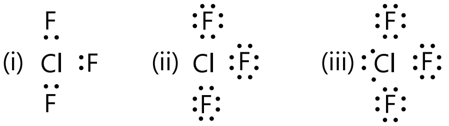
(a) Place two electrons between each bonding pair of atoms.

(b) Place sufficient electrons around each terminal atom so that the terminal atoms satisfy the octet rule.

(c) Assign the remaining valence electrons to the central atom.

Example : ClF_3

Total number of valence electrons = $7_{Cl} + 3(7_F) = 28$ valence electrons



Twenty-four of the twenty-eight valence electrons are displayed in (ii). Four valence electrons remain and these electrons are assigned to the central atom in (iii).

10. NO MOLECULE (IMPORTANT)

In NO molecule, nitrogen contains 5 electrons in outermost shell and oxygen 6. Now oxygen gives 2 electrons for bonding and now nitrogen has 3 electrons for bonding out of which 2 of them form complete bond with oxygen while the odd electron just wanders, contributing partially to the bond. Hence, NO has 2.5 bond order.

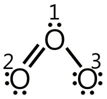
11. FORMAL CHARGE

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom.

It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as:

Formal charge (F.C.) On an atom in a Lewis Structure	=	$\begin{bmatrix}\text{Total number of valence}\\ \text{electron in the free atom}\end{bmatrix} - \begin{bmatrix}\text{Total number nonbonding}\\ \text{(lonepair) electrons}\end{bmatrix}$ $-(1/2)\begin{bmatrix}\text{Total number of}\\ \text{bonding (shared) electrons}\end{bmatrix}$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3, may be drawn as:



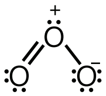
The atoms have been numbered as 1.2 and 3. The formal charge on.

The central O atom marked 1 = $6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 = $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows:



CONCEPTS

It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally, the lowest energy structure is the one with the smallest formal charges on the atoms.

Misconception: The formal charge is a factor based on a pure covalent view of bonding and not ionic. Hence, never apply this concept on ionic compounds where electron pairs are equally shared by neighboring atoms.

Aman Gour (JEE 2012, AIR 230)

12. HYDROLYSIS

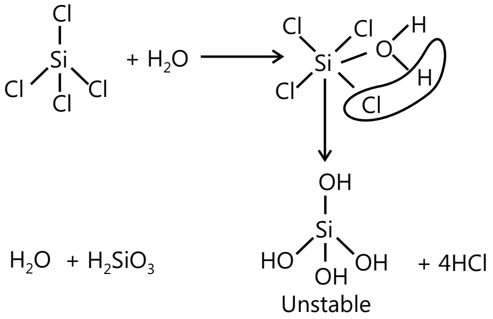
Hydrolysis means a reaction with water molecules ultimately leading to the breaking of O–H bond into H^+ and OH^- ions. While the term hydration means the surrounding of polar molecule or ions by polar molecules of water. In hydrolysis, there is a complex formation with a water molecule or reaction with a water molecule.

Hydrolysis in covalent compounds takes place generally by two mechanisms:

(a) By Coordinate bond formation. Generally in halides of atoms having vacant d-orbitals or of halides of atoms having vacant orbits.

(b) By H-bond formation: For example in nitrogen trihalides.

(a) Hydrolysis via coordinate bond formation: Hydrolysis of $SiCl_4$ (due to presence of vacant d-orbitals on silicon)



(b) By H-bond formation: Hydrolysis of NCl_3(N has no vacant orbitals). By a similar mechanism there will be hydrolysis of NBr_3 and NI_3, but NF_3 does not undergo hydrolysis mainly because it is a polar molecule and also the hydrolysis product FOH is an unstable compound.

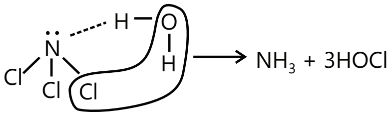
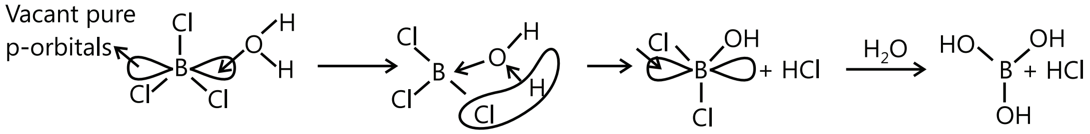


Illustration 3: Explain the hydrolysis in BCl_3 and BF_3.

Sol:



$BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HF$

But the HF produced will react with the reactant BF_3 to form BF_4^- ion

$BF_3 + HF \rightarrow H^+ [BF_4]^-$;

hydrogen tetrafluoroborate (III) (stable species)

13. COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE)

When an anion and cation approach each other, the valence shell of the anion is pulled towards the cation's nucleus and thus the shape of anion gets deformed. This phenomenon of deformation of an anion by a cation is known as polarisation, and the ability of a cation to polarize a nearby anion is called as the polarizing power of the cation.

Fajan's rule points out that greater the polarization of an anion in a molecule, the more covalent it is of character..

CONCEPTS

More the distortion of anion, more the polarization and covalent character will increase.

Vaibhav Krishnan (JEE 2009, AIR 22)

Fajan gives some rules which govern the covalent character in the ionic compounds, which are as follows:

(a) Size of cation: Smaller the cation, more is its polarizing power and thus more will be the polarization of an anion. Hence, greater will be the covalent character of the compound.

Sizer of cation α (1/polarisation)

e.g. $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$

$\longrightarrow$

Size of cation increases Polarisation decreases Covalent character decreases

(b) Size of anion: Larger the anion, greater is its polarisability and, therefore, more will be the polarization. Thus, greater will be the covalent character in the compound.

Size on anion α polarisation

e.g. LiF LiCl LiBr LiI

$\longrightarrow$

-Size of anion increases
-Polarisation increases
-Covalent character increases

(c) Charge on cation: Higher the oxidation state of the cation, more will be the deformation of anion and thus, greater will be the covalent character in the compound.

(d) Charge on anion: Higher the charge on the anion, more will be the polarisation of anion and thus, greater will be the covalent character in the compound.

Charge on cation α polarisation

e.g. NaCl $MgCl_2$ $AlCl_3$

Na^+ Mg^{2-} Al^{3+}

$\longrightarrow$

-Charge of cation increases
-Polarisation increases
-Covalent character increases

Charge on anion $\propto$ polarisation

e.g. AlF_3 Al_2O_3 AlN

F^- O^{2-} N^{-3}

$\longrightarrow$

-Charge of anion increases
-Polarisation increases
-Covalent character increases

(e) Pseudo inert gas configuration of cation: A cation having pseudo inert gas configuration has more polarizing power than a cation with inert gas configuration. Thus, NaCl having inert gas configuration will be more ionic, whereas CuCl having a pseudo inert gas configuration will be more covalent by nature.

Charge on cation $\propto$ polarization.

Cu^+ = [Ne] $3s^2$ $3p^6$ $3d^{10}$	Na^+ = $1s^2$ $2s^2$ p^6
$18e^-$	$8e^-$
Pseudo inert gas configuration	Inert gas configuration
(Poor shielding of d-electrons)	(More shielding of s and p electrons)

13.1 Application and Exceptions of Fajan Rule

(i) Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.

(ii) $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water because Fe^{3+} is smaller than Fe^{2+} and thus charge is more. Therefore, $Fe(OH)_2$ is more covalent than $Fe(OH)_2$.

(iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

For example:

AgCl is white AgBr, AgI, Ag_2CO_3 are yellow. Similarly, $SnCl_2$is white but SnI_2 is black, $PbCl_2$ is white but PbI_2 is yellow.

The bigger anions are more polarised and hence their electrons get excited by the partial absorption of visible light.

(iv) Variation of melting point [melting point of covalent compound < melting point of ionic compound]:

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

$\longrightarrow$

Ionic character increases, melting point increases; since size of cation increases and size of anions is constant.

CaF_2, $CaCl_2$, $CaBr_2$, CaI_2

$\longrightarrow$

Covalent character increases, melting point decreases; since size of anions increases and size of cations is constant.

Illustration 4: Explain why AgCl is colourless whereas AgI is yellow.

Sol: The bigger anions are more polarized and hence their electrons get excited by the partial absorption of visible light. AgCl is colourless whereas AgI is yellow, because of:

(A) Ag^+ has 18 electron shell to screen the nuclear charge.

(B) Ag^+- shows pseudo inert gas configuration.

(C) Distortion of I^- is more pronounced than Cl^- ion.

(D) Existence of d-d transition.

14. THEORIES OF BONDING

Lewis approach helps in writing the structure of molecules, but it fails to explain the formation of a chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 (435.8 kJ mol^-, 74 pm) and F_2(150.6 kJ mol^-, 42 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly, the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

14.1 Valence Bond Theory (Modern Concept of Covalent Bond)

Introduced by Heitler and London (1927) and developed further by Pauling and others, discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configuration of elements, the overlapping criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at a large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between:

(a) Nucleus of one atom and its own electron i.e., $N_A - e_A$ and $N_B - e_B$

(b) Nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

Similarly repulsive forces arise between:

(a) Electrons of two atoms like $e_A - e_B$

(b) Nuclei of two atoms $N_A - N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 14.8)

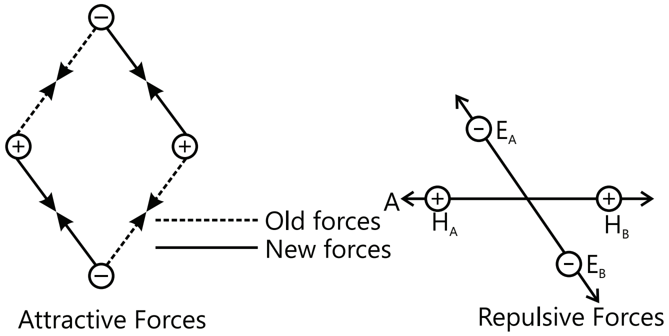


Figure 14.8: Force of attraction and repulsion during the formation of H_2 molecule

Experimentally, it has been found that the magnitude of new attractive forces is more than the new repulsive forces. As a result, two atoms approach each other and the potential energy decreases. Ultimately, a stage is reached where the net force of attraction balances the force of repulsion and the system acquires minimum energy. At this stage, two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

$H_2(g) + 435.8\ kJ\ mol^- \rightarrow H(g) + H(g)$

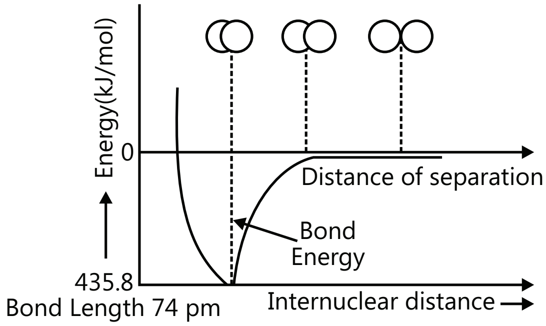


Figure 14.7: The potential energy curve forth formation of H_2 molecule as a function of intermolecular distance of H atoms. The minimum in the curve corresponds to the most stable state of H_2

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in figure. Conversely 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

Orbital Overlap Concept: In the formation of hydrogen molecule there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals, which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap, the stronger is the bond formed between two atoms. Therefore, according to the orbital overlap concept, the formation of a covalent bond between two atoms results by the pairing of electrons present in the valence shell having opposite spins.

Directional Properties of Bonds: The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

Overlapping of Atomic Orbitals: When two atoms come close to each other there is an overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in the given figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4, NH_3 and H_2O, the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral, pyramidal and bent respectively.

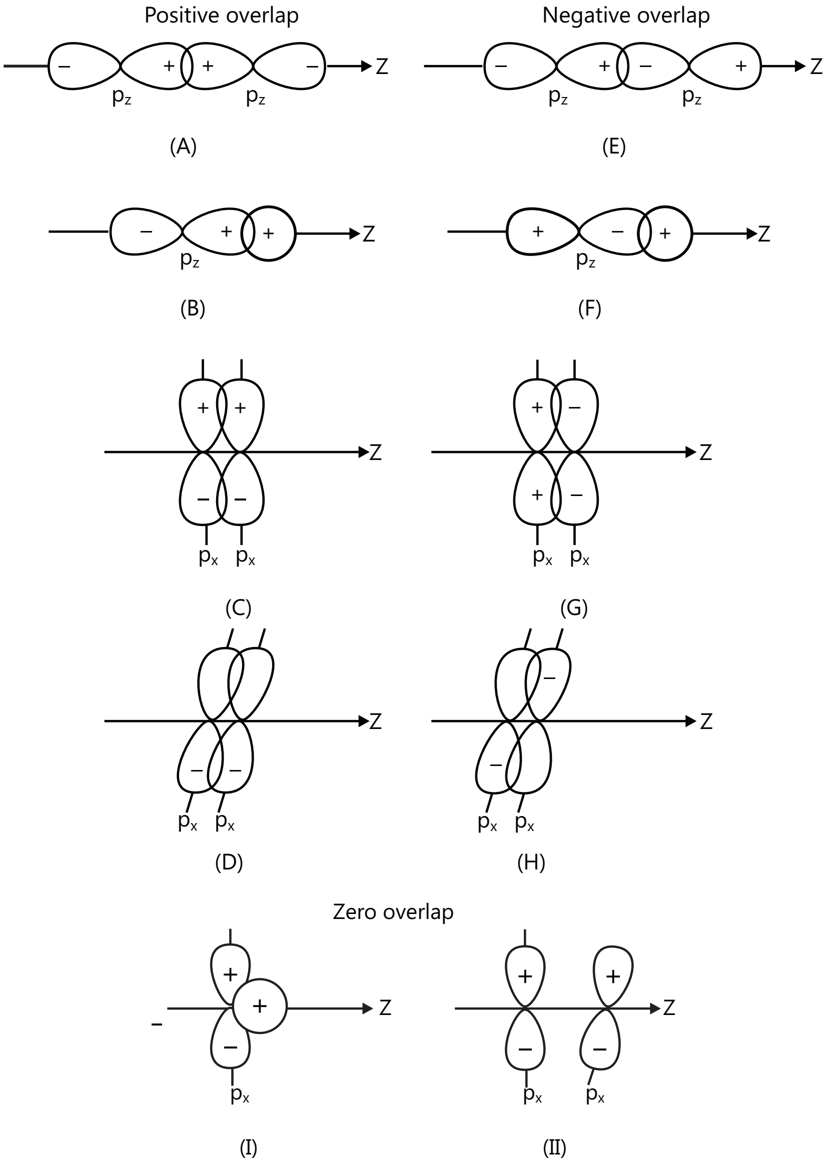


Figure 14.8(a): Positive, Negative and zero overlaps of s and p atomic orbital

Types of overlapping and nature of covalent bonds: The covalent bond may be classified into two types depending upon the types of overlapping: (i) Sigma (σ) bond, and (ii) pi (π) bond

(a) Sigma(σ)bond: This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the internuclear axis. This is called the head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

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

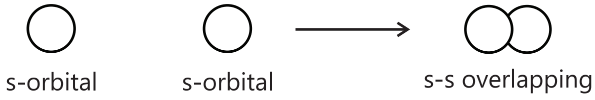


Figure 14.8(b): s-s overlapping

s-p overlapping: This type of overlap occurs between half-filled s-orbitals of one atom and half-filled p-orbitals of another atom.

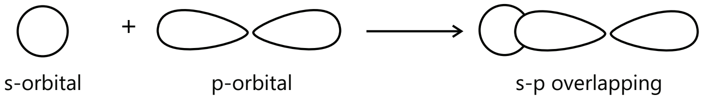
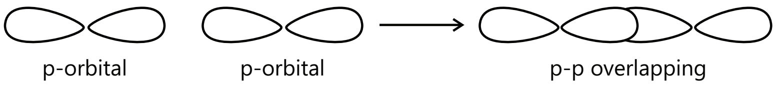


Figure 14.8 (c): s-p overlapping



p-p overlapping: This type of overlap takes place between half-filled p-orbitals of the two approaching atoms.

(b) **Pi (π) bond:** In the formation of π bond, the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals are formed due to sideways overlapping, and consists of two saucer type charged clouds above and below the plane of the participating atoms.

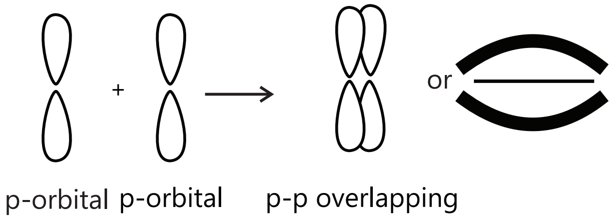
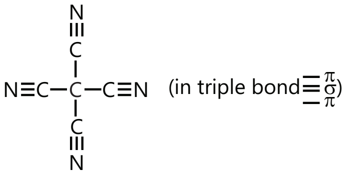


Figure 14.8 (d): p-p overlapping

Strength of Sigma and pi Bonds: Basically, the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that a pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Illustration 5: What are the total number of σ and π bonds in tetracyanomethane.



Sol: From the structure it is clear that it has 8σ and 8π bonds.

CONCEPTS

Bent's rule: In a molecule, smaller bond angles are formed between electronegative ligands, since the central atom to which the ligands are attached tend to direct bonding hybrid orbitals of greater p character towards its more electronegative substituents.

Reason: The rule states :"Atomic s character tends to concentrate in orbitals that are directed toward electropositive groups and atomic p character tends to concentrate in orbitals that are directed toward electronegative groups". Bent based his rule on the perturbation theory, and suggested that isovalent orbital hybridization should transfer more s character to the more electropositive bonding orbital to maximize bonding energy, hybrid orbitals for main group elements consist of one s and three p orbitals, with the s orbital having lower energy. To have more s character means that the bonding orbital is lower in energy and shaped more like an s orbital rather than a p orbital. In other words, ligand orbitals tend to be rich in p character because of higher electronegativity, with s character concentrated on the central metal. However, in cases where the metal has a lone pair, the lone pair orbital is high in s character. This is because s orbitals are closer to the nucleus, allowing for greater stabilization of the lone pair.

Nikhil Khandelwal (JEE 2009, AIR 94)

14.2 Valence Shell Electron Pair Repulsion (VSEPR) Theory

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows:

(a) The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.

(b) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

(c) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

(d) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

(e) 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.

(f) When two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order:

lone pair (ℓp)-lone pair(ℓp) > lone pair (p)-bond pair(bp) > bond pair (bp)-bond pair(bp)

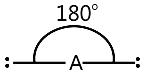
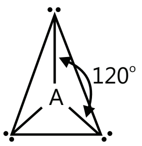
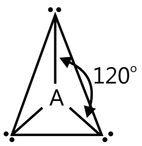
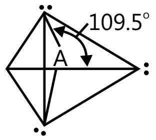
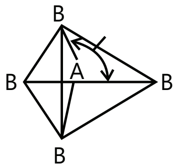
CONCEPTS

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localized on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs, electrons as compared to the lone pair-bond pair and bond pair-bond pair repulsions. These repulsion effects result in deviations from idealized shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair, and (ii) molecules in which the central atom / ion has one or more lone pairs.

Rohit Kumar (JEE 2012, AIR 79)

Table 14.4: Shape (molecular geometry) of some simple molecules / ions with central atom / ion having no lone pairs of electrons (E)

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
2	 Linear	B – A – B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+

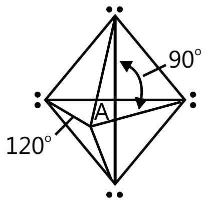
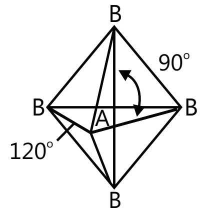
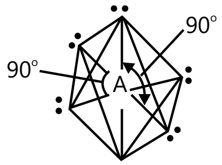
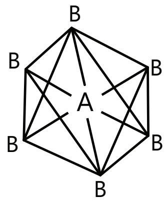
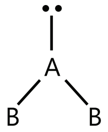
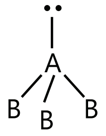
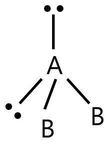
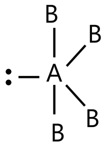
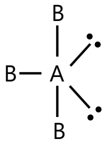
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
5	 Trigonal bipyamidal	 Trigonal bipyamidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

Table 14.5: Electron pair geometries of some simple molecules

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement electron pairs of	Shape	Examples
AB_1E	2	1		Bent	SO_2, O_3
AB_1E	3	1		Trigonal pyramidal	NH_3
AB_2E_2	2	2		Bent	H_2O
AB_4E	4	1		See saw	SF_4
AB_3E_2	3	2		T-shape	ClF_3

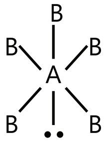
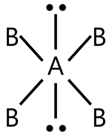
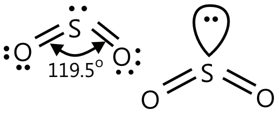
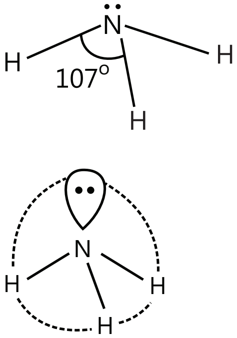
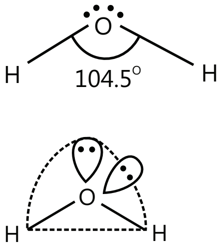
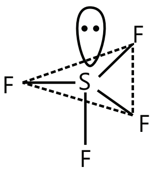
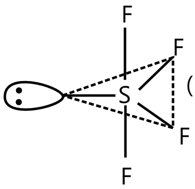
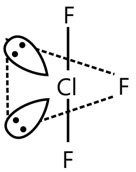
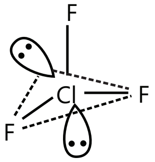
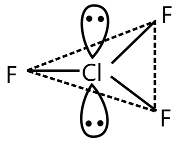
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement electron pairs of	Shape	Examples
AB_5E	5	1		Square pyramidal	BrF_5
AB_4E_2	4	2		Square planar	XeF_4

Table 14.6: Molecular shape of some simple compounds

Molecule type	No.of bonding pairs	No. of lone pairs		Shape	Reason for the shape acquired
AB_2E	4	1		Bent	It is found to be bent or v-shaped. The reason being the lone pair- bond pair repulsion is much more as compared to the bond pair - bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB_3E	3	1		Trigonal pyramidal	It is found to be trigonal pyramidal due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° to 109.5°
AB_2E_2	2	2		Bent	The shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°

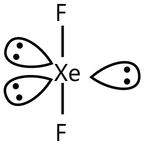
Molecule type	No.of bonding pairs	No. of lone pairs		Shape	Reason for the shape acquired
AB_4E	4	1	(i)  (ii)  (More Stable)	See saw	In (i) the lp is present at axial position so there are three lp-bp repulsion at 90º. In (ii) the lp is an equatorial position and there are two lp-bp repulsion. Hence, arrangement (ii) is more stable. The shape shown in (ii) is called as a distorted tetrahedron, a folded square or a see-saw.
AB_3E_2	3	2	(i)  (ii)  (iii) 	T-shape	In (i) the lone pairs are at equatorial position (120º), so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (i) is most stable. (T shaped)

The VSEPR Theory is able to predict the geometry of a large number of molecules, especially the compounds of p-block elements accurately.

Illustration 6: Use the VSEPR model to predict the geometry of the following (a) XeF_2 (b) ClO_3^-

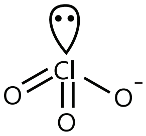
Sol:

(a) XeF_2



Lone pairs occupy the equatorial positions to have minimum repulsion. Thus it is linear.

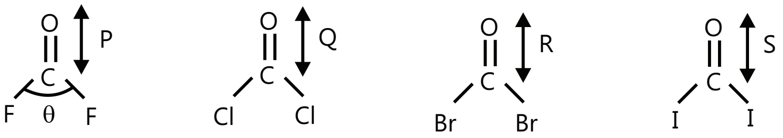
(b) ClO_3–



To minimize the repulsion between lone pair and double bond, species acquires trigonal pyramidal.

Illustration 7: Discuss the bond angle in carbonyl halides COF_2, $COCl_2$, $COBr_2$, COI_2

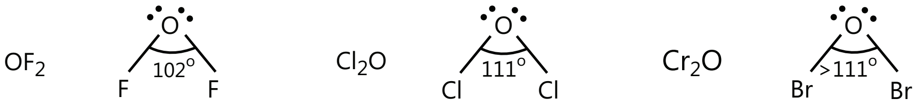
Sol: Extent of electronegativity and the steric crowding of the large halogen atoms contributes in the increasing bond angles.



Double bonds require more room than single bonds. Hence, C = O group compresses the molecule and bond angle decreases maximum in COF_2 ,as bond pairs of electrons are closer to fluorine atoms because of high electronegativity of fluorine. As the size of halogen atoms increase and their electronegativity decreases repulsion between bond pairs increases and therefore θ increases.

Illustration 8: Compare bond angle of OF_2, Cl_2O and Br_2O.

Sol: Extent of electronegativity and the steric crowding of the large halogen atoms contributes in the increasing bond angles.



Bond pair electrons are closer to the fluorine atoms (because of high electronegativity of fluorine). So the lp-lp repulsion is more than bp-bp. Thus the F—O—F bond angle decreases to 102º from 109.5º. In Cl_2O, the bond pair are closer to the oxygen atom because of the high electronegativity of oxygen. So the bp-bp repulsion is more than lp-lp. Thus, the bond angle Cl—O—Cl increases to 111º due to bp-bp repulsion and repulsion between larger Cl atoms.

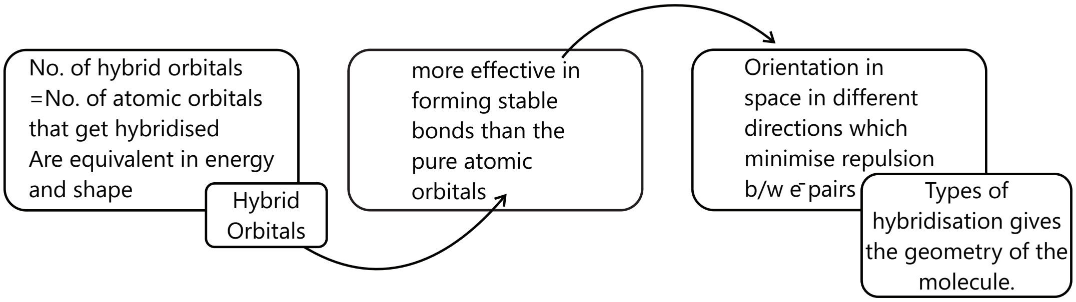
Note : The steric crowding of the large halogen atoms also contributes in the increasing bond angles.

15. HYBRIDISATION

Valence bond theory (overlapping concept) explains the formation of various molecules but it fails to account for geometry and shapes of various molecules. In order to explain the cases of linear $BeCl_2$,planar BF_3 and other such structures, the VBT has been supplemented by the concept of hybridization. This is a hypothetical concept and was introduced by Pauling and Slater.

According to them, the atomic orbitals combine to form a new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation, which can be defined as the process of intermixing of the orbitals of slightly different energies in the formation of a new set of orbitals of equivalent energies and shape.

For example, when one 2s and three 2p-orbitals of carbon hybridise, there is a formation of four new sp^3 hybrid orbitals.



Flowchart 14.1: Salient features of hybridisation

CONCEPTS

Drago’s rule: For any Group in general, the formula for calculating the number of hybrid orbitals in a group is the number of the central element + no. of atoms surrounding the central element (except oxygen) - charge on the central element (consider the charge including its sign) whole divided by 2.

Aman Gour (JEE 2012, AIR 230)

Important conditions for hybridisation:

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridization should have almost equal energy.

(iii) Promotion of electron is not an essential condition prior to hybridization.

(iv) It is the orbital that undergoes hybridization and not the electrons. For example, for orbitals of N atom ($2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) belonging to valence shell, when hybridized to form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each, it is not necessary that only half filled orbitals participate in hybridization. In some cases, even fully filled orbitals of the valence shell take part in hybridization.

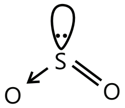
Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie):

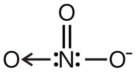
Steric no. of an atom = Number of the atom bonded with that atom + Number of lone pair(s) left on that atom.

Note: This rule in not applicable to molecules/ions which have odd e$^-$ (ClO_2, NO, NO_2), free radicals and compounds like B_2H_2, which involve 3 centre 2e$^-$ bond (banana bond).

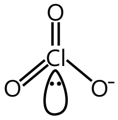
For example: O=C=O S.No. = 2+0=2



S.No. = 2+1=3



S.No. = 3+0=3



S.No. = 2+1=3

Table 14.7: Determination of hybridisation of an atom using steric number

Steric number	Types of Hybridisation	Geometry
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
7	sp^3d^3	Pentagonal bipyramidal

15.1 Types of Hybridisation

(a) **sp hybridisation:** Mixing of one s+one p=Two sp hybrid orbitals. Each sp hybrid orbital has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation. The two sp hybrids point in the opposite direction along the Z-axis with projecting bigger positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of a molecule having sp hybridisation

$BeCl_2$: The ground state electronic configuration of Be is $1s^2\ 2s^2$. In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its divalency. Once 2s and 2p-orbitals get hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and forms two Be-Cl sigma bonds.

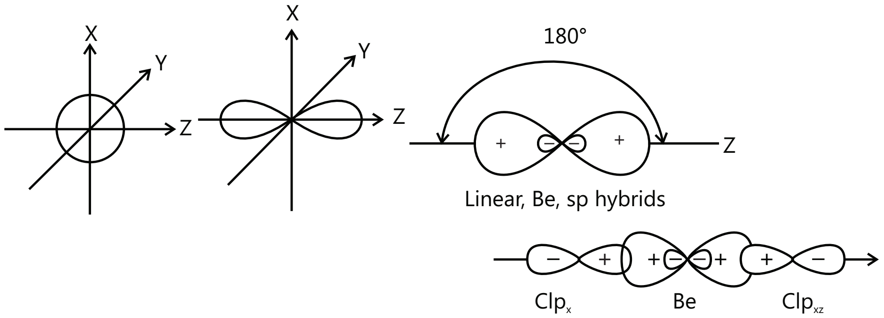


Figure 14.9: Figure (A) formation of sp hybrids from s and p orbitals; (B) Formation of the linear $BeCl_2$ molecule.

More examples of sp hybridisation:

(a) $C \equiv N$, $H - C \equiv C - H$

(b) $H_2C = C = CH_2$

(c) N_3^- (azide ion), BeF_2, $HgCl_2$, NO_2– (nitronium ion), N_2O

Note: In N_3^- there is a total of two σ and two π bonds giving N = N = N and a bond order of two. Both N – N bonds are of the same length, 1.16 Å. The hydrogen azide molecules have a bent structure and two N–N bond lengths are different.

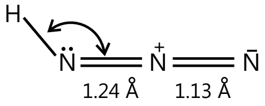


Illustration 9: Which is linear PH_4^+, H_3S^+ or NO_2^+ ?

(A) Phosphonium ion (PH_4^+) (B) Sulphonium (H_3S^+) (C) Nitronium ion (NO_2^+) (D) None of these

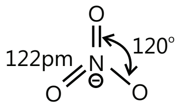
Sol: Phosphonium ion (PH_4^+) is tetrahedral, sulphonium $(H_3S)^+$ is pyramidal, but nitronium ion

(NO_2^+) is linear ; $O = \overset{\oplus}{N} = O$ (sp hybridisation) **Ans.** (C)

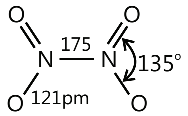
Illustration 10: The ONO angle is maximum in

(A) NO_3^- (B) NO_2^+ (C) N_2O_4 (D) NO_2

Sol:

(A)


(B) $O = \overset{+}{N} = O$ Bond angle is 180° because of sp hybridisation of nitrogen
115pm

(C)


(D)


(b) **sp^2 hybridisation :** Mixing of one s+two p=Three sp^2 hybrid orbitals. For example, in BCl_3 molecule, the ground state electronic configuration of central B(boron) atom is $1s^2\ 2s^2\ 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital. As a result, boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B–Cl bonds. Therefore, in BCl_3, the geometry is trigonal planar with ClBCl bond angle of 120º.

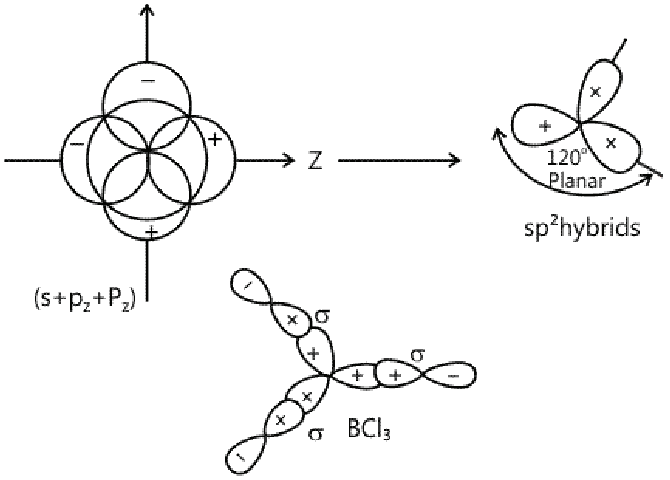


Figure 14.10: Formation of sp^2 hydrids and then BCl_3 molecule steric no-3, Geometry=Trigonal planar, Ideal bond angle=120°

Table 14.8: Examples of molecules showing sp^2 hybridisation

Shape	Trigonal	V-shaped (bent)
Example	$\rangle C = \overset{+}{C}H_3.\overset{\bullet}{C}H_3$ C_6H_6, CO_3^{2-}, HCO_3^- H_2CO_3, graphite, BF_3 $B(OH)_3$, SO_3, NO_3^- C_{60} (Fulleraene)	$-\ddot{C}-$, SO_2, $SnCl_2$ NOCl, O_3, NO_3 NO_2^-

(c) **sp^3 hybridisation:** This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbitals of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5º as shown in figure.

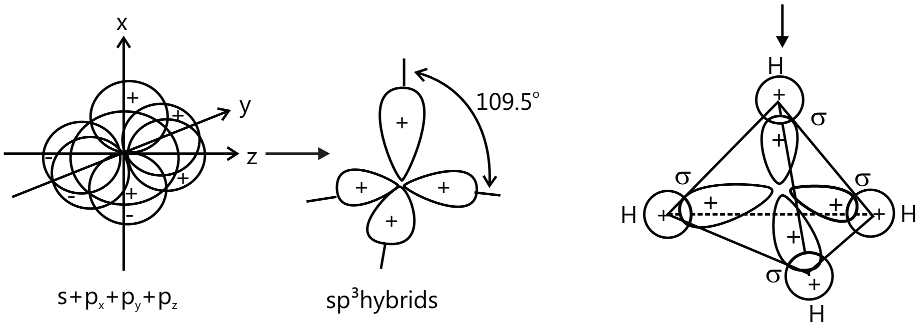


Figure 14.11: Shape of sp^3 hybridised orbital

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation.

In NH_3, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2s^2 2p_x^1 2p_y^1 2p_z^1$ having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. Overlapping of these orbitals with s-orbitals of 3 Hydrogen atoms gives 3 bonds. Since lone pair-bond pair repulsion is more than bond pair-bond pair, the molecule gets distorted and the bond angle is reduced to 107° from 109.5° giving it a pyramidal geometry.

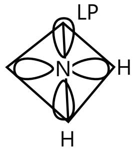


Figure 14.12: Formation of NH_3 molecule

In case of H_2O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° and the molecule thus acquires a V-shape or angular geometry.

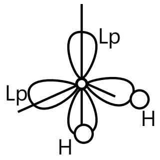


Figure 14.13: Formation of H_2O molecule

Steric No. = 4 Geometry = tetrahedral Ideal bond angle = 109°28′

Table 14.9: Examples of molecule showing sp^3 hybridisation

Type	Shape	Example
AB_4	Tetrahedral	CH_4
AB_3L	Pyramidal	XeO_3
AB_2L_2	V-shape or bent	OBr_2
ABL_3	Linear	–OCl

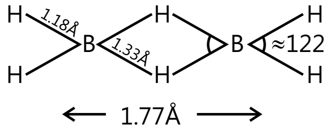
Some other Examples of sp^3 hybridisation

This molecule does not have any B–B bond like C–C bond in C_2H_6 (ethane). Therefore, there is no scope of any conformations in the molecules of B_2H_6.

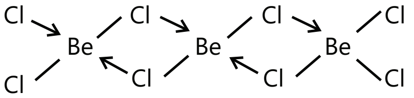
Both the B atoms are in sp^3 hybridization state and each boron contains two types of boron hydrogen bond lengths.

This is an example of 3-centre 2-e^- bond which is also known as Banana bond.

The bridging hydrogen atoms are not in the plane of the molecule, one is above the plane and the other is below the plane.

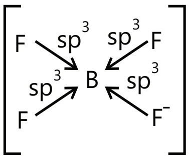


(i) $\boxed{Be}$ ○ $BeCl_2(s)$



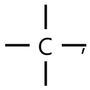
Steric number = 4(i.e.sp^2)

(ii) $\boxed{B}$ ○ BF_4^- ; B= $\boxed{\uparrow\downarrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\ }$
1s 2s 2p
sp^3 hybridisation



○ B_2H_4

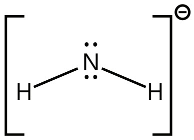
(iii) $\boxed{C}$ ○



$-\overset{|}{\underset{|}{C}}-$, diamond , CCl_4, $:CH_3^{\oplus}$

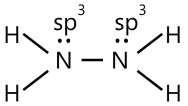
(iv) $\boxed{Si}$ ○ $SiCl_4$, SiO_2, Silicates etc.

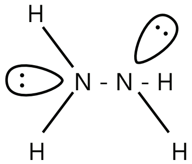
(v) $\boxed{N}$ ○ NH_2^- (amide ion)



V-shape

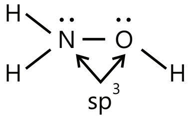
○ NH_2-NH_2 or N_2H_4 (hydrazine)





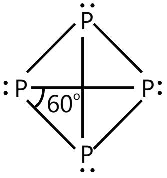
Structure is similar to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecules are rotated 95° about N–N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å.

○ NH_2OH (hydroxylamine)



lp-lp repulsion increases the N-O bond length.

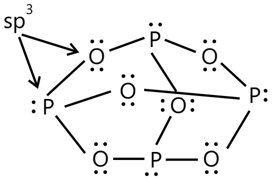
(vi) $\boxed{P}$ ○ P_4 (white phosphorus)



All phosphorus atoms occupy all four vertexes of tetrahedron. There are six P–P bonds and ∠ PPP is 60°.

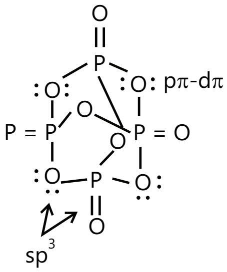
Since bond angle is 60° (against normal tetrahedral bond angle, 109.5°) so, P_4 molecule is a strained molecule. So it is chemically very reactive.

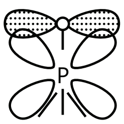
○ P_4O_6



P–O bond length shows that the bridging bonds on the edges are 1.65Å and are normal single bonds. There is no. P–P bonds.

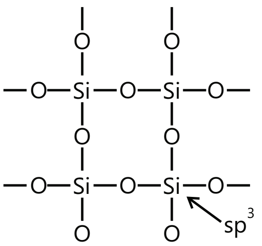
P_4O_{10}



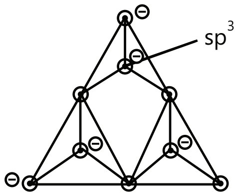


The P–O bond lengths shows that the bridging bonds on the edges are 1.60Å but the P=O bonds on the corners are 1.43 Å and the P = O is formed by p – d back bonding. A full p orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P – P bond.

(vii) $\boxed{Si}$ ○ SiO_2 is a covalent network solid like diamond



○ Structure of cyclic silicates : $[Si_3O_9]^{6-}$



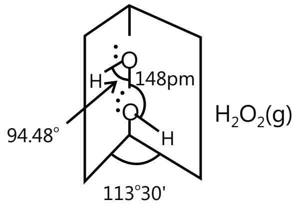
• = Silicon ; ○ = Oxygen

Note: Oxygen atom bonded with two Si atoms cannot have a negative charge. There is no oxygen-oxygen bond. All silicates contain only Si-O bond and there is no Si-Si bond.

O – O bond length (148 pm) is larger than the expected due to the repulsion between the lone pairs on the two oxygen atoms.

It has book like structure (angle between the two pages of the book = 94º) and both the O atoms have two lone pairs each.

○ H_2O_2



The H_2O_2 is the smallest molecule known to show restricted rotation about the O–O bond and this is presumably due to repulsion between the OH groups. A similar structure is retained in the liquid and solid, but bond lengths and angles are slightly changed because of hydrogen bonding.

Table 14.10: Hybridization Involving d-orbital

sp^3d	d_{z^2}
sp^3d^2	$d_{x^2-y^2}$ & d_{z^2}
sp^3d^3	d_{xy}, d_{yx}, d_{zx}
dsp^2	$d_{x^2-y^2}$

(d) sp^3d hybridisation:

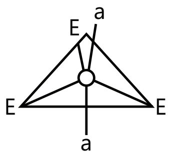
Steric number = 5 Geometry = trigonal bipyramidal

Table 14.11: Examples of molecule showing sp^3d hybridisation

Type	**AB_5**	**AB_4L**	**AB_3L_2**	**AB_2L_3**
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	PCl_5, PBr_5, PF_5 etc	SF_4, XeO_2F_2	ClF_3, $[XeF_3]^+$	XeF_2, I_3^-, $[ICl_2]^-$

Important points regarding sp^3d :

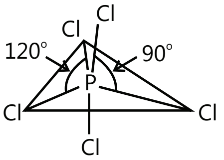
(i) According to VSEPR theory, a lone pair will occupy equatorial positions but not axial.



(ii) More electronegative atoms will prefer to occupy axial positions.

(iii) Since, double bonds occupy more space. Therefore, they will also prefer equatorial positions.

$\boxed{AB_5}$ $PCl_5(g)$

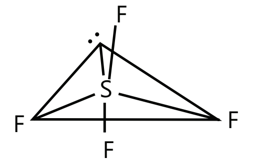


It is covalent in the gas but in solid state exists as an ionic solid consisting of $[PCl_4]^-$ (tetrahedral) and $[PCl_6]^-$ (octahedral). All P–Cl bonds are not of equal lengths. Here, axial bonds are longer and weaker than equatorial bonds.

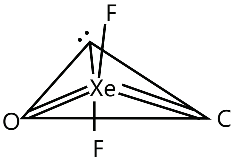
Note: PF_5 (g) is trigonal bipyramidal and the electron diffraction shows that some bond angles are 90º and others are 120º, and axial P – F bond lengths are 1.58 Å, whilst the equatorial P – F lengths are 1.53 Å. But NMR studies suggest that all five atoms are equivalent because of pseudo rotation. PF_5 remains convalent and is trigonal bipyramidal in the solid state. $PBr_5(s)$ exists as $[PBr_4]^+$ Br^- and PI_5 as $[PI_4]^+$ I^- in solution.

$\boxed{AB_4L}$

SF_4

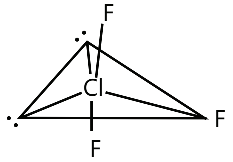


XeO_4F_2



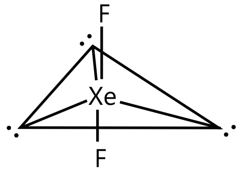
$\boxed{AB_3L_2}$

ClF_3



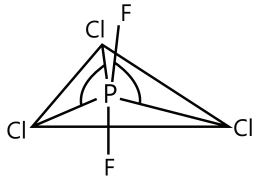
$\boxed{AB_2L_3}$

XeF_2

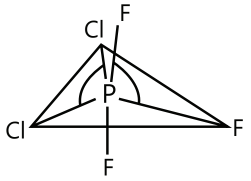


AB_5

PCl_2F_3



μ=zero (non-polar)



μ ≠ zero (polar)

(e) sp^3d^2 hybridization: Steric Number= 6 Geometry = octahedral

Table 14.12: Examples of molecules sowing sp^3d^2 hybridisation

Type	AB_6	AB_5L	AB_4L_2
Shape	Octahedral	Square Pyramidal	Square Planar
Example	SF_6, PF_6^-, $[SiF_6]^{2-}$ $[AlF_6]^{3-}$, $[XeO_6]^{4-}$	BrF_6, IF_6 $XeOF_4$	ICl_4^- XeF_4

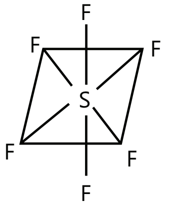
Important : Since, octahedral is a symmetrical figure, hence

(a) Position of a lone pair can be anywhere,

(b) But if there are two lone pairs (max.) then these must be in the trans positions.

$\boxed{AB_6}$

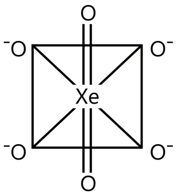
SF_6



Bond angle = 90°

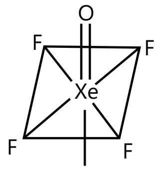
Due to over-crowding and maximum valency of S, SF_4 is much less active (almost inert) than SF_8

$[XeO_6]^{4-}$

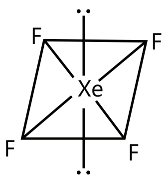


$[XeO_6]^{4-}$ is the perxenate ion and H_4XeO_6 is called perxenic acid. But $H_2[X^{-4}\ eO_4]$ is called xenic acid.

$\boxed{AB_5L}$ $XeOF_4$



$\boxed{AB_4L_2}$ XeF_4



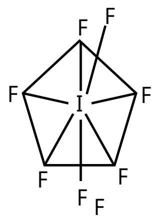
(f) sp²d³ Hybridization:

Steric number = 7 Geometry = Pentagonal bi-pyramidal

Table 14.13: Examples of molecules sowing sp³d³ hybridisation

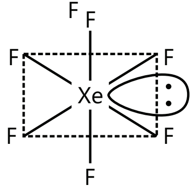
Type	AB_2	AB_6L
Shape	Pentagonal bi-pyramidal	Distorted octahedral
Example	IF_7	XeF_6

$\boxed{AB_7}$ IF_7

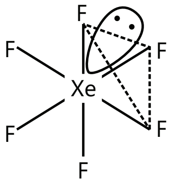


Bond angle = 72° & 90°

$\boxed{AB_6L}$ XeF_6(g)

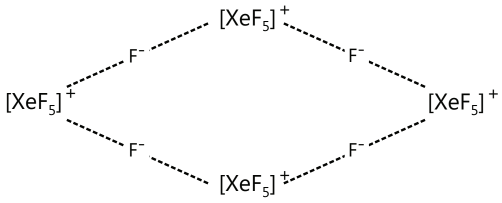


or

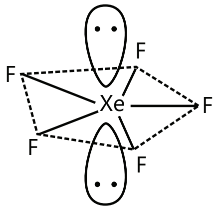


Distorted octahedral with a nonbonding electron pair either at the center of a face or the midpoint of an edge.

- XeF_4 (s) is found to be ionic solid, consisting of $[XeF_5]^+$ and F^- ions. It is found that F^- is forming a bridge between two XeF_5^+ ions.

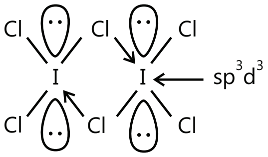


$[XeF_5]^-$



Pentagonal planar ion with two nonbonding electron pairs above and below the plane of the pentagon.

- ICl_3 does not exist, but the dimer I_2Cl_6 is a bright yellow solid. Its structure is planar. The terminal I – Cl bonds are normal single bonds of length 2.38 Å and 2.39 Å. The bridging I – Cl bonds are appreciably longer (2.68 Å and 2.72 Å) suggesting delocalized bonding, rather than a simple halogen bridge formed by coordinate bonds from Cl_2 to I.



The liquid has an appreciable electrical conductance due to self-ionization.

$I_2Cl_6 \rightleftharpoons [ICl_2]^+$ (bent) + $[ICl_4]^-$ (square planar)

Illustration 11: The triodes ion $[I_3^-]$ in which the I atoms are arranged in a straight line is stable, but the corresponding F_3^- ion does not exist.

Sol: F_3^- and I_3^- are of same group. Iodine can expand its octet but F cannot and thus, in I_3^- octet rule is not violated, but in F_3^-, the octet rule is violated.

15.1 Molecular Orbital Theory (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(a) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(b) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(c) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule.

Thus an atomic orbital is monocentric, while a molecular orbital is polycentric.

(d) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called bonding molecular orbital and anti-bonding molecular orbitals are formed.

(e) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(f) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by the molecular orbital.

(g) The molecular orbitals like the atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli Exclusion Principle and the Hund's Rule of Maximum Multiplicity. But the filling order of these molecular orbitals is always experimentally decided, there is no rule like (n + 1) rule in case of atomic orbitals.

Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

Let us begin by discussing the case of molecular hydrogen. An approximate description of the molecular orbitals in H_2 can be obtained by considering them as a Linear Combination of Atomic Orbitals (LCAOs). Let us label the nuclei A and B. The lowest energy orbital associated with each nucleus is the 1s orbital, and each of these atomic orbitals may be represented by wave function φ_A or φ_B. Now each molecular orbital may also be represented by a wave function which is a suitable linear combination of atomic orbitals; since A and B are identical atoms, their atomic orbitals obviously contribute equally to molecular orbitals. In this case we can write down two molecular orbitals derived by combining the 1s atomic orbitals, these being represented by:

$$\varphi m = \left[\varphi A + \varphi B\right]'\varphi m = \left[\varphi A - \varphi B\right]$$

The molecular wave functions φ_A and φ^+_m are bonding and antibonding molecular orbitals; orbitals of the type, in which the line joining the two nuclei is a symmetrical axis for the electron distribution, are known as σ orbitals if bonding and σ^* orbitals if antibonding, so we may alternatively denote them as σ 1s and σ^*_{1s} orbitals. When the two 1s wave functions are added, they reinforce one another everywhere, and especially in the region between the two nuclei; the build-up of electron density, there diminishes the internuclear repulsion and a strong bond results. When one of the two 1s wave functions is subtracted from the other, they exactly cancel in a plane, midway between the nuclei, and the molecular wave function changes sign at this nodal plane. This lack of electron density raises the internuclear repulsion, the total energy becomes higher, the two nuclei are not bonded together, and the orbital is described as antibonding.

Pictorial representations of this LCAO method are given in figure, in the first of these, the relative energies of 1s molecular orbitals and their constituent atomic orbitals are shown, note that the antibonding orbital is correctly shown as somewhat more destabilised relative to the atomic orbitals than the bonding orbital is stabilised (N is not strictly equal to N^+, but is rather smaller, as we mentioned earlier).

In the hydrogen molecule in its ground state, both electrons occupy the σ 1s orbital in the hydrogen molecule ion, H_2^+. Formed by the action of an electric discharge on hydrogen at low pressures, only a single electron is in this orbital and the total bonding energy being 269 kM mol^{-1} compared with 458 kJ mol^{-1} for H_2.

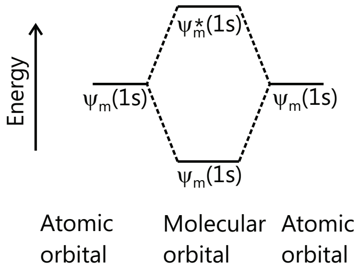


Figure 14.14: The relative energy levels of molecular orbitals and their constituent atomic orbitals for H_2

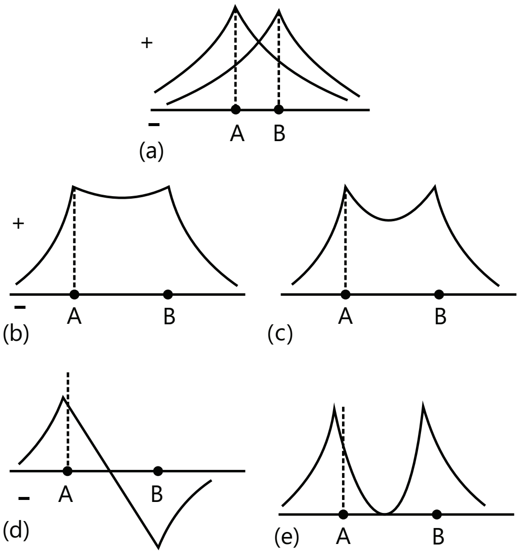


Figure 14.15: The formation of molecular orbitals for H_2. (a) Ψ_A and Ψ_B for individuals. (b) $\Psi_A + \Psi_B = \Psi_m$. (c) Probability function for the bonding orbital, $(\Psi_m)^2$. $\Psi_A - \Psi_B = \Psi^*_m$. (e) Probability function for the antibonding orbital, $(\Psi_m)^2$.

Figure: Another representation of the formation of molecular orbitals for H_2. Since the σ and σ* orbitals are respectively centrosymmetric and non-centrosymmetric these orbitals may also be denoted by the symbols σ_g and σ^*_u.

Molecular orbital wave functions are designated as φ_g and φ_u, g and u refer to the symmetry of the orbital about its centre. If the wave function is centrosymmetric, i.e., has the same sign at the same distance in opposite directions from the centre of symmetry. The orbitals is said to gerade (German, even); if it changes sign on inversion about the centre, it is said to ungerade (German, uneven).

Alternative method for determining the symmetry of the molecular orbital is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remain the same, the orbital is gerade, and if the sign changes, the orbital is ungerade.

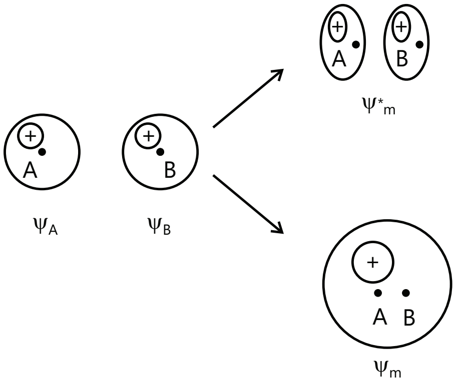


Figure 14.16 : Combination of atomic orbital

Thus σ and π* molecular orbitals are gerade and σ* and π molecular orbitals are ungerade.

Condition for the combination of atomic orbitals: The linear combination of atomic orbitals to form molecular orbital takes place only if the following conditions are satisfied.

1. **The combining atomic orbitals must have the same or nearly the same energy.** This means that the 1s orbital can combine with another 1s orbital but not with the 2s orbital because the energy of the 2s orbital is appreciably higher than that of the 1s orbital. It, therefore, means that only a limited number of combinations of atomic orbitals are possible.
2. **The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having the same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbitals of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.
3. **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

Types of molecular orbitals: Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pie), δ (delta) etc. In this nomenclature, the sigma (σ) molecular orbitals are symmetrical around the bond-axis, while pi (π) molecular orbitals are not symmetrical. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbital's are of the σ type and are designated as σ 1s and σ^* 1s. If internuclear axis is taken to be in the direction, it can be seen that a linear combination of $2p_z$-orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma\ 2p_z$ and σ^*2p_z. [Fig.(b)]. Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of a positive lobes plane. Such molecular orbitals, are labelled as π and π^* [Fig(c)]. A π bonding MO has large electron density above and below the internuclear axis. The π^* anti-bonding MO has a node between nuclei and δ -type of molecular orbitals are obtained by involvement of d-orbitals into bonding.

Difference between π molecular orbitals and the σ orbitals

(a) For π overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for σ overlap the lobes point along the line joining the two nuclei.

(b) For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is in contrast to σ orbitals.

(c) The symmetry of π molecular orbitals is different from that shown by σ orbitals. If the bonding π MO is rotated about the internuclear line, a change in the sign of lobe occurs. The π bonding orbitals are therefore ungerade, whereas all bonding MO's are gerade. Conversely, the antibonding π MO's are gerade, while all σ antibonding MO's are ungerade.

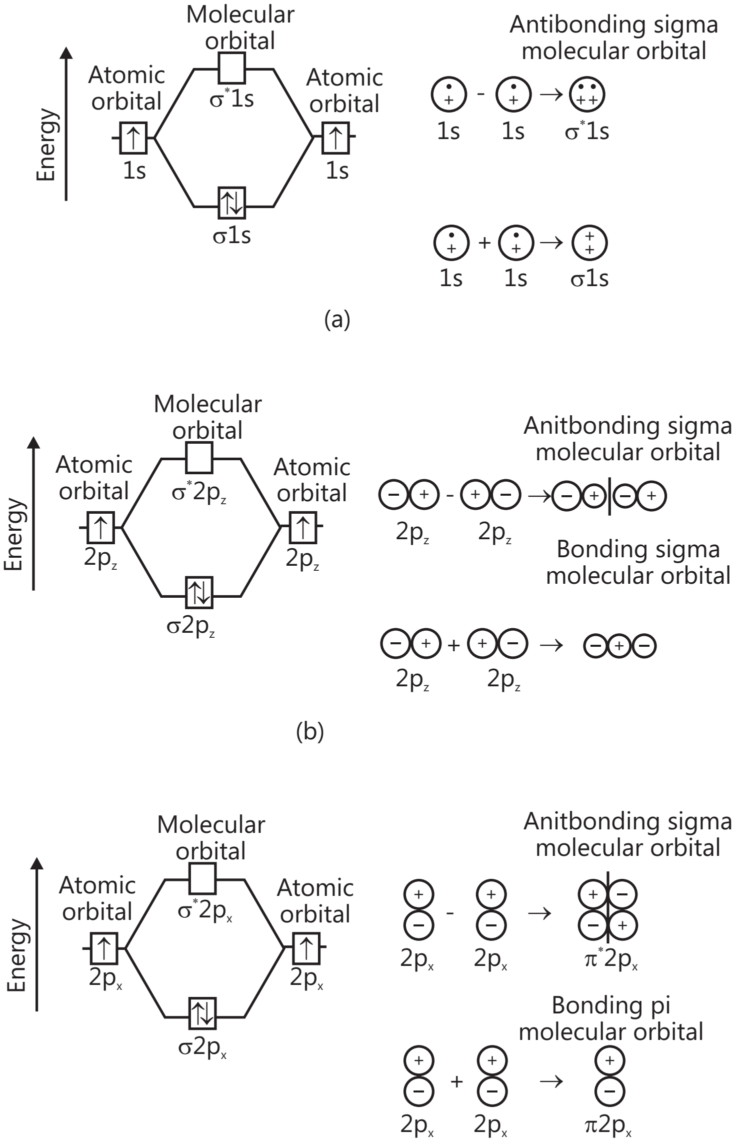
Energy level diagram for molecular orbitals: The energy level of molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_y) < \sigma^* 2p_z$$

The increasing order of energies of various molecular orbitals for Be_2, B_2, C_2, N_2 etc. is :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z\ (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

The important characteristic feature of this order in that the energy of $\sigma\ 2p_z$ molecular orbital is higher than that of $\pi\ 2p_x$ and $\pi\ 2p_y$ molecular orbitals.



(a)

(b)

Figure 14.17: Bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals (b)$2p_z$ orbital and (c) $2p_x$ atomic orbitals

Electronic configuration and molecular behaviour: The distribution of electrons among molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecules as discussed below:

(i) The molecule is stable, if N_b is greater than N_a, and

(ii) The molecule is unstable, if N_b is less than N_a

In (i) more bonding orbitals are occupied, so the bonding influence is stronger and a stable molecule results. In (ii) antibonding influence is stronger and therefore the molecule is unstable.

N_b is the number of electrons in bonding molecular orbitals and N_a is the number of electrons in antibonding molecular orbitals.

Bond order: Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e., Bond order (b.o.) = $\frac{1}{2}(N_b - N_a)$.

A positive bond order (i.e. $N_b > N_a$) means a stable molecule while a negative (i.e. $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

Nature of the bond: Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

Bond-Length: The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic nature: If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N_2 molecule. However if one or more molecular orbitals are single occupied it is paramagnetic (attracted by magnetic field), e.g. O_2 molecule.

Bonding in Some Homonuclear Diatomic Molecules:

(a) Hydrogen molecule (H_2) : $H_2 : (\sigma\,1s)^2$

Bond order : $\dfrac{N_b - N_a}{2} = \dfrac{2-0}{2} = 1$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

(b) Helium molecule (He_2): $He_2 : (\sigma\,1s)^2\,(\sigma^*1s)^2$

Bond order of He_2 is ½(2 – 2) = 0

The molecular orbital description of He_2 predicts two electrons in a bonding orbital and two electrons in an antibonding orbital, with a bond order of zero,in other words, no bond. This is what is observed experimentally. The noble gas He has not a significant tendency to form of free atoms. He2 has a very low binding energy, approximately 0.01 J/mol; for comparison, H_2 has a bond energy of 436 kJ/mol.

(c) Lithium molecule (Li_2) : $(\sigma\,1s)^2\,(\sigma^*1s)^2\,(\sigma\,2s)^2$

Its bond order, therefore is ½(4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2, the molecules are known to exist in the vapour phase. The M.O. model predicts a single Li-Li bond in Li_2, in agreement with gas phase observations of the molecule.

(d) Beryllium (Be_2) : $(\sigma\,1s)^2\,(\sigma^*1s)^2\,(\sigma 2s)^2\,(\sigma^*2s)^2$

Be_2 has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like He_2, Be is not a stable chemical species.

(e) Boron (B_2) : $(\sigma\,1s)^2\,(\sigma^*1s)^2\,(\sigma 2s)^2\,(\sigma^*2s)^2\;\;(\sigma 2p^1{}_x = \sigma 2^1{}_y)(\sigma p_z)^0$

Here is an example in which the Molecular orbital model has distinct advantage over the Lewis dot picture. B_2 is found only in the gas phase, solid boron is found in several very hard forms with complex bonding, primarily involving B_{12} icosahedra, B_2 is paramagnetic. This behaviour can be explained if its two higher energy electrons occupy separate p-orbitals. The Lewis dot model cannot account for the paramagnetic behaviour of this molecule.

B_2 is also a good example of the energy level shift caused by the mixing of s and p orbitals. In the absence of mixing, the σ_g (2p) orbital is expected to be lower in energy than the π_u(2p) orbitals and the resulting molecule would be diamagnetic. However, mixing of σ_g(2s) orbital with the σ_g (2p) orbital lowers the energy of σ_g(2s) orbital and increases the energy of the σ_g(2p) orbital to a higher level than the π orbitals, giving the order of energies shown above. As a result, the last two electrons are unpaired in the degenerate (having the same energy) π orbitals, and the molecule is paramagnetic. Overall, the bond order is 1, even though the two p electrons are in different orbitals. The bond order of B_2 is 1/2(6 – 4) = 1.

(f) Carbon molecule (C_2) : $(\sigma\ 1s)^2\ (\sigma\ {}^*1s)^2\ (\sigma\ 2s)^2\ (\sigma\ {}^*2s)^2\ (\pi\ 2p^2_x = \pi\ 2p^2_y)$ or $(\sigma\ 2s)^2\ (\pi\ 2p^2x = \pi\ 2p^2_y)$. The simple MO picture of C_2 predicts a doubly bonded molecule with all electrons paired, but with both the highest occupied molecular orbitals (HOMOs) having π symmetry. It is unusual because it has two π bonds and no σ bond. The bond dissociation energies of B_2, C_2 and N_2 increase steadily, indicating single, double, and triple bond with increasing atomic number. Although C_2 is not a commonly encountered chemical species (carbon is more stable as diamond, graphite, and fullerene), the acetylide ion, C_2^{2-}, is well known, particularly in compounds with alkali metals, alkaline earths, and lanthanides. According to the molecular orbital model, C_2^{2-} should have order of 3 (configuration $\pi_a^2\ \pi_u^2\ \sigma_g^2$). This is supported by the similar C–C distances in acetylene and calcium carbide (acetylide).

Table14.14: C-C bond distance in different molecule

C – C Distance (pm)	
H – C = C – H	120.5
CaC_2	119.1

The bond order of C_2 is 1/2 (8 – 4) = 2 and C_2 should be diamagnetic. C_2 molecules have indeed been detected in the vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

(g) Nitrogen molecule (N_2): $(\sigma\ 1s)^2\ (\sigma\ {}^*1s)^2\ (\sigma\ 2s)^2\ (\sigma\ {}^*2s)^2\ (\pi\ 2p^2_x = \pi\ 2p^2_y)\ (\sigma\ 2p_z)^2$

N_2 has a triple bond according to both the Lewis and the molecular orbital models. This is in agreement with its very short N–N distance (109.8 pm) and extremely high bond dissociation energy (942 kJ/mol). Atomic orbitals decrease in energy with increasing nuclear charge Z; as the effective nuclear charge increases, all orbitals are pulled to lower energies. The shielding effect and electron-electron interactions cause an increase in the difference between the 2s and 2p orbital energies as Z increases, from 5.7 eV for boron to 8.8 eV for carbon and 12.4 eV for nitrogen. As a result, the $\sigma_g(2s)$ and $\sigma_g(2p)$ levels of N_2 interact (mix) less than the B_2 and C_2 levels, and the $\sigma_g(2p)$ and $\pi_u(2p)$ are very close in energy and C_2 levels. And the $\sigma_g(2p)$ and $\pi_u(2p)$ are very close in energy. The bond order of N_2 is 1/2 (10 – 4) = 3. It contains one sigma and two π bonds.

(h) Anionic nitrogen species (N_2^-): Though 15 electrons, but derived from N_2. Hence electronic configuration will be according to N_2.

Electronic configuration: $(\sigma\ 1s)^2\ (\sigma\ {}^+1s)^2\ (\sigma\ 2s)^2\ (\sigma\ {}^*2s)^2\ (\pi\ 2p^2_x = \pi\ 2p^2_z)\ (\sigma\ 2p_z)^2$, $(\pi\ {}^*2px)^1$ The bond order of N_2 is 1/2(10 – 5) = 2.5. It is a paramagnetic species.

(i) N_2^+: Bond order = 2.5 . Out of N_2^+ and N_2^-, N_2^- is less stable though both have equal bond order but N_2^- has greater number of antibonding electrons.

(j) Oxygen molecule (O_2): O_2 : $(\sigma\ 1s)^2\ (\sigma\ {}^*1s)^2\ (\sigma\ 2s)^2\ (\sigma\ {}^+2s)^2\ (\sigma\ 2p_g)^2\ (\pi\ 2p_x^{\ 2} = \pi\ 2p_y^{\ 2})\ (\pi\ {}^*2p_x^{\ 1} = \pi\ {}^*2p_y^{\ 1})$ O_2 is paramagnetic. This property, as for B_2, cannot be explained by the traditional Lewis dot $\underset{\cdot\cdot}{\ddot{O}}=\underset{\cdot\cdot}{\ddot{O}}$ structure, but is evident from the molecular orbital picture, which assigns two electrons to the degenerate π_{*g} orbitals. The paramagnetism can be demonstrated by pouring liquid O_2 between the poles of a strong magnet: some of the O_2 will be held between the pole faces until it evaporates. The bond order of O_2 is $\frac{1}{2}\ [N_b - N_a] - \frac{1}{2}\ [10 - 0] = 2$.

So in the oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in $\pi\ {}^*2p_x$ and $\pi\ {}^*2p_y$ molecular orbitals, therefore, O_2 molecule should be paramagnetic, a prediction that corresponds to the experimental observations. Several ionic forms of diatomic oxygen are known, including O_2^+ and O_2^{2-}. The internuclear O – O distance can be conveniently known, including O_2^- and O_2^{2-}. The internuclear O – O distance can be conveniently correlated with the bond order predicted by the molecular orbital model, as shown in the following table.

Table 14.15: Bond order predicted by the molecular orbital model

	Bond Order	**Internuclear Distance (pm)**	**Number of unpaired(s) Electrons**
O_2^+ (dioxygenyl)	2.5	112.3	1
O_2 (dioxygen)	2.0	120.07	2
O_2^- (superoxide)	1.5	128	1
O_2^{2-} peroxide	1.0	149	0

Note : Oxygen-oxygen distances in O_2^- and O_2^{2-} are influenced by the cation. This influence is especially strong in the case of O_2^{2-} and is one factor in its unusually long bond distance. The extent of mixing is not sufficient in O2 to push the $\sigma 2(2p)$ orbital to higher energy than the π_g (2p) orbitals. The order of molecular orbitals shown is consistent with the photoelectron spectrum.

(k) **Fluorine molecule (F_2):** $(\sigma\, 1s)^2(\sigma\, {}^*1s)^2(\sigma{}^*\, 2s)^2(\sigma\, 2s)^2(\sigma\, {}^*2s)^2(\sigma\, 2p_z)^2(\pi\, 2p_x^2 = \pi\, 2p_y^2)(\pi\, {}^*2p_x^2 = \pi\, {}^*2p_y^2)$ The molecular orbital picture of F_2 shows a diamagnetic molecule having a single fluorine-fluorine bond, in agreement with experimental data on this very reactive molecule.

The net bond order in N_2, O_2 and F_2 is the same whether or not mixing is taken into account, but the order of the filled orbitals is different. The switching of the order of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals can occur because these orbitals are so close in energy ; minor changes in either orbital can switch their order. The energy difference between the 2s and 2p orbitals of the atoms increases with increasing nuclear charge, from 5.7 eV in boron to 27.7eV in fluorine. Because the difference becomes greater, the s-p interaction decreases and the normal order of molecular returns in O_2 and F_2. The higher σ_g orbital is seen again in CO.

(l) **Neon molecule (Ne_2):** $(\sigma\, 1s)^2(\sigma\, {}^*1s)^2(\sigma\, 2s)^2(\sigma\, {}^*2s)^2(\sigma\, 2p_z)^2(\pi\, 2p^2_x = \pi\, 2p^2_y)(\pi\, {}^*2p_x^2 = \pi{}^*2p^2_y)(\sigma\, {}^*2p_z)^2$ All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons and the bond order is therefore zero. The Ne_2 molecule is a transient species, if it exists at all.

Note: HOMO : Highest Occupied Molecular Orbital, LUMO : Lowest Unoccupied Molecular Orbital

Bond lengths in homonuclear diatomic molecules: Figure shows the variation of bond distance with the number of valence electrons in the second period, p block homonuclear diatomic molecules. As the number of electrons increases, the number in bonding orbitals also increases, the bond strength becomes greater, and the bond length becomes shorter. This continues with up to 10 valence electrons in N_2 and then the trend reverses because the additional electrons occupy antibonding orbitals. The ions N_2^+, O_2^+, O_2^{2+} are also shown in the figure and follow a similar trend.

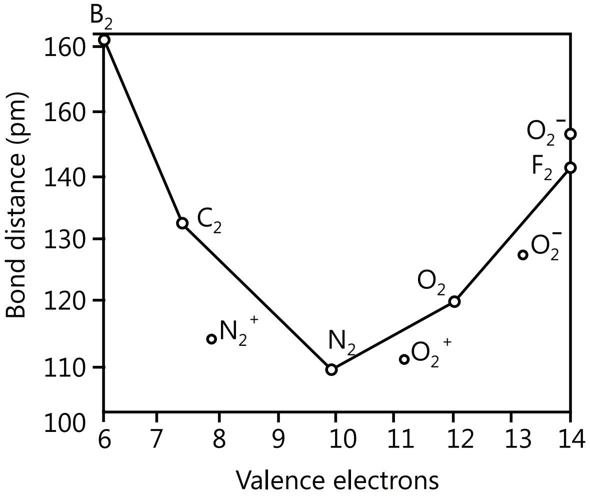


Figure 14.18: Plot of Bond distance Vs Valence electrons for homonuclear diatomic orbital

The same principles apply when combining atomic orbitals from two different atoms as applied when the atoms are identical, that is:

(1) Only atomic orbitals of about the same energy can combine effectively.

(2) They should have the maximum overlap.

(3) They must have the same symmetry.

Since the two atoms are different, the energies of their atomic orbitals are slightly different. A diagram showing how they combine to form molecular orbitals after considering the symmetry interaction of 2s and $2p_x$ orbitals is given in figure (where the molecule is XY and Y is more electronegative than X).

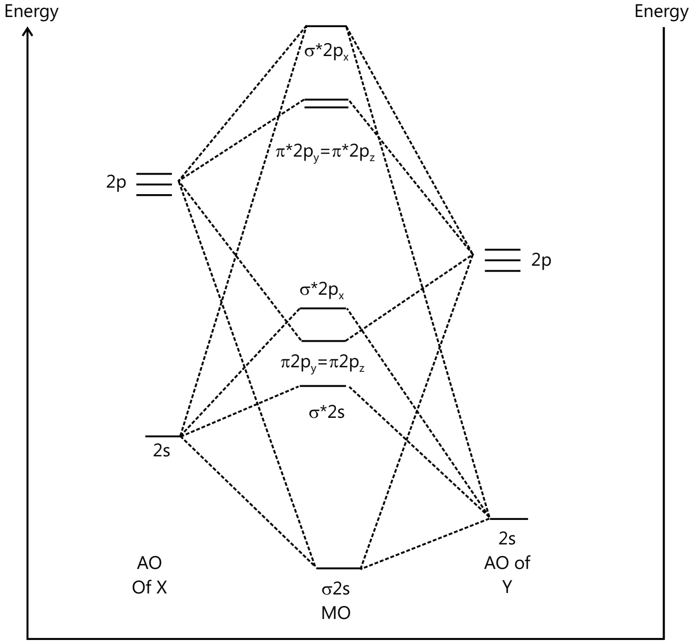


Figure 14.19: Electronic configuration, atomic and molecular orbital for a heteronuclear molecule XY

There are a total of 15 electrons in the molecule and the order of energy levels of the various MOs is

$$\sigma1s^2, \sigma*1s^2, \sigma2s^2, \sigma*2s^2, \left\{\begin{matrix}\pi2p_y^2, \\ \pi2p_z^2,\end{matrix}\right. \sigma2p_x^2 \left\{\begin{matrix}\pi*2p_y^1 \\ \pi*2p_z^0,\end{matrix}\right.$$

An unpaired electron is present in the $\pi*$ orbital and is delocalized over the whole molecule, hence NO molecules is paramagnetic. Since the highest occupied molecular orbital (HOMO) is $\pi*$ and the energy of which is higher than the atomic orbitals of N atom and O atom, the ionization energy of NO is less than that of both N and O atoms.

Table 14.16: Ionization enthalpies of some elements

Species	**Ionization energy (in kJ mol^{-1})**
N	1402
O	1314
NO	894

On ionization, the bond order 2.5 of NO is increased to 3.0 in NO^+, as a result of which bond length decreases from 113 pm in NO to 106 pm in NO^+.

Some special features are introduced in the MO diagram of CO because the electronegativity difference between C and O atom is large. Since the $\Delta E_{(2p-2s)}$ for C atom (5.3 eV) is much less compared to $\Delta E_{(2p-2s)}$ for O atom (15.0 eV), the participation of s – p hybrid orbitals are considered for the formation of MO diagram of CO, which is shown in the figure.

In ionization of CO, i.e. $CO \rightarrow CO^+$, the removal of the electron takes place from the non-bonding orbital of C atom (HOMO). Hence the interelectronic repulsion decreases and finally the bond length decreases from 112.8 pm to 111.5 pm.

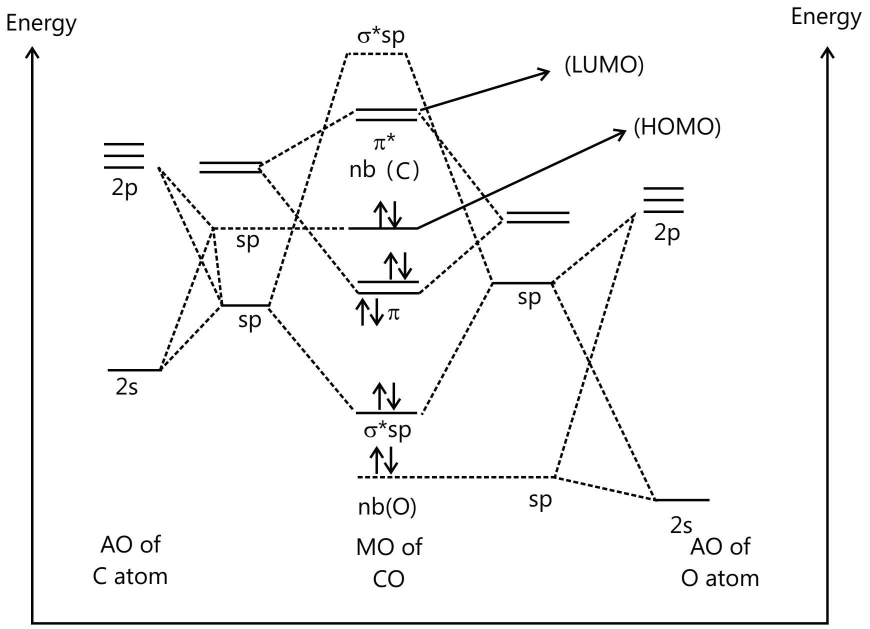


Figure 14.20: Molecular orbital diagram for CO molecule

Illustration 12: Though O_2 molecule is paramagnetic yet it is a colourless gas. Why ?

Sol : It is because the energy gap between HOMO and LUMO levels in O_2 molecule is so large that the radiation of visible light cannot excite e^- from HOMO to LUMO. In fact O_2 gas shows absorption in UV zone. So it is colourless.

Illustration 13: Correct order of bond energy is-

(A) $N_2 > N_2^+ > N_2^- > N_2^{2-}$
(B) $N_2^+ > N_2^- > N_2^{2-} > N_2$
(C) $N_2 > N_2^- = N_2^+ > N_2^{2-}$
(D) $N_2^- > N_2 = N_2^- > N_2^{2-}$

Sol: (A) Bond order is directly proportional to the bond energy.

Bond order of N_2 = 3, N_2^- = 2.5 N_2^{2-} = 2

But N_2^- has more electrons in antibonding MO's and thus N_2^+ is more stable than N_2^-. So correct order of bond energy will be $N_2 > N_2^+ > N_2^- > N_2^{2-}$

Illustration 14: Which of the following species have a bond order of 3 ?

(A) CO (B) CN^- (C) NO^+ (D) O_2^-

Sol: Bond order = $\frac{1}{2}$ $[N_b - N_a]$

Where N_b- No of electron in bonding energy level

N_a - no of electron in anti-bonding level.

(A, B, C). Species CO, CN^-, NO^- are isoelectronic with 14 electrons to N_2 which has bond order of 3 (i.e. $\frac{10-4}{3}$ = 3), so their bond order will be equal to three.

Illustration 15: Which of the following are diamagnetic ?

(A) C_2 (B) O_2^{3-} (C) Li_2 (D) N_2^+

Sol: (A, B, C). Species C_2, O_2^{2-}, Li_2 have all the electrons paired but N_2^- has one unpaired electron in the bonding molecular orbital, it is paramagnetic.

Polarity of bonds: In reality no bond or compound is either completely covalent or Ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2 N_2 or F_2 the shared pair of electrons is equally attracted by the atoms. As a result, electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine, since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

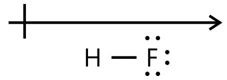
As a result of polarisation, the molecule possesses the dipole moment which can be defined as the product of magnitude of the partial charge $\left(\delta^+ \text{ or } \delta^-\right)$ developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d)

Dipole moment is usually expressed in Debye units (D). The conversion factors are 1D = 3.33564×10^{-10} Cm, where C is coulomb and m is meter.

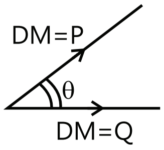
1 Debye = 1×10^{-18} e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with a tail on the positive centre and the head pointing towards the negative centre. For example, the dipole moment of HF may be represented as



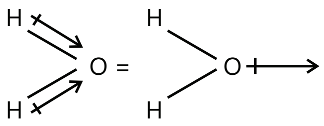
The shift in electron density is represented by crossed arrow ($+\!\!\!\longrightarrow$) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules, the dipole moment not only depends upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such a case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e., a molecule will have a dipole moment if the summation of all of the individual vectors is non-zero.



$$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$$, where R is resultant dipole moment

For example, H_2O molecule, which has a bent structure, the two O–H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17×10^{-30} cm (1D = 3.33564×10^{-30} cm) is the resultant of the dipole moments of two O–H bonds.



Net dipole moment, μ = 1.85 D = $1.85 \times 3.33564 \times 10^{-30}$ cm = 6.17×10^{-30} cm.

Following compounds have zero dipole moment:

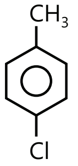
BF_3, CO_2, SO_2, CF_4, $PF_5(g)$, SF_6, XeF_2, CS_2, CCl_4, $PCl_5(g)$, XeF_4

Some important orders

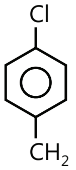
HF >	HCl >	HBr >	HI
1.92 D	1.08	0.78	0.38
CH_3Cl >	CH_2Cl_2 >	$CHCl_3$ >	CCl_4
1.86	1.6	1.0	0

Usually for distributed Benzene order is o > m > p

But it all depends on the substituents

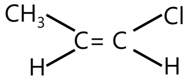


D.M ≠ 0

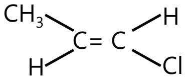


D.M = 0

Note: For geometrical isomers, usually the dipole moment of cis is more than trans, but again there can be exceptions.

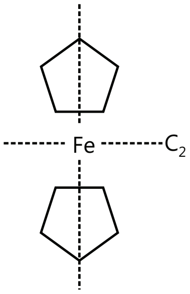


cis-form (low dipole moment)

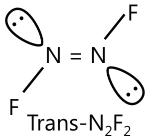


tras-form (high dipole moment)

For example: The presence of a centre of symmetry, I, requires that the dipole moment be zero, since any charge on one side of the molecule is cancelled by an equal charge on the other side of the molecule. Thus, $[CoF_6]^{3-}$, trans $-N_2F_2$ and the staggered conformer of ferrocene do not have moments.



Staggered-ferrocene (μ=0)



Trans-N_2F_2

Some Important points about dipole moment: A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B–F bonds are polar in BF_3, but BF_3 has $\mu = 0$ due to its symmetrical geometry.

If the molecule has $\mu \neq 0$, then it should be linear or having symmetrical geometry.

E.g. linear – CO_2, CS_2, $BeCl_2$(g) ; symmetrical geometry –BF_3, CH_4, PCl_5, SF_6, IF_7, XeF_4

If the molecule has $\mu = 0$, then it should be angular or having unsymmetrical geometry

$SnCl_2$, $PbCl_2$, SO_2, angular molecular geometry NH_3, H_2O, NF_3, SF_4, H_2S, unsymmetrical molecular geometry

○ % Ionic character = $\frac{\mu_{\text{experimental}}}{\mu_{\text{theoritical}}} \times 100 = \frac{\mu_{\text{(Observed)}}}{\mu_{\text{(100\% inoiccompound)}}} \times 100$

Illustration 16: The resultant dipole moment of water is 1.85 D, ignoring the effects of lone pair calculate, the dipole moment of each OH bond (given that bond angle in H_2O = 104°, cos 104° = –0.25)

Sol: $R^2 = P^2 + Q^2 + 2PQ \cos$

$$(1.85)^2 = x^2 + x^2 + 2x^2\left(-\frac{1}{4}\right)$$

$$(1.85)^2 = 2x^2 - \frac{x^2}{2} \Rightarrow \frac{3x^2}{2}$$

$$\therefore\ x = 1.51\ \text{D}$$

Illustration 17: For a HCl molecule, the observed dipole moment is 1.03 D and bond length is 1.275Å. Calculate % ionic character.

Sol: first determine the theoretical dipole moment by using distance of separation and magnitude of charge.

% ionic character can be calculated as follows :

$$\frac{\text{experimental dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Dipole moment = $4.8 \times 10^{-8} \times 1.275 \times 10^{-8} = 4.8 \times 1.275$

$$\%\ \text{ionic character} = \frac{1.03 \times 100}{1.275 \times 4.8} \approx 17\%$$

Illustration 18: Why does NH_3 is have more dipole moment than NF_3?

Sol: In NH_3 molecule, nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards nitrogen atom, but in NF_3 molecule, fluorine is more electronegative than nitrogen so that net dipole moment is towards fluorine atoms. In NH_3 ,the bond pair moments and lone pair moments are in the same direction, while in NF_3 ,the lone pair moment and bond pair moments are in opposite direction.

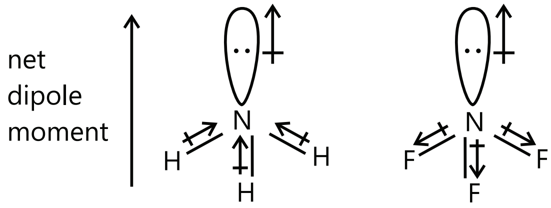
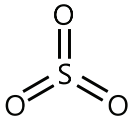


Illustration 19: The geometry of SO_3 and its dipole moment are :

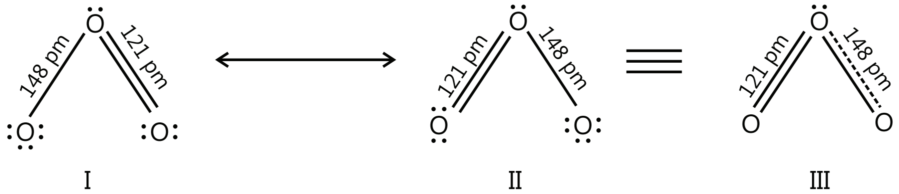


(A) pyramidal and non-zero
(B) trigonal and non-zero
(C) trigonal planar and zero
(D) T-shaped and zero

Sol: (C) The steric number of sulphur = 3 ; so hybridization in sp^2. There is no lone pair on sulphur atom., therefore, according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence, the molecule will be symmetrical (trigonal planar) with zero dipole moment.

16. RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone,



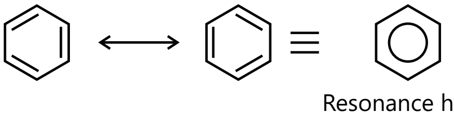
(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

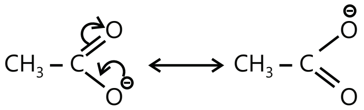
In both structures we have a O–O single bond and a O = O double bond. The normal O – O and O = O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_2 molecule are same (128 pm). Thus, the oxygen-oxygen bonds in the O_2 molecule are intermediate between a double and a single bond.

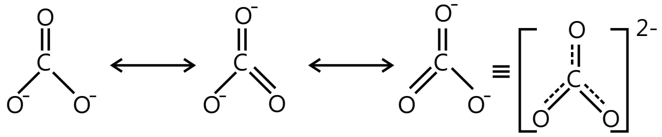
Obviously, this cannot be represented by either of the two Lewis structures shown above. The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3.

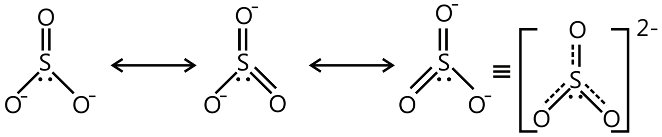
Definition: Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound.

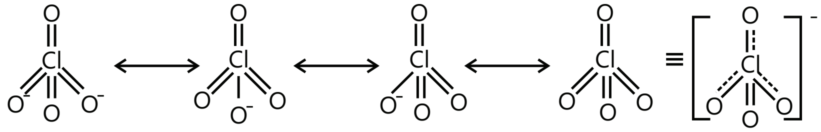
Resonance Hybrid: It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



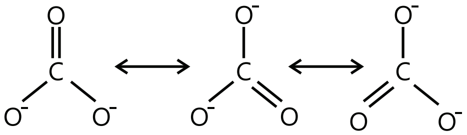
(i) 

(ii) 

(iii) 

(iv) 

Example:



$$\text{Bond order} = \frac{2 + 1 + 1}{3} = 1.33$$

Resonance energy = Actual bond energy – Energy of most stable resonating structure.

Stability of molecule of resonance energy.

More the number of covalent bonds in a molecule, greater will be its resonance energy.

(Resonance energy) α (number of resonating structures).

17. HYDROGEN BOND

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied to a hydrogen atom to form a covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially, positively charges the hydrogen atom forming a bond with the other more electronegative atom. This bond is called a hydrogen bond and is weaker than a covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below :

$– – – H^{\delta+}\ F^{\delta-}– – – H^{\delta+}\text{-}F^{\delta-}\ – – – H^{\delta+}\text{-}F^{\delta-}– – –$

Here, the hydrogen bond acts as a bridge between atoms which holds one atom by covalent bond and the other by a hydrogen bond. Hydrogen bond is represented by a dotted line (– – –), while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds the hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pair tend to line up and hold the molecules together. Other atom with high electronegativity, such as Cl, can also form hydrogen bonds in strongly polar molecules such as chloroform, $CHCl_3$.

Conditions required for H-bond :

(i) Molecule should have a more electronegative atom (F, O, N) linked to H-atom.

(ii) Size of electronegative atom should be smaller.

(iii) A lone pair should be present on a electronegative atom.

Strength of H-bond: The strength of H-bond is usually very low (5 – 10 kJ/mol,) but in some cases this value may be as high as 50 kJ/mol. The strongest H-bonds are formed by F atoms. Deuterium is more electropositive than H, therefore it also forms stronger bonds. The strength of the H-bond can be compared by the relative bond energies and the geometry of the various compounds as given below :

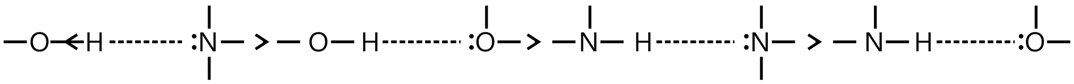
$$F^- + HF \rightarrow \left[FHF\right]^- ; \Delta H = -161 \pm 6 \text{ kJ mol}^{-1}$$

$$(CH_3)_2CO + HF \rightarrow (CH_3)_2CO \ldots\ldots HF; \Delta H = -46 \text{ kJ mol}^{-1}$$

$$H_2O + HOH \rightarrow H_2O \ldots\ldots HOH; \Delta H = -25 \text{ kJ mol}^{-1}$$

$$HCN + HCN \rightarrow HCN \ldots\ldots HCN; \Delta H = -12 \text{ kJ mol}^{-1}$$

The magnitude of H-bonding depends on the physical state of the compounds. H-bonding is maximum in the solid state and minimum in the gaseous state. Thus, hydrogen bonds have a strong influence on the structure and properties of the compounds. Order of H-bond strength



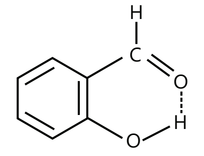
$$-O\leftarrow H\cdots\cdots :\overset{|}{\underset{|}{N}}- \;>\; -O-H\cdots\cdots :\overset{|}{O}- \;>\; -\overset{|}{N}-H\cdots\cdots :\overset{|}{\underset{|}{N}}- \;>\; -\overset{|}{N}-H\cdots\cdots :\overset{|}{O}-$$

Types of H-Bonds:

(a) Intramolecular H-Bonding:

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.

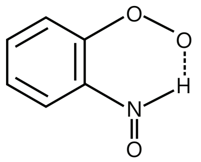
(i)



O-hydroxy benzaldehyde

It has a lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

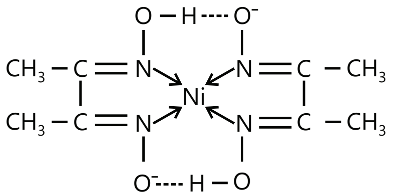
(ii)



O-nitro phenol

It has a lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

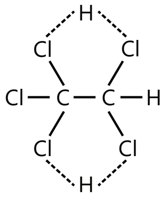
(iii)



Nickel dimethyl glyoximate (a chelate)

Extra stability of the complex is because of intermolecular hydrogen bonding in addition to the chelating effect.

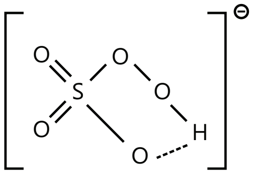
(iv)



Chloral hydrate

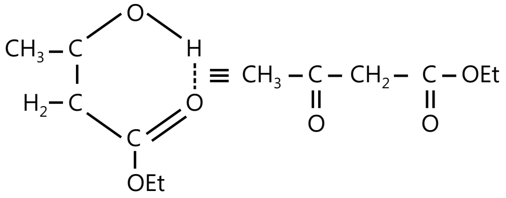
Chlorat hydrate is stable only on account of intramolecular hydrogen bonding.

(v)



Persuphate ion HSO_5^-

(vi)



Aceto acetic ester (enolic form)

K_1 of peroxomono sulphuric acid (i.e., caros acid) is greater than K_2. After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult. The intramolecular hydrogen bonding attributes the stability of the enolic form of acetoacetic ester.

Necessary conditions for the formation of intramolecular hydrogen-bonding:

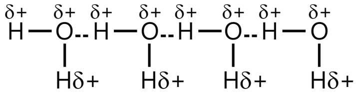
(a) The ring formed as a result of hydrogen bonding should be planar.

(b) a 5- or 6- membered ring should be formed.

(c) Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

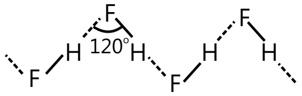
(a) **Intermolecular H-Bonding:** Exists between the negative and positive ends of different molecules of the same or different substances i.e., it is formed between two different molecules of the same or different compounds.

(i) In water molecules due to the polar nature of H_2O there is an association of water molecules giving a liquid abnormally high boiling point.



When ice is formed from liquid water, some air gaps are formed (in tetrahedral packing of water molecules). The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules. Due to this, volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Conversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks. Hence, volume increases and density decreases. Thus, water has maximum density at 4°C.

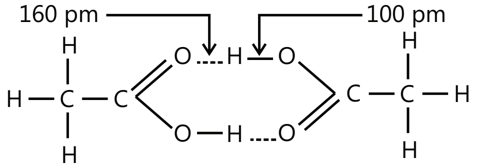
(ii) The hydrogen bonds in HF link the F atom of one molecules with the H-atom of another molecule, thus forming a zig-zag chain $(HF)_n$ in both the solid and also in the liquid.



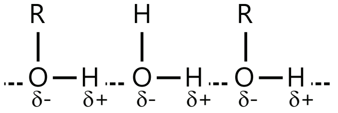
Some hydrogen bonding also occurs in the gas, which consists of a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$, and monomeric HF. Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $M(HF_2)$; For example, in KHF_2 an X-ray diffraction study together with a neutrons diffraction study shows that there is a linear symmetrical anion having an over all, F–H–F distance of 2.26Å, which may be compared with the H–F bond length of 0.92 Å in hydrogen fluoride monomer.

(iii) There is also similar H-bonding in alcohol (R–OH), ammonia (NH_3) and phenol (C_6H_5OH) molecules

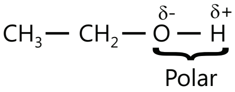
(iv) Carboxylic acid dimerises in gaseous state due to H-bonding



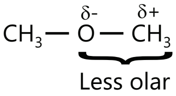
(v) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding H_2O and R–OH molecules)



However, isomeric ether is less soluble in water due to the less polar nature of ether.

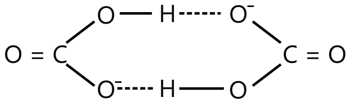


$CH_3-CH_2-\underbrace{\overset{\delta-}{O}-\overset{\delta+}{H}}_{\text{Polar}}$



$CH_3-\underbrace{\overset{\delta-}{O}-\overset{\delta+}{CH_3}}_{\text{Less olar}}$

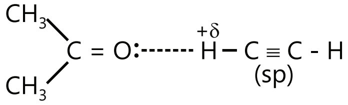
(vi) HCO_3^- ions exist as dimer in $KHCO_3$



In $Na^-HCO_2^-$, the HCO_3^- ions are linked in to an infinite chain through intermolecular H-bonding.

Illustration 20: C_2H_2 is not soluble in H_2O, but it is highly soluble in acetone.

Sol: As %s character increases, electronegativity increases, due to Hydrogen bonding C_2H_2 becomes soluble in acetone



In hybridisation, as s character increases, electronegativity increases, hence C_2H_2 forms H-bonds with O–atom of acetone and dissolves. But H_2O molecules are so linked that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O.

Illustration 21: Why $SnCl_2, 2H_2O$ readily loses one molecule of water at 80ºC ?

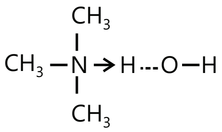
Sol : One water molecule is coordinated to a lone pair of electrons on $SnCl_2$ and the other is hydrogen bonded to coordinate water molecules.

Illustration 22: Why does crystalline sodium lose one molecule of water at 80ºC ?

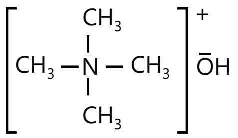
Sol : Na_2O_2 forms stable hydrates on account of H-bonding

$\cdots\cdots O_2^{2-}\cdots\cdots(H_2O)_8\cdots\cdots O_2^{2-}\cdots\cdots(H_2O)_8\cdots\cdots$

Illustration 23: Explain why tetramethyl ammonium hydroxide is a stronger base than trimethyl ammonium hydroxide.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}\rightarrow H\cdots O-H$$



$$\left[CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_3\right]^{+}\overset{-}{O}H$$

Sol : Due to hydrogen bonding in trimethyl ammonium hydroxide ,ionization becomes difficult and thus OH^- is not formed with ease.

In the trimethyl compound, the O–H group is hydrogen bonded to Me_3NH group and this makes it more difficult for the OH group to ionize and hence it is a weak base.

In the tetramethyl compound, hydrogen building cannot occur, so the OH^- group ionizes easily and thus it is a much stronger base.

18. INTERMOLECULAR FORCES (VAN DER WAAL'S FORCES)

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

(a) Ion-dipole attraction,

(b) Dipole-dipole attraction,

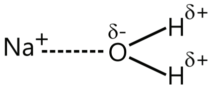
(c) Ion-induced dipole attraction,

(d) Dipole-induced dipole attraction,

(e) Instantaneous dipole-Instantaneous induced dipole attraction (Dispersion force or London forces)

Strength of Van der Waal's forces a > b > c > d > e

(a) Ion-dipole attraction: Exists between an ion and a polar molecule. Its strength depends on (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule. It is thought to be directional. Ion-dipole forces are important in solutions of ionic compounds in polar solvents, where solvated species such as $Na(OH_2)_x^-$ and $F(H_2O)_y^+$ (for solution of NaF in H_2O) are found. Hence, this force is responsible for hydration.



(b) Dipole-dipole attraction: These are electrostatic attractions between the oppositely charged ends of permanent dipoles. Exists between polar molecules and due to this force, gas can be liquefied.

$$\overset{\delta+}{H}-\overset{\delta-}{Cl}\qquad\overset{\delta+}{H}-\overset{\delta-}{Cl}$$

(c) Ion-induced dipole attraction: Exists between ion and non-polar molecules (e.g. an atom of a noble gas such as Xenon)

(d) Dipole-induced dipole attraction: Exists between polar and non-polar molecules.

Head to tail arrangement of dipoles

Antiparallel arrangement of dipoles

Figure 14.17: Different arrangements of dipole

$$\overset{\delta^+}{H}-\overset{\delta^+}{Cl}\qquad\overset{\delta\delta\delta^+}{Cl}-\overset{\delta\delta\delta^+}{Cl}$$

(Polar) (Non-polar)

(e) **Instantaneous dipole-Instantaneous induced attraction:** Exists among the non-polar molecules like H_2, O_2, Cl_2 etc. in solid or liquid states. Even in atoms or molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary unbalances in electron distribution.

London forces are extremely short range in action and the weakest of all attractive forces. The London forces increase rapidly with molecular weight, or more properly with the molecular volume and the number of polarizable electrons.

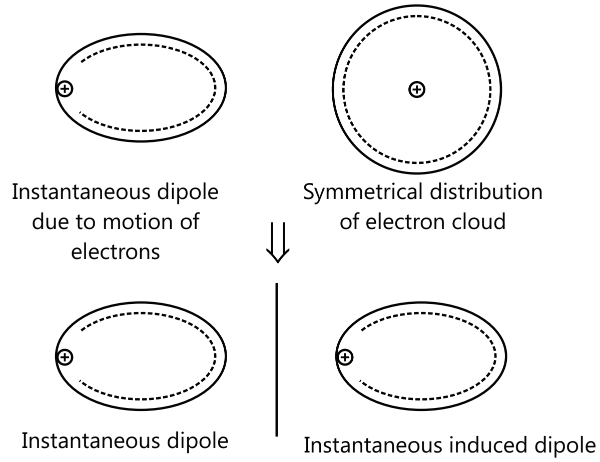


Figure 14.18: Instantaneous dipole-Instantaneous induced attraction

Note : Fluoro carbons have usually low boiling points because tightly bound electrons in the fluorine atoms have a small polarizability.

a) Strength of Van der waal force $\propto$ molecular mass.

b) van der Waal's force $\propto$ boiling point.

Illustration 24: Give the order of boiling point of following Cl_2, HCl.

Sol: $Cl_2 - Cl_2 < HCl - HCl$ (boiling point)

As dipole-dipole attraction is stronger than dispersion force.

Illustration 25: Arrange the inert gases, according to their increasing order of boiling points.

Sol : strength of van der Waal's force increases down the group with increase in molecular mass.

He < Ne < Ar < Kr < Xe (boiling point)

Metallic bond: Most metals crystallise in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electron interactions among 8 to 12 nearest neighbours (which is also called coordination number). Bonding in metals is called metallic bonding. It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole. Two models are considered to explain metallic bonding:

(a) Band model

(b) Electron-sea model

(a) **Band Model:** The interaction of two atomic orbitals, say the 3s-orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one antibonding orbital. If N atomic orbitals interact, N molecular orbitals are formed. Atoms interact more strongly with nearby atoms than with those farther away. The energy that separates bonding and antibonding molecular orbitals decreases as the interaction (overlap) between the atomic orbitals decreases. When we consider the possible interactions among one mole of Na atoms, there is a formation of a series of very closely spaced molecular orbitals (3 σ s and 3 σ *s). They consist of a nearly continuous band of orbitals belonging to the crystal as a whole. One mole of Na atoms contributes one mole (6.02×10^{23}) of valence electrons, thus 6.02×10^{23} orbitals in the band are half-filled.

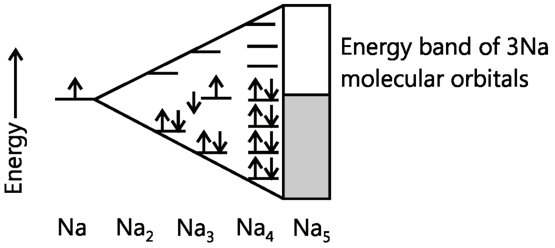


Figure 14.19: The band of orbitals resulting from interaction the 3s-orbitals in a crystal of sodium.

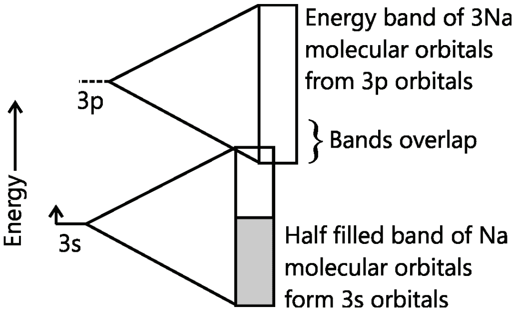


Figure 14.20: Overlapping of a half-filled 3s band with an empty 3p band of Na crystal.

The empty 3p atomic orbitals of Na atoms also interact to form a wide band of $3 \times 6.07 \times 10^{23}$ orbitals. The 3s and 3p atomic orbitals are quite close in energy, so that these bands of molecular orbitals overlap. The two overlapping bands contain $4 \times 6.02 \times 10^{23}$ orbitals. Because each orbital can hold two electrons, the resulting combination of bands is only-eight full.

According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band which (or into which) electrons must move to allow electrical conduction is called a conduction band. The electrical conductivity of a metal decreases as temperature increases. The increases in temperature cause thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

Crystalline non-metals, such as diamond and phosphorus, are insulators, they do not conduct electricity. It is due to the fact their highest-energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty bond (conduction band) by an energy difference called the band gap. In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band.

Elements that are semiconductors have filled bands that are only slightly below, but do not overlap with empty bands. They do not conduct electricity at low temperature, but a small increase in temperature is sufficient to excite some of the highest-energy electrons into the empty conduction band.

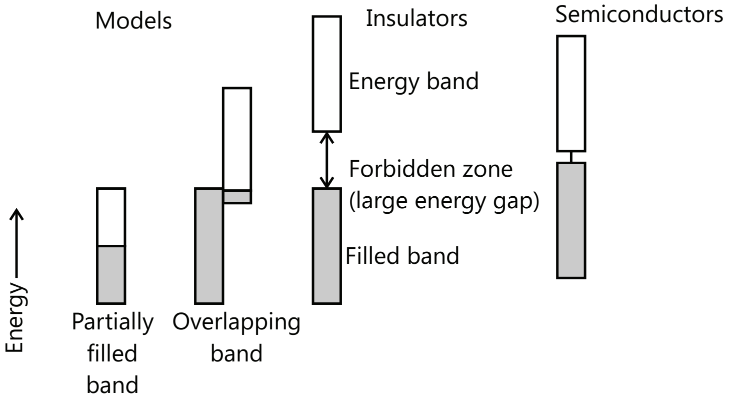


Figure 14.21: Distinction among metal, insulator and semiconductors.in each case an unshaded area represents a conduction band.

(b) Electron-Sea Model: Metals have the ability to conduct electricity, ability to conduct heat, ease of deformation that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility) and a lustrous appearance.

One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured as a network of positive ions immersed in a "sea of electrons". In lithium, the ions would be Li^+ and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

In thermal conductivity, no electrons leave or enter but those in the region being heated gain kinetic energy and transfer this to other electrons.

According to the electron-sea model, the case of deformation of metals can be thought of in this way : If one layer of metal ions is forced across another, perhaps by hammering, the structure remains unchanged as the sea of electrons rapidly adjusts to the new situation.

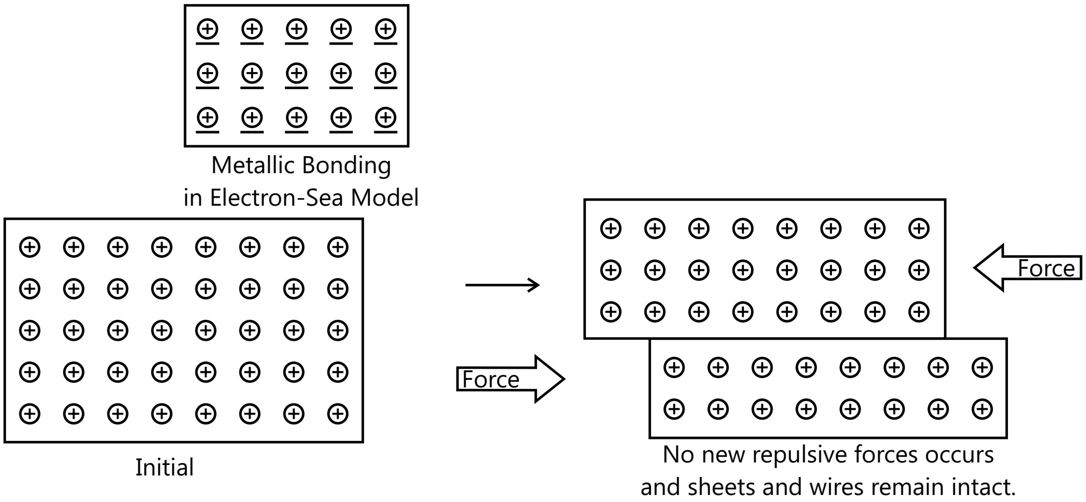
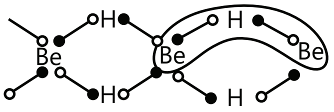


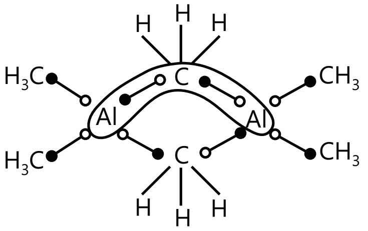
Figure 14.22: Effect of distortion on metal sheet

Some Special Bonding Situations:

(a) **Electron deficient boding:** There are many compounds in which some electron deficient bonds are present from normal covalent bonds or coordinates which are 2c-2e bonds (two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected, such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6, $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.

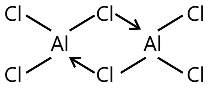


$BeH_2(S)$

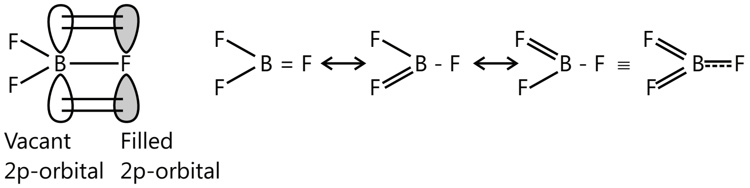


$Al_2(CH_3)_6$

But Al_2Cl_6 has a covalent bond only and there is no electron deficient bonding as depicted in the given structure.



(b) **Back Bonding:** Back bonding generally takes place when out of two bonded atoms has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair (generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3 ,the boron atom completes its octet by accepting two 2p-electrons from fluorine into 2p empty orbital.



(i) Decrease in B – F bond length is due to delocalised pπ–pπ bonding between filled p-orbitals of F atom and vacant p-orbital of B atom. The extent of back bonding is much larger if the orbitals involved in the back are of same size, for example the extent of back bonding in boron trihalides is as follows: $BF_3 > BCl_3 > BBr_3$

There is pπ–pπ back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

(ii) The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pair on it. So among the atoms of third period the extent of back bonding follows the order Si > P > S > Cl. The extent of pπ–pπ overlapping $\propto \dfrac{1}{\text{Lewis acid character}}$

(c) Bond Lengths and $p\pi - d\pi$ bonding: The bonds between S and O, Se and O, are much shorter than might be expected for a single bond. In some cases, they may be formulated as localized double bonds. A σ bond is formed in the usual way. In addition a π bond is formed by the sideways overlap of a p orbital on the oxygen with a d orbital on the sulphur giving a p-d interaction. This $p\pi - d\pi$ bonding is similar to that found in the oxides and oxo-acids of phosphorus, and is in contrast to the more $p\pi - d\pi$ type double bond found in ethene.

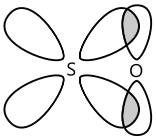


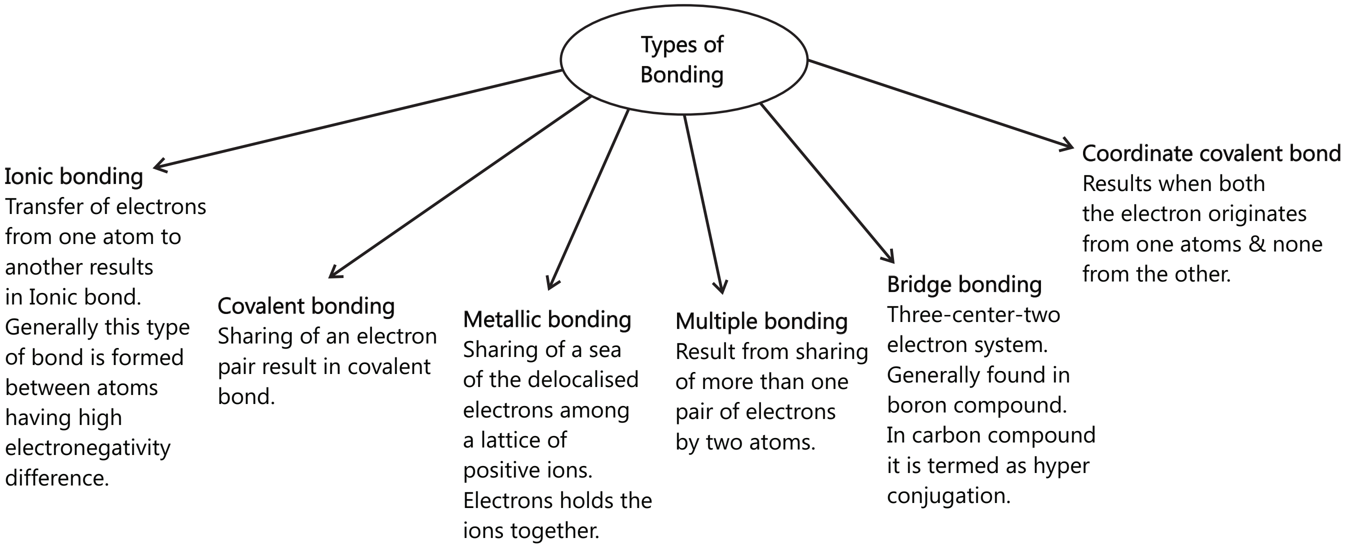
Figure 14.23: p-d interaction between S and O

To obtain effective $p\pi - d\pi$ overlap the size of the d orbital must be similar to size of the p orbital. Thus sulphur forms stronger π bonds than the larger elements in the group. On crossing a period in the periodic table, the nuclear charge is increased, as more s and p electrons are added. Since, these s and p electrons shield the nuclear charge incompletely, the size of the atom and the size of the 3d orbitals in this series of elements leads to progressively stronger $p\pi - d\pi$ bonds. Thus, in the silicates there is hardly any $p\pi - d\pi$ bonding and SiO_4^{4-} units polymerize into an enormous variety of structures by Si–O–Si σ bonds. In the phosphates, π bonding is stronger, but a large number of polymeric phosphates exist. In the oxo-acids of sulphur, π bonding is even stronger and has become a dominant factor. Thus only a small amount of polymerization occurs, and only a few polymeric compounds are known with S–O–S linkages. For chlorine, $p\pi - d\pi$ bonding is so strong that no polymerization of oxo-anions occurs.

POINTS TO REMEMBER

Bond parameters

Bond length	Bond angle	Bond enthalpy	Bond order
Equilibrium distance between the nuclei of two bonded atoms in a molecule.	Angle between the orbitals containing bonding electron pair around the central atom in a molecule.	Amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.	It is given by the number of bonds between the two atoms in a molecule.



Ionic bonding
Transfer of electrons from one atom to another results in Ionic bond. Generally this type of bond is formed between atoms having high electronegativity difference.

Covalent bonding
Sharing of an electron pair result in covalent bond.

Metallic bonding
Sharing of a sea of the delocalised electrons among a lattice of positive ions. Electrons holds the ions together.

Multiple bonding
Result from sharing of more than one pair of electrons by two atoms.

Bridge bonding
Three-center-two electron system. Generally found in boron compound. In carbon compound it is termed as hyper conjugation.

Coordinate covalent bond
Results when both the electron originates from one atoms & none from the other.

- **Electronegativity:** Electronegativity is a measure of the relative tendency of a bonded atom to attract electrons.
- **Oxidation Number:** The oxidation number (oxid. No.) of an atom is the number of valence electrons on the neutral atom minus the number of valence electrons assigned to the atom in the compound on the basis that the bonding electrons belong to the more electronegative atom.
- **Dipole Moment:** $\mu = q \times r$

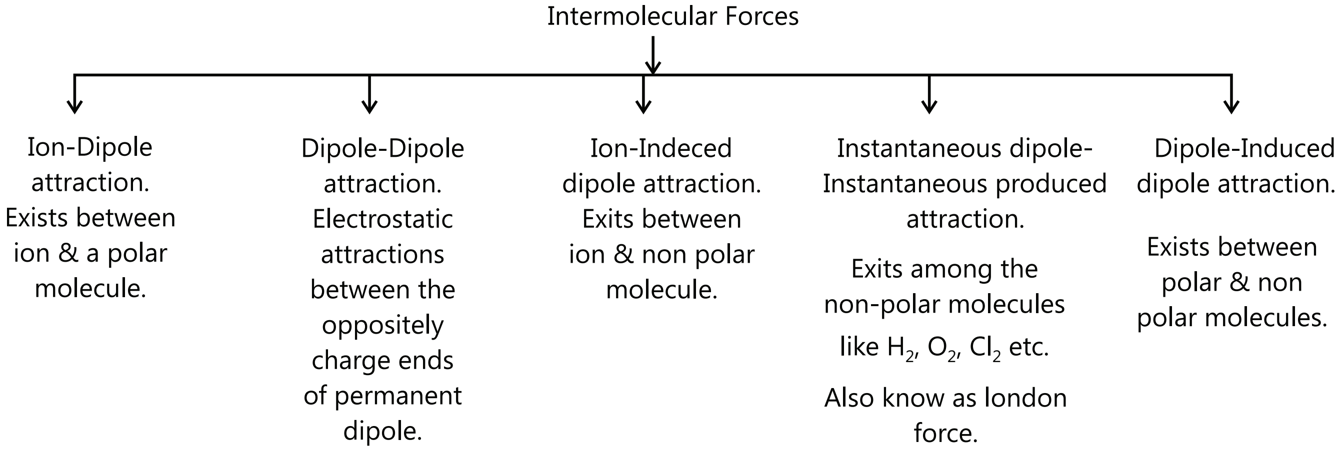
  Where, q is the magnitude of the charge in esu (electrostatic units) and r is the distance between the positive and negative charges in centimeter.
- **Formal Charge** = (Total no. of valence electron in the free atom)- (Total no of nonbonding electron)

  -1/2 (Total no of bonding electron)
- **Polarization :** When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarization and the ability of cation to polarize a nearby anion is called as polarizing power of cation.
- **Fajan's Rule :** Greater is the polarization of anion in a molecule, more is covalent character in it.
- **Theories of Bonding :**

  (a) Valence Bond Theory

  (b) Valence shell Electron Pair repulsion theory

  (c) Molecular Orbital theory
- **Hydrogen bond:** Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pair tend to line up and hold the molecules together.
- **Back Bonding:** Back bonding generally takes place when out of two bonded atoms has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair (generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length.



Solved Examples

JEE Main/Boards

Example 1: Classify the following bonds as ionic, polar covalent and give your reasons :

(i) SiSi bond in $Cl_3SiSiCl_3$

(ii) SiCl bond in $Cl_3SiSiCl_3$

(iii) CaF bond in CaF_2

(iv) NH bond in NH_3

Sol: Atoms having more electronegativity difference form ionic bond whereas atoms having similar electronegativity value forms covalent bond**.**

(i) Covalent, due to identical Electronegativity.

(ii) Covalent, due to less electronegativity difference.

(iii) Ionic, due to more electronegativity difference.

(iv) Covalent, due to nearly similar electronegativity

Example 2: (i) Which one has highest and lowest melting point and why? NaCl KCl RbCl CsCl

(ii) Why does the melting point of cesium halide (CsX) decrease in the order given below? CsF > CsCl > CsBr > CsI.

Sol: Molecule having higher lattice energy show higher melting point.

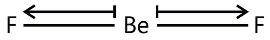
Lattice energy can be defined as energy that is given out when infinitely-separated ions in gas phase come together to form a crystal.

(i) NaCl will have the highest lattice energy on account of the smaller Na^+ while CsCl has lowest lattice energy on account of the larger Cs^+. Hence, NaCl has the highest melting point and CsCl has the lowest melting point.

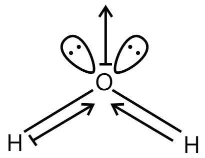
(ii) As the size of anions increases their polarisability increases, thus their covalent character increases and melting point decreases.

Example 3: Why does BeF_2 have a zero dipole moment whereas H_2O has some dipole moment ?

Sol: symmetrical stretching in BeF_2 causes cancelation of dipole moment whereas in H_2O, due to asymmetrical stretching net dipole gets added up.



$\mu = 0$

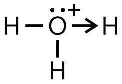


$\mu \neq 0$

BeF_2 has linear molecule and H_2O has bent molecule.

Example 4: Which type of hybridization is found in H_3O^+?

Sol: According to steric no. rule Steric number = Number of bond pair(s) +number of lone pair(s) at central atom So, steric number = 3 + 1 = 4



Thus the hybridization of oxygen in H_3O^+ is sp^3

Example 5: Why are crystals of hydrated calcium sulphate soft and easily cleaved, whereas anhydrous calcium sulphate is very hard and very difficult to cleave?

Sol: Hydrated calcium sulphate involves hydrogen bonding. Within the Ca^{2+}/SO_4^{2-} layer the ions are held together by strong electrovalent bonds but these separated Ca^{2+} / SO_4^{2-} layers are linked by relative weak H-bond. The weak H bonds link SO_4^{2-} ion in the intermediate region.

Example 6: Super oxides are coloured and paramagnetic. Why?

Sol: Super oxides contain on unpaired electron in anti-bonding molecular orbital and are coloured due to transition of HOMO orbital electron within the visible region.

Example 7: Of the species O_2^+, O_2^-, O_2 and O_2^{2-} which would have the maximum bond strength?

Sol: Bond strength is directly proportional to bond order.

O_2^+has higher bond order i.e. 2.5 than

O_2 (2) and O_2^- (1.5) and bond strength is directly proportional to bond order.

Example 8: A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is equal to 1.0 Å, then the fraction of an electronic charge on each atom is

(A) 25% (B) 37% (C) 52% (D) 42%

Sol: (A) Assuming complete charge transfer dipole moment = $(4.8\times10^{-10}\text{esu})(10^{-8}\text{cm})$ = 4.8 D.

So % ionic character = $\frac{1.2}{4.8} \times 100\% = 25\%$

Example 9: The dipole moment of KCl is 3.336×10^{-29} coulomb meter. The interionic distance in KCl is 2.6 Å. Find the % ionic character in KCl.

Sol: First determine the theoretical dipole moment by using distance of separation and magnitude of charge.

% ionic character can be calculated as follows :

The theoretical dipole moment in

KCl = $e\times d = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

= 4.1652×10^{-29} C meter % ionic character

$$= \frac{\text{experimental dipole moment}}{\text{The ratical dipole moment}} \times 100$$

= $(3.336 \times 10^{-29} / 4.1652 \times 10^{-29}) \times 100$

JEE Advanced/Boards

Example 1: Which of the compounds $MgCO_3$ and $ZnCO_3$ is thermally more stable? Explain.

Sol: Polarizing power of an ion affect the stability of its carbonate compound. More the polarizing power less stable is the carbonate compound.

Mg^{+2} has less polarising power due to inert gas configuration, while Zn^{+2} has higher polarising power due to pseudo inert gas configuration . A cation i.e. Zn^{2+} with a greater, polarizing power exercises a strong pull on the electron cloud of the neighbouring O-atom of the CO_3^{2-} ion, as such the metal carbonate ($ZnCO_3$) gets readily decomposed into CO_2 and the oxide of the metal, ZnO. Thus $ZnCO_3$ is less stable than $MgCO_3$.

Example 2: Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in its aqueous solution?

Sol: It exists as HCl (bond formed by equal sharing of electrons) but in an aqueous solution ionises as H^+ (or H_3O^+) and Cl^- due to polarity of HCl.

Example 3: Which is an incorrect statement?

(A) In $CF_2 = C = CF_2$ molecule all the four fluorine atoms are not in the same plane.

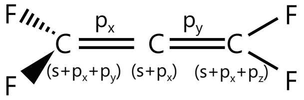
(B) Ka_2 of fumaric acid is more than Ka_2 of maleic acid due to intra molecular hydrogen bonding in maleic acid

(C) The O–O bond length in $O_2[AsF_4]$ is longer than KO_2.

(D) The bond angle order in halogen – S – halogen is $OSF_2 < OSCl_2 < OSBr_2$

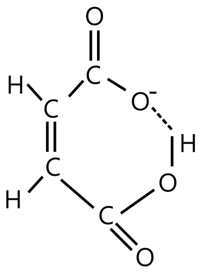
Sol: (C)

(A)

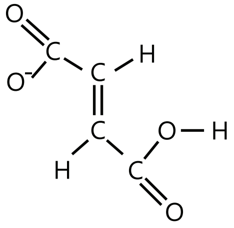


As both carbon atoms are in different planes, all the four fluorine atoms are not in the same plane.

(B) Maleic acid



Fumaric acid



Due to intramolecular hydrogen bonding the maleate ion gets stabilized and thus the removal of second hydrogen becomes quite difficult.

(C) $O_2[AsF_4] = O_2^+$ B.O= 2.5

$KO_2 = O_2^-$ B.O= 1.5

Bond order $\propto \frac{1}{\text{Bondlength}}$;

So, O_2^+ has smaller bond length than O_2^-

(D) Greater the size of the halogen atoms, greater will be the steric repulsions and thus larger will be the bond angles.

Example 4: The gaseous potassium chloride molecule has a measured dipole moment of 10.0 D, which indicates that is a very strong molecule. The separation between the nuclei in this molecule is 2.67×10^{-8} cm. Calculate the percentage ionic character in KCl molecule.

Sol: First determine the theoretical dipole moment by using distance of separation and magnitude of charge.

% ionic character can be calculated as follows :

$$\frac{\text{experimental dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Dipole moment of compound would have been completely ionic

$= (4.8\times 10^{-10}\text{ esu})(2.67 \times 10^{-8}\text{ cm}) = 12.8\text{ D}$

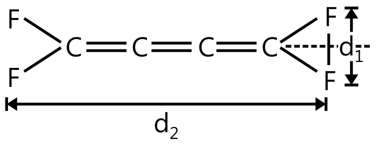
So % ionic character = $\frac{10.0}{12.8} \times 100\% = 78.125\% \approx 78\%$

Example 5: There will be three different fluorine-fluorine distances in molecule $CF_2(C)_2CF_2$. Assuming ideal bond angles for a particular hybridisation (assume no distortion due to double bonds). Find out the two smaller fluoride-fluorine distances and fill the result (in pm) in the increasing order in your answer sheet. Round off your answer to the nearest whole number.

(Given that C – F bond length = 134 pm,

C = C bond length = 134 pm $\sqrt{3}$ = 1.73)

Sol:



$d_1 = 2 \times 134 \times \sin 60^\circ$ pm = 231.8 pm = 232 pm

$d_2 = 134 \times 3 + 2 \times 134 \cos 60^\circ$ pm = 536 pm

Example 6: For an ionic compound AX_3 (s) formed between a metal A and a non-metal X (outermost shell configuration of X = ns^2np^5). Find the enthalpy of formation (magnitude) of AX_3(s) in k cal mol^{-1}, with the help of the following data. (Non-metal X is found to exist in nature as a diatomic gas)

$\Delta H_{\text{Sublimation}}$ A(s) = 100 Kcal/mol

ΔH_{IE1}, A(g) = 60 Kcal/mol

ΔH_{IE2}, A(g) = 150 Kcal/mol

ΔH_{IE3}, A(g) = 280 Kcal/mol

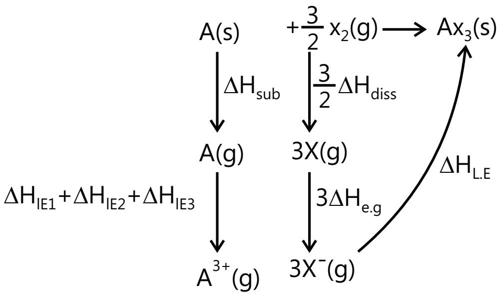
ΔH_{diss} X_2(g) = 80 Kcal/mol

$\Delta H_{e.g.}$ X(g) = – 110 Kcal/mol

$\Delta H_{\text{Lattice energy}}$ A X_3(s) = –470 Kcal/mol

Sol: This problem can be solved using born Heber cycle. Break the complete reaction to different step.

$\Delta H_f = \Delta H_{sub} + \Delta H_{IE1} + \Delta H_{IE2} + \Delta H_{IE3} + \frac{3}{2} + \Delta$
$H_{diss} + 3\Delta H_{e.g} + \Delta H_{LE}$



$\Delta H_f = \Delta H_{sub} + \Delta H_{IE1} + \Delta H_{IE2} + \Delta H_{IE3} + \frac{3}{2}\ \Delta$
$H_{diss} + 3\Delta H_{e.g} + \Delta H_{LE}$

$= 100 + 60 + 150 + 280 + \frac{3}{2} \times 80 - 3 \times 110 - 470$

$= 100 + 60 + 150 + 280 + 120 - 330 - 470$

= – 90 Kcal/mol

Example 7: CO forms weak bonds to Lewis acid such as BF_3. In contrast, CO forms strong bonds to transition metals. Explain.

Sol:

$$CO \underset{\sigma}{\longleftarrow} BF_3$$

$$\text{Transition metal} \underset{\sigma}{\overset{\pi}{\rightleftarrows}} CO$$

This is called synergic interaction and because of it the bond between CO and transition metal is stronger.

Example 8: Which of the following will be the strongest Lewis base?

(A) CH_3CN (B) CH_3NH_2

(C) N_2 (D) None of these

Sol: Lewis base is a compound that donates lone pair of electron. Hybridization also play an important role. As s character increases the electronegativity of atom increases and electron donating ability decreases, (B) In CH_3NH_2 , hybridisation of N sp^3 while in CH_3CN hybridisation of N is sp. N_2 is also sp hybridised. We know that in hybridisation, as s-character increases the electronegativity of atom also increases. Due to this tendency the release of lone pair of electrons becomes somewhat difficult. In methyl amine, the nitrogen is in sp^3 hybridisation and therefore the donation of the lone pair of electron will be quite easier, so it is the strongest Lewis base.

JEE Main/Boards

Exercise 1

Q.1 Why do atoms of noble gases not react with other atoms to form compounds?

Q.2 Why ionic bond is called a non- directional bond but a covalent bond is a called directional bond

Q.3 Why is MgO more stable than NaCl?

Q.4 Why is NaCl more stable than CsCl?

Q.5 Why ionic compounds do not conduct electricity when they are in solid state?

Q.6 Why do elements show variable covalency?

Q.7 Why do covalent compounds consist of discrete molecules?

Q.8 Why are some covalent compounds good conductors of electricity?

Q.9 Why are covalent solids soluble in nonpolar solvents?

Q.10 Why do covalent solids have giant molecules insoluble in all solvents?

Q.11 Why is metallic bond weaker than covalent bond?

Q.12 Why only O, N and F are capable of forming H-bonds?

Q.13 Why is NH_3 a better electron donor than PH_3, H_2S&H_2O?

Q.14 Why do metals have a high density?

Q.15 Why are alkaline earth metals harder than alkali metals?

Q.16 Why does Ag^+ (cation) $4s^2p^6d^{10}$ have a greater polarising power than K^+ (cation) $3s^2p^6$?

Q.17 Why are Li^+ compounds soluble in non-polar solvents but not in polar solvents?

Q.18 Explain the following sequences of solubility? $AlF_3 > AlCl_3 > AlBr_3 > AlI_3$

Q.19 Why is a co-ordinate bond called a semi polar bond?

Q.20 Why is H - atom alone not capable of forming hydrogen bond?

Q.21 Methanoic acid, HCOOH, has one carbon-oxygen bond of length 123 pm, and another of 136 pm. Which bond has which length?

Q.22 Both carbon-oxygen bonds in the methanoate ion, HCOO, have the same length (127 pm). What does this tell about bonding?

Q.23 Water can react with hydrogen ion to make the oxonium ion, H_3O^+ What is present in water molecule that allows it to react with a hydrogen ion ? Describe the bonding in the oxonium ion. Draw a dot and cross diagram for the molecule?

Q.24 Why is $MgCl_2$ linear but $SnCl_2$ is angular?

Q.25 Why NCl_5 does not exist while PCl_5 does?

Q.26 The electronegativities of nitrogen and chlorine are same but NH_3 exists as liquid whereas HCl as gas. Why?

Q.27 Although CO_2 has no dipole moment, SO_2 and H_2O have considerable dipole moments. Why'?

Q.28 Nitrogen trifluoride (NF_3) and ammonia (NH_3) have identical shape and a lone pair of electrons on nitrogen and further the electronegativity difference between the elements is nearly the same but the dipole moment of NH_3 is very high in comparison to NF_3.Why?

Q.29 Why three carbon-oxygen bonds are equal in carbonate ion?

Q.30 Why NF_3 is weaker base than NH_3, NCl_3, NBr_3 and NI_3?

Exercise 2

Single Correct Choice Type

Q.1 The electronic configuration of four elements L, P, Q and R given in brackets

$$L\left(1s^2, 2s^2, 2p^4\right), P\left(1s^2, 2s^2, 2p^6, 3s^1\right),$$

$$Q\left(1s^2, 2s^2, 2p^6, 3s^2, 3p^5\right), R\left(1s^2, 2s^2, 2p^6, 3s^2\right).$$

The formula of ionic compounds that can be formed between these elements are:

(A) L_2P, RL, PQ and R_2Q (B) LP, RL, PQ and RQ

(C) P_2L, RL, PQ and RQ_2 (D) LP, R_2L, P_2Q and RQ

Q.2 Lattice energy of an ionic compound depends upon:

(A) Charge on the ion only

(B) Size of the ion only

(C) Packing of ions only

(D) Both (A) and (B)

Q.3 The high melting point and insolubility in organic solvents of sulphanilic acid are due to its structure.

(A) Simple ionic (B) Cubic

(C) Bipolar ionic (D) Hexagonal

Q.4 What is the effect of more electronegative atom on the strength of ionic bond?

(A) Increases (B) Decreases

(C) Remains the same (D) None of these

Q.5 Which of the following hybrids are ionic?

I. CaH_2 II. BaH_2 III. SrH_2 IV. BeH_2

(A) I and IV (B) II and IV

(C) III and IV (D) I, II and III

Q.6 With which of the given pairs CO_2 resembles?

(A) $HgCl_2, C_2H_2$ (B) C_2H_2, NO_2

(C) $HgCl_2, SnCl_4$ (D) N_2O, NO_2

Q.7 Ionic and covalent bonds are present in:

(A) CCl_4 (B) $CaCl_2$ (C) H_2O (D) NH_4Cl

Q.8 Among the species $CO_2, CH_3COO^-, CO, CO_3^{2-}, HCHO$ which has the weakest C – O bond?

(A) CO (B) CO_2 (C) CO_3^{2-} (D) CH_3COO^-

Q.9 Number of electronic in the valence orbit of nitrogen in an ammonia molecule are:

(A) 5 (B) 6 (C) 7 (D) 8

Q.10 Which bond angle θ would result in the maximum dipole moment for the triatomic molecule yxy?

(A) $\theta = 90°$ (B) $\theta = 120°$

(C) $\theta = 150°$ (D) $\theta = 180°$

Q.11 The dipole moment of HBr is 1.6×10^{-30} C.m and interatomic spacing is 1 Å. The % ionic character of HBr is:

(A) 7 (B) 10 (C) 15 (D) 27

Q.12 In a polar molecule, the ionic charge is 4.8×10^{-10} esu. If the interionic distance is 1 Å unit, then the dipole moment is:

(A) 0.48 debye (B) 4.18 debye

(C) 4.8 debye (D) 41.8 debye

Q.13 If HCl molecule is completely polarized, so expected value of dipole moment is 6.12 (debye), but experimental value of dipole moment is 1.03 D. Calculate the percentage ionic character.

(A) 17 (B) 50 (C) 83 (D) Zero

Q.14 In which of the following there exists a $p\pi - d\pi$ bonding?

(A) Graphite (B) Diamond

(C) Dimethyl amine (D) Trisilyamine

Q.15 Number of sigma bonds in P_4O_{10} is:

(A) 6 (B) 9 (C) 16 (D) 20

Q.16 The correct order of hybridization of the central atom in the following species $NH_3, [PtCl_4]^{2-}, PCl_5$ and BCl_3 is:

(A) sp^3, dsp^2, dsp^3, sp^2 (B) dsp^2, dsp^3, sp^2, sp^3

(C) sp^2, sp^3, dsp^2, dsp^3 (D) sp^2, dsp^2, sp^3, dsp^3

Q.17 As the s-character of hybridization orbital increases, the bond angle.

(A) Increases (B) Decreases

(C) Becomes zero (D) Does not change

Q.18 Which has the least bond angle?

(A) NH_3 (B) H_2O (C) CH_4 (D) BeF_2

Q.19 The molecular shapes of SF_4, CF_4 and XeF_4 are:

(A) The same with 2, 0 and one lone pair of electron on the same central atom, respectively

(B) The same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively

(C) Different with 0, 1 and 2 lone pair of electrons on the central atom, respectively

(D) Different with 1, 0 and 2 lone pair of electrons on the central atom, respectively

Q.20 The maximum number of 90° angles between bond pair-bond pair of electrons is observed in following hybridization:

(A) dsp^3 (B) dsp^2 (C) sp^3d (D) sp^3d^2

Q.21 When two atoms of chlorine combine to form one molecule of chlorine gas, the energy of the molecule:

(A) Equal to that of separate atoms

(B) Lower than that of separate atoms

(C) Greater than that of separate atoms

(D) None of the above

Q.22 Which of the following molecule has highest bond energy?

(A) C – C (B) N – N (C) O – O (D) F – F

Q.23 According to MO theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+ ?

(A) Paramagnetic and bond order < O_2

(B) Paramagnetic and bond order > O_2

(C) Diamagnetic and bond order < O_2

(D) Diamagnetic and bond order > O_2

Q.24 The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for those two species?

(A) Bond length in NO^+ is equal to that in NO

(B) Bond length in NO is greater than in NO^+

(C) Bond length is NO^+ is greater than in NO

(D) Bond length is unpredictable

Q.25 The reason for exceptionally high boiling point of water is:

(A) Its high specific heat

(B) Its high dielectric constant

(C) Low ionization of water molecule

(D) Intermolecular H-bonding

Q.26 The maximum possible number of hydrogen bonds in a H_2O molecule can participate is:

(A) 1 (B) 2 (C) 3 (D) 4

Q.27 The high density of water compare to ice is due to:

(A) Dipole-dipole interaction

(B) Dipole-induced dipole interaction

(C) Induced dipole-induced dipole interaction

(D) Hydrogen bonding interaction

Q.28 Which of the following hydrogen bonds are strongest in vapour phase?

(A) HF---HF (B) HF---HCl

(C) HCl---HCl (D) HF---HI

Q.29 The value of electronegativity of atoms A and B are 1.20 and 4.0 respectively. The percentage of ionic character of A - B bond is:

(A) 43% (B) 50 % (C) 55.3 % (D) 72.24 %

Q.30 The number of electron that are paired in oxygen molecule is:

(A) 7 (B) 9 (C) 16 (D) 14

Q.31 Which combination is best explained by the coordinate covalent bond?

(A) $H^+ + H_2O$ (B) Cl + Cl

(C) $Mh + \frac{1}{2} O_2$ (D) $Mg + \frac{1}{2} O_2$

Q.32 In which of the following the central atom does not use sp^3 hybrid orbitals in its bonding?

(A) NH_2^- (B) OH_3^+ (C) BeF_3^- (D) NF_3

Q.33 Which of the following molecules/ions does not contain unpaired electrons?

(A) O_2^{2-} (B) B_2 (C) N_2^+ (D) O_2

Q.34 Among the following mixtures, dipole-dipole as the major interaction, is present in:

(A) Benzene and ethanol

(B) Acetonitrile and acetone

(C) KCl and water

(D) Benzene and carbon tetrachloride

Q.35 A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?

(A) MCl_2 is more volatile than MCl_4

(B) MCl_2 is more soluble in anhydrous ethanol than MCl_4

(C) MCl_2 is more ionic than MCl_4

(D) MCl_2 is more easily hydrolysed than MCl_4

Q.36 In which of the following molecules/ions all the bonds are not equal?

(A) SF_4 (B) SiF_4 (C) XeF_4 (D) BF_4

Previous Years' Questions

Q.1 The common features among the species CN^-, CO and NO^+ are ***(2001)***

(A) Bond order three and isoelectronic

(B) Bond order three and weak field ligands

(C) Bond order two and acceptors

(D) Isoelectronic and weak field ligands

Q.2 The correct order of hybridisation of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is ***(2001)***

(A) dsp^2,dsp^3,sp^2 and sp^3 (B) sp^3, dsp^2 ,sp^3d and sp^2

(C) dsp^2,sp^2,sp^3,dsp^3 (D) dsp^2,sp^3,sp^2,dsp^3

Q.3 Specify the coordination geometry around and hybridisation of N and B atoms in a 1: 1 complex of BF_3 and NH_3 ***(2002)***

(A) N : tetrahedral, sp^3 ; B: tetrahedral, sp^3

(B) N : pyramidal, sp^3;B: pyramidal, sp^3

(C) N: pyramidal, sp^3 ; B: planar, sp^2

(D) N: pyramidal, sp^3; B: tetrahedral, sp^3

Q.4 The nodal plane in the π-bond of ethane is located in ***(2002)***

(A) The molecular plane

(B) A plane parallel to the molecular plane

(C) A plane perpendicular to the molecular plane which bisects the carbon-carbon bond at right angle

(D) A plane perpendicular to the molecular plane which contains the carbon-carbon σ bond

Q.5 Which of the following molecular species has unpaired electron(s)? ***(2002)***

(A) N_2 (B) F_2 (C) O_2^- (D) O_2^{2-}

Q.6 Among the following, the molecule with the highest dipole moment is: ***(2003)***

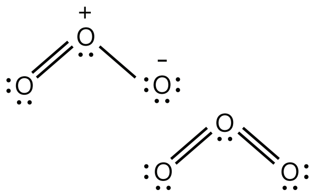
(A) CH_3Cl (B) CH_2Cl_2 (C) $CHCl_3$ (D) CCl_4

Q.7 Which of the following are isoelectronic and isostructural? NO_3^-,CO_3^{2-}, ClO_3^- , SO_3 ***(2003)***

(A) NO_3^-,CO_3^{2-} (B) SO_3,NO_3^-,

(C) ClO_3^-,CO_3^{2-} (D) CO_3^{2-}, SO_3

Q.8 Statement-I: The electronic structure of O_3 is



Statement-II: Structure is not allowed because octet around O cannot be expanded. ***(1998)***

Q.9 Statement-I: LiCl is predominantly a covalent compound

Statement-II: Electronegativity difference between Li and Cl is too small ***(1998)***

Q.10 Based on VSEPR theory, the number of 90° F—Br—F angles in BrF_5 is: ***(2010)***

Q.11 Which one of the following molecules is expected to exhibit diamagnetic behaviour ? ***(2013)***

(A) C_2 (B) N_2 (C) O_2 (D) S_2

Q.12 Stability of the species Li_2,Li_2^- and Li_2^+ increases in the order of: ***(2012)***

(A) $Li_2 < Li_2^+ < Li_2^-$ (B) $Li_2^- < Li_2^+ < Li_2$

(C) $Li_2 < Li_2^- < Li_2^+$ (D) $Li_2^- < Li_2 < Li_2^+$

Q.13 The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is : ***(2015)***

(A) Ion-ion interaction (B) Ion-dipole interaction

(C) London force (D) Hydrogen bond

JEE Advanced/Boards

Exercise 1

Q.1 In solid $NaCl^-$,one Na^+ is surrounded by six Cl^- ions. Find out total number of directional bonds formed by each Na^+ with Cl^- ions.

Q.2 Find out total number of $p\pi$–$d\pi$ bonds present in any one of its structures in case of PO_4^{3-}

Q.3 Find out total number of $p\pi$–$p\pi$ bonds present in ClO_3^-

Q.4 How many number of atomic orbitals are required, so that their mixing produces hybrid orbitals each having % of s-character equal to 17%?

Q.5 $AgNO_3$ gives a white precipitate with NaCl but not with CCl_4. Why?

Q.6 Using VSEPR theory identify the type of hybridisation and draw the structure of OF_2

Q.7 What should be the structure shape of the following as per VSEPR theory ?

(A) XeF_2 (B) XeF_4

(C) PBr_5 (D) OF_2

(E) I_3^- and (F) I_3^+

Q.8 The percent ionic character in HCl is 18.08. The observed dipole moment is 1.08 D. Find the inter-nuclear distance in HCl.

Q.9 Assuming that all the four valences of carbon atoms in propane point towards the corners of a regular tetrahedron, calculate the distance between the terminal carbon atom in propane. Given, C–C single bond length is 1.54 Å

Q.10 The dipole moment of HBr is 7.95 Debye and the intermolecular separation is 1.94×10^{-10}m. Find the % ionic character in HBr molecule.

Q.11 HBr has dipole moment 2.6×10^{-30} C–m. If the ionic character of the bond is 11.5 %, Calculate the interatomic spacing

Q.12 Dipole moment of LiF was experimentally determined and was found to be 6.32 D. Calculate percentage ionic character in LiF molecule Li -F bond length is 156 pm.

Q.13 A diatomic molecule has a dipole moment of 1.2 D. If bond length is 1.0 A, what percentage of an electronic charge exists on each atom.

Q.14 Which will have a higher boiling point, Br_2 or ICl, & Why ?

Q.15 Arrange noble gases in the increasing order of b.p. Xe, Ar, Ne, Kr, He, Ra

Exercise 2

Multiple Correct Choice Type

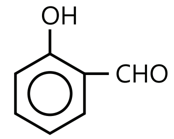
Q.1 Shape of NH_3 is very similar to :

(A) SeO_3^{2-} (B) CH_3^- (C) BH_3 (D) CH_3^+

Q.2 Which of the following have same shape as NH_2^+ ?

(A) CO_2 (B) $SnCl_2$ (C) SO_2 (D) $BeCl_2$

Q.3



(A) Has intermolecular H - bonding

(B) Has intramolecular H- bonding

(C) Has low boiling point

(D) Is steam-volatile

Q.4 Which of the following bonds/forces is/are weakest?

(A) Covalent bond (B) Vander Waals force

(C) Hydrogen bond (D) London force

Q.5 Which of the following factors are responsible for van der Waals forces?

(A) Instantaneous dipole-induced dipole interaction

(B) Dipole-induced dipole interaction and ion-induced dipole interaction

(C) Dipole-dipole interaction and ion induced dipole interaction

(D) Small size of molecule

Q.6 Atoms combine so that

(A) They can always attain stable configuration to that of nearest noble gas.

(B) They can attain stable configuration if possible, to that of nearest noble gas.

(C) Their potential energy can increase and hence bond energy may increase.

(D) Their potential energy can decrease and hence bond energy may increase.

Q.7 Which of the following statement(s) is/are correct regarding ionic compounds?

(A) They are good conductors of electricity at room temperature in aqueous solution.

(B) They are generally soluble in polar solvents.

(C) They consist of ions.

(D) They generally have high melting and boiling points.

Q.8 Which of the following compounds contain ionic, covalent and coordinate bonds?

(A) NH_4Cl (B) KCN (C) $NaBF_4$ (D) NaOH

Q.9 sp^3 hybridisation is in:

(A) AlH^-_4 (B) CH_3^- (C) ClO_2^- (D)NH_2^-

Q.10 Which of the following has (have) regular octahedral geometry :

(A) $SbCl_6^-$ (B) $SnCl^{2}_{6}{}^{-}$ (C)XCF_6 (D) $IO^{5}_{6}{}^{-}$

Q.11 Which of the following species are linear?

(A) ICl_2^- (B) I_3^- (C) N_3^- (D) ClO_2

Q.12 Which of the following compounds possesses zero dipole moment?

(A) Water (B) Benzene

(C) Carbon tetrachloride (D) Boron trifluoride

Q.13 Which of the following statements are correct?

(A) The crystal lattice of ice is formed by covalent as well as hydrogen bonds

(B) The density of water increases when heated from 0°C to 4°C

(C) Above 4°C, the thermal agitation of water molecules increases. Therefore, intermolecular distance increases and water starts expanding

(D) The density of water decreases from 0°C to a maximum at 4°C

Q.14 Which of the following compounds has bond angle as nearly 90°?

(A) NH_3 (B) H_2S (C) H_2O (D) SF_6

Q.15 For propadiene $H_2C_1=C_2=C_3H_2$, correct statement(s) is/are:

(A) Molecule is non planar

(B) Molecule is nonpolar

(C) Nodal plane of π-bond formed by C_1 and C_2 is perpendicular to that of formed by C_2 and C_3

(D) Nodal plane of π-bond formed by C_1 and C_2 is coplanar with that of formed by C_2 and C_3.

Q.16 Molecule(s) having both polar and non- polar bonds is/are

(A) O_2F_2 (B) S_2Cl_2 (C) N_2H_4 (D) S_2F_{10}

Q. 17 Which of the following are true?

(A) Vander Waals forces are responsible for the formation of molecular crystals

(B) Branching lowers the boiling points of isomeric organic compounds due to weaker Vander Waals forces of attraction

(C) In graphite, Vander Waals forces act between the carbon layers

(D) In diamond, Vander Waals forces act between the carbon layers

Q.18 Intermolecular hydrogen bonding increases the enthalpy of vaporization of a liquid due to the:

(A) Decrease in the attraction between molecules

(B) Increase in the attraction between molecules

(C) Decrease in the molar mass of unassociated liquid molecules

(D) Increase in the effective molar mass of hydrogen - bonded molecules

Q.19 Which of the following molecules have intermolecular hydrogen bonds?

(A) KH_2PO_4 (B) H_3BO_3

(C) $C_6H_5CO_2H$ (D) CH_3OH

Q.20 Which of the following have dipole moment?

(A) Nitrobenzene (B) p-chloronitrobenzene

(C) m-dichlorobenzene (D) o-dichlorobenzene

Comprehension Type

Paragraph 1: During the formation of a covalent bond each participating atom usually acquires electronic configuration to that of nearest noble gas, and the shared electron pair remains localized between the bonded nuclei. Besides these shared electrons there are certain electron pairs which remain localized on C.A. or on substituent or both and are called nonbonding or lone pair electrons.

Q.21 Which of the following species does / do not follow octet rule:

(A) Hypovalent (B) Hypervalent

(C) Odd electron molecules (D) All of the above

Q.22 In SO_3^{2-} the total number of lone pairs and bond pairs are respectively

(A) 18 and 4 (B) 9 and 8 (C) 9 and 4 (D) 7 and 4

Paragraph 2: Hybridisation is a theoretical concept, as state of hybridisation cannot be detected even by spectroscopically; unlike intermediates or transition state in various reactions, but it corrects the predictions which are based on simple overlapping of pure atomic orbitals. VSEPR theory predicts precisely shape and bond angle in a given molecule.

Q.23 In which pair of molecules bond angles are not same:

(A) CCl_4 and $SiCl_4$ (B) NH^{+}_{4} and NF_4^-

(C) ClF_6^- and SF_6 (D) None

Q.24 The molecules / ions which are planar as well as polar.

(A) BF_3, H_2O, HF, NH_2^- (B) $SnCl_2$, I_3^+, NH_2^-, IF_3

(C) $CO_3^-, I_3^-, SF_2, XeF_2$ (D) $NO_2^-, XeF_4, ICl_4, NH_2^+$

Q.25 The correct order of energy levels of hybrid orbitals.

(A)$sp > sp^2 > sp^3$ (B)$sp < sp^2 < sp^3$

(C)$sp^2 > sp^3 > sp$ (D)$sp^3 > sp > sp^2$

Paragraph 3: As one moves from sp hybridisation to sp^3, % of s-character in hybrid orbital decreases from 50% to 25% and p-character increases from 50% to 75% and in any hybrid orbital total % of s and p-character remains 100%. By increasing p-character the hybrid orbitals become elongated hence, their overlapping extent decreases that is results into weak bond energy also bond angle decreases.

Q.26 Statement-I: On decreasing s-character in hybrid orbitals, bond angle decreases.

Statement-II: p-orbitals are at 90° to one another.

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I.

(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true.

Q.27 The type of overlapping which produces bond of maximum bond energy is:

(A) sp^3 - 1s (B) sp^2 - 1s

(C) sp - 1s (D) All have same bond energy

Q.28 The molecule having bond pair in which % of s and p character is different from rest bond pairs.

(A) SiF_4 (B) BCl_3 (C) CF_3H (D) CCl_4

Q.29 State whether each statement is true or false. If false, write the correct statement.

(i) An element with low ionization potential is most likely to form a covalent bond with another element having a high electron gain enthalpy

(ii) Ionic interactions are always stronger than covalent bonds.

(iii) Two non-metal atoms are likely to form covalent

(iv) Ionic interactions are directional.

Q.30 State whether each statements is T or F, If F rectify

(i) All diatomic molecules are non-polar

(ii) All molecules having polar bonds are polar

(iii) The lone pairs of electrons do not contribute to the net dipole of a molecule.

(iv) The CH_2Cl_2 molecule may be polar or nonpolar depending on its geometry

(v) The net dipole in the water molecule is the resultant of its bond dipoles.

(vi) SO_2 is polar whereas CO_2 is non-polar.

(vii) NH_3 is less polar than NF_3

(viii) If a co-ordinate bond neutralizes charge separation of a polar bond, then dipole moment of the bond decreases.

Q.31 Fill in the blanks.

(i) π bonds are formed by the lateral overlap of a p-orbital with another _____ orbital in same phase.

(ii) Free rotation is possible if two atoms are bonded together only by a ______ bond.

(iii) The maximum number of σ bonds that can be formed between two atoms is _____

(iv) The repulsion between _______ is greater than the repulsion between two bonded pairs

(v) In nitro benzene the total number of bonded electrons equals _______

Paragraph 4: An ionic compound is formed by electrostatic attraction between gaseous cation(s) and gaseous anion(s) which are formed by complete removal and acceptance of electrons respectively

Q.32 The correct order of lattice energies of given ionic compounds is/are

(A) $LiF < NaF < KF < RbF < CsF$

(B) $MgO > CaO > SrO > BaO$

(C) $LiF > LiCl > LiBr > LiI$

(D) $MgO > MgF_2 > LiF > NaF$

Q.33 The correct statement about ionic bond/ compound is/are:

(A) One cation can attract more than one anion at a time and vice versa.

(B) One cation can attract only one anion at a time.

(C) Brittle character is caused by repulsion between same type of ions that come in contact by external force.

(D) They conduct electricity both in Molten & solid state.

Match the Columns

Q.34

Column I	Column II
(A) BrF_3	(p) One angle ≤90°
(B) TeF_5	(q) Central atom is sp^3d^2 hybridised
(C) IF_7	(r) Non planar
(D) XeF_4	(s) Polar

Q.35

Column I	Column II
(A) $I(CN)_2^-$,	(p) Having pπ–pπ bond and $\mu_D = 0$
(B) CO_3^{2-}	(q) Having pπ–dπ bond and $\mu_D = 0$
(C) XeO_2F_2	(r) Planar
(D) SOF_4	(s) Central atom is sp^3d

Q.36

Column I	Column II
(A) $H_2S_2O_5$ sp^3 hybridised	(p) Central atom is S
(B) $H_6B_2O_7^{2-}$	(q) M-O-M i.e., oxo linkage is present
(C) $H_4P_2O_6$	(r) M-M i.e., oxo linkage is absent
(D) $H_6Si_2O_7$	(s) Non planar

Assertion Reasoning Type

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I.

(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true.

Q.37 Statement-I: Higher the lattice energy greater will be the ease of formation of an ionic compound.

Statement-II: Lattice energy is evolved during formation of an ionic compound.

Q.38 Statement-I: Lattice energy of an ionic solid cannot be infinite

Statement-II: As inter ionic distance tends to zero, repulsive forces dominate over attractive forces.

Q.39 Statement-I: If all substituents and lone pairs are symmetrically placed around central atom, the molecule will be non- polar.

Statement-II: The direction of bond moment is from positive pole towards negative pole.

Q.40 Statement-I: During formation of coordinate bond, the acceptor accepts electron pair only when its octet has not been completed

Statement-II: Inspite of having completed octet, acceptor can accept electron pair provided it has empty 'd' orbitals.

Q.41 Statement-I: On the basis of overlapping of pure atomic orbital, the shape of NH_3 molecule will be trigonal pyramidal.

Statement-II: According to pure atomic orbital overlapping, each $\angle$ HNH is 90°.

Q.42 Statement-I: lone pair-lone pair repulsion is found to be greater than lone pair b.p. repulsion.

Statement-II: lone pair is under the influence of one nucleus while b.p. is under that of two nuclei.

Q.43 Statement-I: Phosphorus exists asP_4 not as P_2

Statement-II: Side wise overlapping between two 3p orbitals is less effective.

Q.44 Statement-I: Inorganic benzene ($B_3N_3H_6$) and organic benzene (C_6H_6) are isoelectronic & hence are iso-structural.

Statement-I: d_{C-C} in benzene is greater than d_{B-N} in inorganic benzene (borazine).

Q.45 Statement-I: Compounds, like graphite, H_3BO_3, boron nitride (inorganic graphite etc.), which are composed of layers in solid state have lubricating action.

Statement-II: Two dimensional layers are bonded to one another by weak Vander Waals forces.

Previous Years' Questions

Q.1 The species having bond order different from that in CO is ***(2007)***

(A) NO^- (A) NO^+ (C) CN^- (D) N_2

Q.2 Hyper-conjugation involves overlap of the following orbitals ***(2008)***

(A) $\sigma - \sigma$ (B) $\sigma - p$ (C) p - p (D) $\pi - \pi$

Q.3 Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is ***(2010)***

(A) 1 and diamagnetic (B) 0 and diamagnetic

(C) 1 and paramagnetic (D) 0 and paramagnetic

Q.4 The species having pyramidal shape is ***(2010)***

(A) SO_3 (B) BrF_3 (C) SiO_3^{2-} (D) OSF_2

Q.5 The linear structure assumed by ***(1991)***

(A) $SnCl_2$ (B) CS_2 (C) NO_2^+ (D) NCO^- (E) SO_2

Q.6 Which of the following have identical bond order? ***(1992)***

(A) CN^- (B) O_2^- (C) NO^+ (D) CN^+

Q.7 The molecules that will have dipole moment are ***(1992)***

(A) 2, 2-dimethyl propane

(B) trans-2-pentene

(C) cis-3-hexene

(D) 2, 2, 3, 3-tetramethyl butane

Q.8 Match the reactions in column I with nature of the reactions/type of the products in column II ***(2007)***

Column I	**Column II**
(A) $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) Redox reaction
(B) $CrO^{2-}_4 + H^+ \rightarrow$	(q) One of the products has trigonal planar structure
(C) $MnO_4^- + NO_2^- + H^+$	(r) Dimeric bridged tetrahedral metal ion
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s) Disproportionation

Q.9 Draw the shape of XeF_4 and OSF_4 according to VSEPR theory. Show the lone pair of electrons on the central atom. ***(2004)***

Q.10 On the basis of ground state electronic configuration arrange the following molecules in increasing O- O bond length order, KO_2, O_2, $O_2[AsF_6]$ ***(2004)***

Q.11 Predict whether the following molecules are iso-structural or not. Justify your answer. ***(2005)***

(i) NMe_3 (ii) $N(SiMe_3)_3$

Q.12 The shape of XeO_2F_2 molecules is ***(2012)***

(A) trigonal bipyramidal (B) square planar

(C) tetrahedral (D) see – saw

Q.13 According to Molecular Orbital Theory, ***(2016)***

(A) C_2^{2-} is expected to be diamagnetic

(B) O_2^{2+} is expected to have a longer bond length than O_2

(C) N_2^+ and N_2^- have the same bond order

(D) He_2^+ has the same energy as two isolated He atoms

Questions

JEE Main/Boards

Exercise 1

Q.2 Q.8 Q.16
Q.23 Q.27

Exercise 2

Q.1 Q.5 Q.10
Q.12 Q.29 Q.35

Previous Years' Questions

Q.1 Q.4 Q.10

JEE Advanced/Boards

EXERCISE 1

Q.2 Q.4 Q.10

Exercise 2

Q.9 Q.13 Q.19
Q.23 Q.26 Q.36
Q.38 Q.44

Previous Years' Questions

Q.2 Q.7 Q.8

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 C	**Q.2** D	**Q.3** C	**Q.4** A	**Q.5** D	**Q.6** A
Q.7 D	**Q.8** C	**Q.9** D	**Q.10** A	**Q.11** B	**Q.12** C
Q.13 A	**Q.14** D	**Q.15** C	**Q.16** A	**Q.17** A	**Q.18** B
Q.19 D	**Q.20** D	**Q.21** B	**Q.22** B	**Q.23** B	**Q.24** B
Q.25 D	**Q.26** D	**Q.27** D	**Q.28** A	**Q.29** D	**Q.30** D
Q.31 A	**Q.32** C	**Q.33** A	**Q.34** B	**Q.35** C	**Q.36** A

Previous Years' Questions

Q.1 A	**Q.2** B	**Q.3** A	**Q.4** A	**Q.5** C	**Q.6** A
Q.7 A	**Q.8** A	**Q.9** C	**Q.11** C	**Q.12** B	**Q.13** B

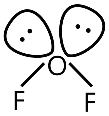
JEE Advanced/Boards

Exercise 1

Q.1 6 **Q.2** 1 **Q.3** 0 **Q.4** 6

Q.5 NaCl ionic compound which dissociate to give Cl^- ions where as CCl_4 cannot be ionised to give Cl^-

Q.6 Hybridisation of O : sp^3



Q.7 (a) Linear, (b) square planar, (c) T.B.P (d) bent, (e) linear, (f) bent **Q.8** 1.2 Å **Q.9** 2.514 Å

Q.10 85% **Q.11** 1.4 Å **Q.12** 84.5% **Q.13** 25% **Q.14** ICl

Exercise 2

Multiple Correct Choice Type

Q.1 A, B **Q.2** B, C **Q.3** B, C, D **Q.4** B, D **Q.5** A, B, C **Q.6** B, D

Q.7 A, B, C, D **Q.8** A, C **Q.9** A, B, C, D **Q.10** A, B, D **Q.11** A, B, C **Q.12** B, C, D

Q.13 A, B, C **Q.14** B, D **Q.15** A, D **Q.16** A, B, C, D **Q.17** A, B, C **Q.18** B, D

Q.19 A, B, C, D **Q.20** A, B, C, D

Comprehension Type

Q.21 A **Q.22** C **Q.23** D **Q.24** B **Q.25** B **Q.26** D

Q.27 C **Q.28** C **Q.29** (i) F, (ii) T , (iii) T, (iv) F

Q.30 B (i) F, (ii) F, (iii) F, (iv) F, (v) F, (vi)T , (vii)F, (viii) T

Q.31 (i) p-orbital (ii) σ-bond. (iii) 1, (iv) lp.lp & lp-bp (v) 36

Q.32 B, C, D **Q.33** A, C

Match the Columns

Q.34 A → p, s; B → p, q, r, s; C → p, r; D → p, q **Q.35** A → p, r, s; B → p, r; C → q, s; D → q, s

Q.36 A → p, r, s ; B → p, q, s; C → p, r, s; D → p, q, s

Assertion Reasoning Type

Q.37 A **Q.38** D **Q.39** B **Q.40** D **Q.41** A **Q.42** A

Q.43 A **Q.44** C **Q.45** A

Previous Years' Questions

Q.1 A **Q.2** B **Q.3** A **Q.4** D **Q.5** B, C, D **Q.6** A, C

Q.7 B, C **Q.8** A → p, s; B → r; C → p, q; D → p **Q.12** D **Q.13** A, C

Solutions

JEE Main/Boards

Exercise 1

Sol 1: Noble gases don't react with other atoms because of the stable ns^2 np^6 outer shell configuration. (Octet).

Sol 2: Two ions can attract each other in any direction but that is not possible in case of covalent bonds.

Ex. F_2. The bond must be along the orbital containing the unpaired e^-.

Sol 3: Lattice energy $E \propto \frac{q_1q_2}{r_+ + r_-}$.

$q_1q_2 = 4$ for MgO, whereas it's 1 for NaCl.

So Lattice energy of MgO is high.

Sol 4: As lattice energy $\propto \frac{q_1q_2}{r_+ + r_-}$ r_+ of Cs is very high compared to that of the Na. So, LE of NaCl is higher.

Sol 5: To conduct electricity, we need movement of charges. But in ionic solids. The ions are at fixed positions in a crystal lattice. So, it cannot conduct electricity.

Sol 6: Some elements show variable covalency because of presence of 2 or more stable O. S., some can show variable covalency because of presence of lone pairs. Ex. PCl_3, PCl_5

Sol 7: There is a force of attraction between ions of different molecules of ionic compounds. But there are no such interactions among most of covalent compounds.

Sol 8: Some covalent compounds are good conductors of electricity because of the presence of free e^-.

Sol 9: Ionic compounds are soluble in polar solvents where as covalent compounds are soluble in non-polar solvents.

Sol 10: Solubility depends on the interactions between solute and solvent. The large covalent molecules need not interact with all solvents. Ex. Starch is not soluble in water at normal temperature.

Sol 11: In metallic bond, the e^- are delocalized, so there isn't strong attraction between nucleus and those electrons. But, in covalent molecules, electrons are localised.

Sol 12: O, N, F are very highly electro-negative elements. So, they have partial –ve charge & H will have partial +ve charge.

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

Another condition is that, the element size must be small, so that the H-bonding is significant.

Sol 13: NH_3 is a better electron donor than H_2O because the electro-negativity of H_2O is high. H_3O^+ is less stable than NH_4^+.

Sol 14: Metals atoms are closely packed in a crystal due to the presence of metallic bonding.

Sol 15: Alkaline earth metals are stronger as each atom contributes $2e^-$ for metallic bonding whereas in IA metals, each atom contributes only 1 e^-. So, metallic bonding is weaker in IA elements. So they are softer compared to II A elements.

Sol 16: Cations with pseudo noble gas configuration have higher polarization power compared to noble gas configuration element. (of similar sizes).

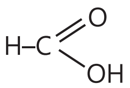
Sol 17: Due to high polarising power of Li^+, its compounds have high covalent character. So. solubility of Li^+ salts is high in non-polar solvents than in polar solvents.

Sol 18: The more the ionic character, more is the solubility in this case & hydration energy of $F^- > Cl^- > Br^- > I^-$. So, solubility of $AlF_3 > AlCl_3$ $AlBr_3 > AlI_3$

Sol 19: $X: \rightarrow Y$ is equivalent to $X^+ - Y^-$ So, it's called as semi-polar bond. $X^{\delta+} - Y^{\delta-}$

Sol 20: To form H-bonding, we need an electronegative atom which has δ– charge on it to attract $H^{\delta+}$. In H_2, there are no partial charges.

Sol 21:



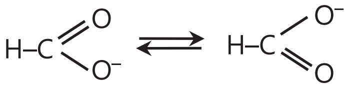
Single bond will be longer than double bond.

C–OH → 136pm.

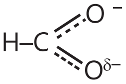
C=O → 123pm.

double bond is shorter because of presence of 2e⁻pairs between 2 atoms.

Sol 22:

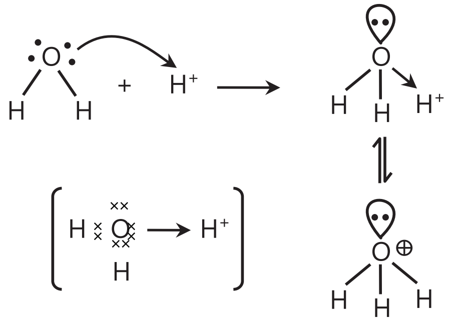


So, the resultant structure would be like



It is called Resonance

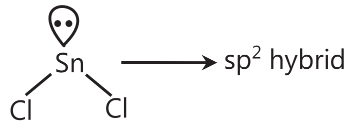
Sol 23: Lone pair on O.



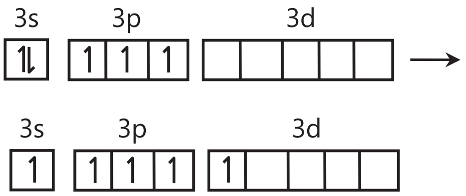
Sol 24: $MgCl_2$ has no lone pairs.

$Cl^- – Mg^{2+} – Cl^-$

In this structure, the repulsions would be minimum. But, Sn has a lone pair in $SnCl_2$



Sol 25: PCl_5 exists because of empty 3d orbitals of P.

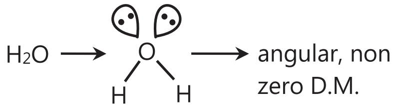


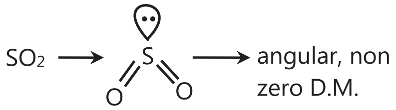
So, it can form 5 bonds.

But, outer orbit in N is 2. It doesn't have 2d orbitals.

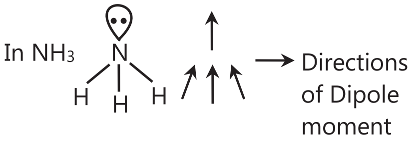
Sol 26: NH_3 has H-bonding but not HCl. It because of large size of Cl. H-bonding is HCl is very-very –very weak.

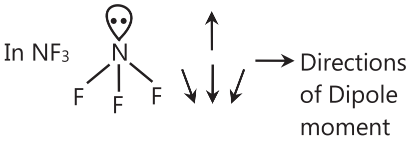
Sol 27: CO_2 is linear O=C=O. So, no dipole moment





Sol 28:



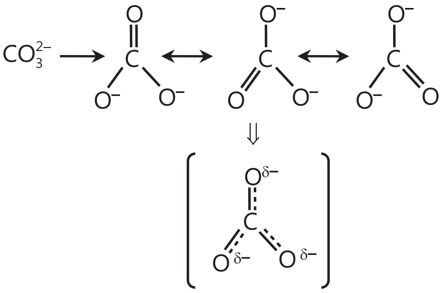


In NF_3, they are in opposite direction, so, they try to cancel each other.

In NH_3, all are in nearly same direction.

So, dipole moment of NH_3 is very high compared to NF_3.

Sol 29: Resonance



Sol 30: In NF_3, the highly electro negative F atom tries to take e⁻ toward it. So, N has δ+ charge. So, it's donation capacity decreases.

Exercise 2

Single Correct Choice Type

Sol 1: (C) Valencies of L, Q, P and R is -2, -1, +1, and +2 respectively so they will form P_2L, RL PQ, and RQ_2.

Sol 2: (D) The value of lattice energy depends on the charges present on the two ions and distance between them. It shell be high if charges are high and ionic radii are small.

Sol 3: (C) Sulphanilic acids have dipolar structure so their, ionic bond strength increases.

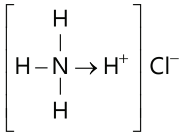
Sol 4: (A) As soon as the electronegativity increases, ionic bond strength increases.

Sol 5: (D) CaH_2, BaH_2, SrH_2 are ionic hydride.

Sol 6: (A) All have linear structure.

$O=C=O, Cl-Hg-Cl, H-C\equiv C-H$

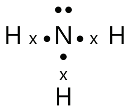
Sol 7: (D) NH_4Cl has covalent as well as ionic bond



$$\left[\begin{array}{c} H \\ | \\ H-N\rightarrow H^+ \\ | \\ H \end{array}\right] Cl^-$$

Sol 8: (C) Among the given species the bond dissociation energy of C – O bond is minimum in case of CO_3^{2-} by which C – O bond become more weaker in CO_3^{2-} or the bond order of CO_3^{2-} (1.33) is minimum so the bond become weaker.

Sol 9: (D) The electronic configuration of nitrogen is $N_7 = 1s^2, 2s^2, 2p^3$. It has 5 electrons in valency shell, hence in ammonia molecule it complete its octet by sharing of three electrons with three H-atoms, therefore, it has 8 electrons in its valence shell in ammonia molecule.



Sol 10: (A) The dipole moment of two dipole inclined at an angle θ is given by the equation $\mu = \sqrt{x^2+y^2+2xy\ \cos\theta}$, cos 90 = 0, Since, the angle increases from 90-180, the value of cos θ becomes more and more –ve and hence resultant decreases. Thus dipole moment is maximum, when $\theta = 90°$.

Sol 11: (B) Charge of $e^- = 1.6\times10^{-19}C$

Dipole moment of HBr $= 1.6\times10^{-30}C.m$

Interionic spacing = 1 Å = 1×10^{-10} m

% of ionic character in

$$HBr = \frac{\text{Dipole moment of HBr}\times100}{\text{Interspacing distance }\times q}$$

$$= \frac{1.6\times10^{-30}\times100}{1.6\times10^{-19}\times10^{-10}}$$

$$= 10^{-30}\times10^{29}\times100 = 0.1\times100 = 10\%$$

Sol 12: (C) Given, ionic charge $= 4.8\times10^{-10}$ esu and, ionic distance = 1 Å $= 10^{-8}$ cm

We know that

Dipole moment = Ionic charge × ionic distance

$= 4.8\times10^{-10}\times10^{-8}$

$= 4.8\times10^{-18}$ esu cm^{-1}

= 4.8 debye

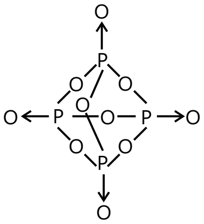
Sol 13: (A) % of ionic character =

$$\frac{\text{Experimental value of dipole moment}}{\text{Expected value of dipole moment}} = \frac{1.03}{6.12}\times100$$

$= 16.83\% \approx 17\%$

Sol 14: (D) We know that trisilylamine is sp^2 hybridized, therefore, $p\pi-d\pi$ bonding is possible due to the availability of vacant d-orbitals with silicon.

Sol 15: (C) Structure of P_4O_{10} is:



Each phosphorus is attached to 4-oxygen atoms.

Sol 16: (A) Hybridization of N in NH_3 is sp^3 that of Pt in $[PtCl_4]^{2-}$ is dsp^2 that of P in PCl_5 is sp^3d and that of B in BCl_3 is sp^2.

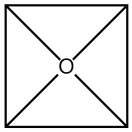
Sol 17: (A) s-character increases with increase in bold angle.

Hybridization	**s %**	**Angle**
sp	50	180°
sp^2	33.3	120°
sp^3	25	109°28'
sp^3d^1	20	90° and 120°

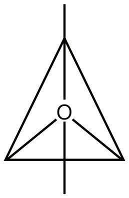
Sol 18: (B) Due to lp-lp repulsion, bond angle in H_2O is lower (145°5') than that in NH_3 (107°) and CH_4 (109°28'). BeF_2 on the other hand, has sp-hybridization and hence has a bond angle of 180°.

Sol 19: (D) The molecular shapes of SF_4, CF_4 and XeF_4 are different with 1, 0 and 2 lone pair of electrons on the central atom, respectively.

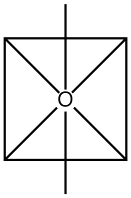
Sol 20: (D)



dsp^2 hybridization (Four 90^o angles between bp-bp)



sp^2 hybridization (Six 90^o angles between bp-bp)



sp^2 hybridization (Twelve 90^o angles between bp-bp)

Sol 21: (B) when bond forms between two atoms then their energy get lower than that of separate atoms because bond formation is an exothermic process.

Sol 22: (B) Nitrogen molecule has highest bond energy due to presence of triple bond.

Sol 23: (B)

$$O_2 = \sigma 1s^2, \sigma * 1s^2, \sigma 2s^2, \sigma * 2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2$$

$$\pi * 2p_y^1 = \pi * 2p_z^1$$

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{10-6}{2} = 2$$

Paramagnetic (Two unpaired electrons)

$$O_2^+ = \sigma 1s^2, \sigma * 1s^2, \sigma 2s^2, \sigma * 2s^2, \sigma * 2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2$$
$$\pi * 2p_y^1 = \pi * 2p_z^0 .$$

$$\text{BO} = = \frac{N_b - N_a}{2} = \frac{10-5}{2} = 2.5$$

Paramagnetic (One unpaired electron)

Sol 24: (B) Higher the bond order, shorter will be the bond-length, thus NO^+ having the higher bond order that is 3 as compared to NO having bond order 2, so NO^+ has shorter bond length.

Sol 25: (D) Hydrogen bonding increases the boiling point of compound.

Sol 26: (D) In case of water, five water molecules are attached together through four hydrogen bonding.

Sol 27: (D) Water is dense than ice because of hydrogen bonding interaction and structure of ice.

Sol 28: (A) A compound having maximum electronegative element will form strong hydrogen bond.

Sol 29: (D) We know that:

$$\text{Ionic character} = 16\left[E_A - E_B\right] + 3.5 \times \left[E_A - E_B\right]^2$$

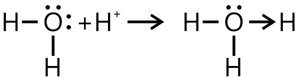
Or ionic characters = 72.24 %

Sol 30: (D)

$$O_2 : \sigma 1s^2, \sigma * 1s^2, \sigma 2s^2, \sigma * 2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2$$
$$\pi * 2p_y^1 = \pi * 2p_z^1$$

Total number of paired electrons = 14

Sol 31: (A)



$$H-\ddot{O}(H): + H^+ \longrightarrow H-\ddot{O}(H) \rightarrow H$$

Sol 32: (C) BeF_2^- does not show sp^3 hybridization because this compound is not formed.

Sol 33: (A) O_2^{2-} (total number of electrons = 18)

$$\sigma 1s^2, \sigma * 1s^2, \sigma 2s^2, \sigma * 2s^2, \sigma 2p_z^2, \pi 2p_x^{1+1} = \pi 2p_y^{1+1}$$

Sol 34: (B)

Molecules	Interaction
Benzene and ethanol	Dispersion force
Acetonitrile and acetone	dipole-dipole
KCl and water	ion-dipole
Benzene and carbon tetrachloride	Dispersion (London) force

Sol 35: (C) MCl_2 oxidation state M = +2

MCl_4 oxidation state of M = + 4

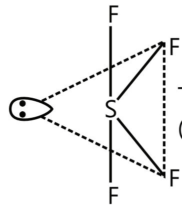
Higher the oxidation state, smaller the size.

Greater the polarizing power, greater the covalent characteristics.

Hence, MCl_4 is more covalent and MCl_2 is more ionic.

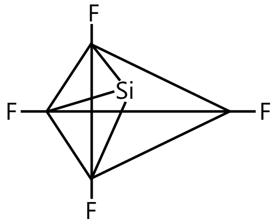
Sol 36: (A) SF_4 has distorted trigonal bipyramidal geometry, lone pair of electrons repels the axial bond pair and decreases the bond angle to 89° and 177° (from 90° and 180°)

SF_4

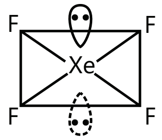


Trigonal bipyramidal (distorted)

SiF_4 Regular tetrahedral

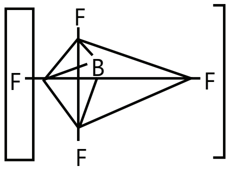


XeF_4



Square planar

BF_4



Tetrahedral

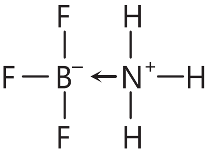
Previous Years' Questions

Sol 1: (A) All three have 14 electrons (iso-electronic) with bond order of three.

Sol 2: (B) NH_3 = sp^3,$[PtCl_4]^{2-}$ = dsp^2,

PCl_5= sp^3d, BCl_3 = sp^2

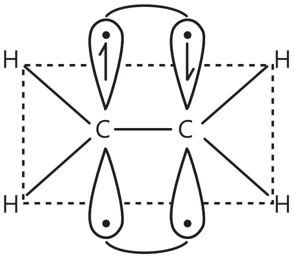
Sol 3: (A)



$$\begin{array}{ccc} & F & & H & \\ & | & & | & \\ F- & B^- & \leftarrow & N^+ & -H \\ & | & & | & \\ & F & & H & \end{array}$$

Both 'B' and 'N' are sp^3 tetrahedral

Sol 4: (A)



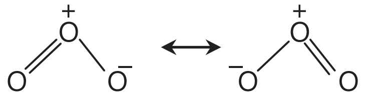
Pi bond is formed by the p-orbitals whose lobes have minima in the plane of molecule, hence molecular plane is the nodal plane of pi-bond.

Sol 5: (C) O_2^- has odd number (17) of electrons, therefore it must contain at least one unpaired electron.

Sol 6: (A) CH_3Cl has the highest dipole moment

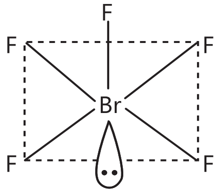
Sol 7: (A) NO_3^- and CO_3^{2-} both have 32 electrons, central atom sp^2 hybridised, triangular planar.

Sol 8: (A) Assertion is correct, given structure is one of the resonance structure of ozone



Sol 9: (C) Assertion is correct but reason is wrong. The covalency in LiCl is due to small size of Li^+ ion which brings about large amount of polarization in bond.

Sol 10:



Lone pair would push the Br—F bond pairs in upward directions and all Br—F bond angles will contract.

Sol 11: (C) O_2 is expected to diamagnetic in nature but actually it is paramagnetic.

Sol 12: (B) B.O. of $Li_2^+ = 0.5$

B.O. of $Li_2^- = 0.5$

Hence stability order $= Li_2^- < Li_2^+ < Li_2$

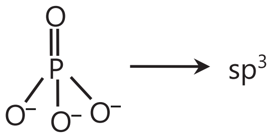
Sol 13: (B) Conceptual fact.

JEE Advanced/Boards

Exercise 1

Sol 1: In the lattice, each Na^+& Cl^- ion is surrounded by 6 oppositely charged ions. But, ionic bond is non-directional. So, no. of directional bonds = 6

Sol 2:

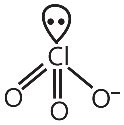


$p\pi - d\pi$ is in P =O as P is sp^3 hybridised.

So, s and p will from σ bonds

$\therefore$No. of $p\pi$-$d\pi$ bonds = 1

Sol 3: ClO_3^-



Cl ⟶ sp^3 hybrid

Sol 4: Let the total no. of orbital's be x.

$$\% \text{ of s character} = \frac{1}{x}\times 100\% \Rightarrow \frac{100}{x} = 17$$

$\Rightarrow x = 6.$

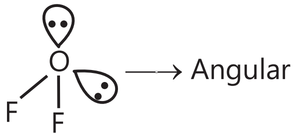
Sol 5: $AgNO_3 + NaCl \to AgCl\downarrow + NaNO_3$

AgCl is formed because of the presence of Ag^+ & Cl^- Ions in the solution.

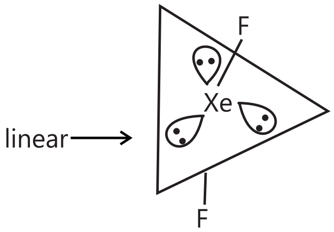
CCl_4 is covalent, So Ag^+ will not have Cl^- ion to form the precipitate.

Sol 6: $OF_2 \to x = \frac{1}{2}(V + M - C + A) = \frac{1}{2}(6 + 2) = 4$

i.e. sp^3.



Sol 7: (A) XeF_2 $x = \frac{1}{2}(V + M - C + A) = \frac{1}{2}(8 + 2)$ = 5(sp^3d)



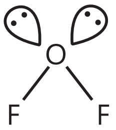
(B) $XeF_4 x = \frac{1}{2}(V + M - C + A) = \frac{1}{2}(8 + 4)$ planar, 2 LP.

$= 6 \to sp^3d^2$

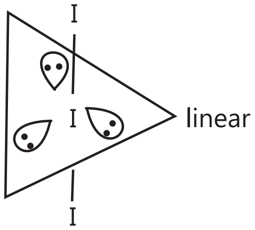
(C) PBr_5 $x = \frac{1}{2}(5 + 5) = 5 \to sp^3d$ Trigonal Bipyramidal

(D) $OF_2 \to \frac{1}{2}(6 + 2) = 4 \to sp^3$

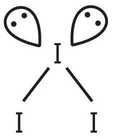
Angular



(E) $I_3^- \to \frac{1}{2}(7 + 2 + 1) = 5 \to sp^3d$



(F) $I_3^+ \to \frac{1}{2}(7 + 2 + 0 - 1) = 4 \to sp^3$

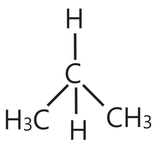


Sol 8: Partial charge = $4.8 \times \frac{18.08}{100} \times 10^{-18}$

$= 0.86 \times 10^{-18}$

$\therefore$ Distance (A°) = $\frac{DP}{\delta C} = \frac{1.08}{0.86} = 1.2$ A°

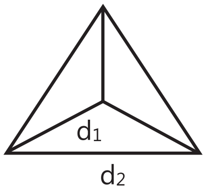
Sol 9:



$d_{c-c} = 1.54$ A°

$d_1 = d_{c-c}$ Cos(109.28° – 90°).

$d_2 = \sqrt{3}\, d_1 = 2.517$ A°



Sol 10: $\delta C = \frac{DM}{R} = \frac{7.95}{1.94\,A^\circ} = 4.097.$

$\therefore$ % of Ionic character = $\frac{4.098}{4.8} = 8.5$ i. e. 85%

Sol 11: $\Delta C = \frac{11.5}{100} \times 1.67 \times 10^{-17} = \mathbf{1.92 \times 10^{-20}}$

$d = \frac{2.6 \times 10^{-30}}{1.92 \times 10^{-20}} = 1.35\ A^\circ$

Sol 12: $\Delta C = \frac{6.32}{1.56} = 4.05.$

% of Ionic Character = $\frac{4.05}{4.8} = 0.844$ i. e. 84. 4%

Sol 13: $\Delta C = \frac{1.2}{1} = 1.2$

% of Ionic character = $\frac{1.2}{4.8} = 0.25$ i. e. 25%

Sol 14: ICl. Because of Vander waal's inductions between ICl molecular

$\overset{\delta+}{I} - \overset{\delta-}{CI} - - - \overset{\delta+}{I} - \overset{\delta-}{CI}$

Sol 15: Vander waal's forces ∝ Surface Area.

So, BP of He < Ne < Ar < Kr < Xe < Ra

Exercise 2

Multiple Correct Choice Type

Sol 1: (A, B) NH_3 similar to CH_3^-, SeO_3^{2-} [Pyramidal]

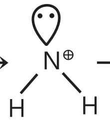
Sol 2: (B, C) $CO_2 \rightarrow$ Linear

Sn → Has a lone pair → Angular

$SO_2 \rightarrow$ Angular.

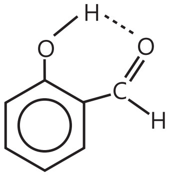
$BeCl_2 \rightarrow$ Linear.

$\overset{+}{N}H_2 \longrightarrow$



⟶ Angular

Sol 3: (B, C, D)



Intramolecular H-bonding.

So Low BP and steam volatile

Sol 4: (B, D) Vander waal's forces & London forces are very weak. They are due to induced charges.

Sol 5: (A, B, C) Possible chances for Vander waal's forces is interaction between Instantaneous, induced dipoles, Ion-induced dipoles. It's not due to sizes of molecules.

Sol 6: (B, D) Atoms combine to decrease their potential energy. In order to do this, they try to attain stable configurations (closest inert gas configuration).

Sol 7: (A, B, C, D) In case of ionic compounds

→ They are soluble in polar solvent.

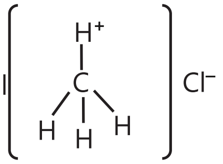
→ Good conductors in aqueous state

→ They have ions.

→ High BP and MP due to stable crystal lattice.

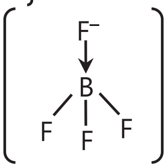
Sol 8: (A, C)

NH_4Cl



$KCNK^+[:C{\equiv}N:]^-$

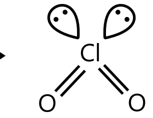
$NaBF_4Na^+$



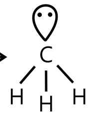
$NaOH \longrightarrow Na^+\ OH^-$

Sol 9: (A, B, C, D) $sp^3 \rightarrow AlH_4$

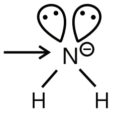
$sp^3\ ClO_2^- \longrightarrow$



sp^3 CH_3^- ⟶



sp^3 NH_3^- ⟶



Sol 10: (A, B, D) Sb → 5A group

$SbCl_6^-$ ✓Sb has 6e$^-$

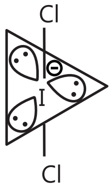
$SnCl_6^{2-}$ ✓

XeF_6 ✓ It has a lone pair

IO_6^{5-} ✓

Sol 11: (A, B, C)

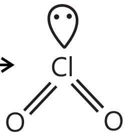
ICl_2^- ⟶



I_3^- → linear.

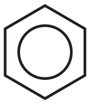
$N_3^- \rightarrow \overset{-}{N} = \overset{+}{N} = \overset{-}{N} \rightarrow$ linear.

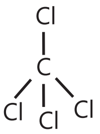
ClO_2 ⟶

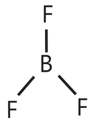


not linear

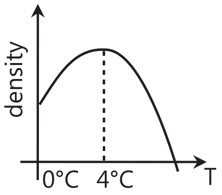
Sol 12: (B, C, D) Benzene. CCl_4, BF_3 NO dipole moment.

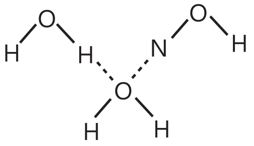






Sol 13: (A, B, C)





Above 4°C thermal agitation of H_2O, molecules increase.

∴ Intermolecular distance increases and water starts expanding.

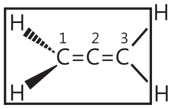
Sol 14: (B, D) H_2O, NH_3 → Sp^3 → nearly 109°

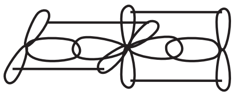
SF_6 → Sp^{3}d^2 →90°.

H_2S → no hybridization → Bond angle is the angle b/w 2 bond-forming p-orbital's i. e. 90°.

Sol 15: (A, D) Molecule is non-planar.

Nodal planes for $C_1 - C_2$ and $C_2 - C_3$ are perpendicular.

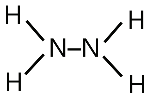




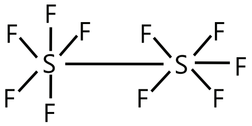
Sol 16: (A, B, C, D) O_2F_2 → F – O – O –F

S_2Cl_2 → Cl – S – S –Cl

N_2H_4 ⟶



S_2F_{10} ⟶



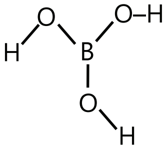
Sol 17: (A, B, C) In graphite, Vander waal's forces act b/w carbon layers. Linear compounds have larger surface area and large Vander waals forces.

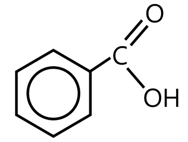
Sol 18: (B, D) Intermolecular H-bonding, increases the attraction b/w the molecules.

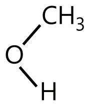
So, it increases the effective molar mass of H-bonded molecules.

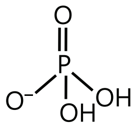
Sol 19: (A, B, C, D)

H_3BO_3 ⟶

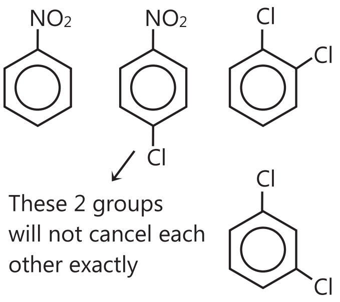








Sol 20: (A, B, C, D)



Comprehension Type

Sol 21: (A) Hypovalent → less than octet.

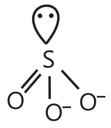
(E.g. $BeCl_2$)

Hyper valent → more than octet

(E.g. PCl_5)

Odd e^- → there will be unpaired e^-.

Sol 22: (C) SO_3^{2-}



LP = 1 + 2 + 3 + 3 = 9

BP = 4

Sol 23: (D) CCl_4, $SiCl_4$ → Tetrahedral.

NH_4^+, NF_4^+ → Tetrahedral.

ClF_6, SF_6 → Octahedral.

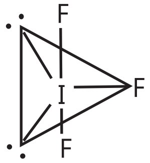
Sol 24: (B) BF_3 → Non polar

$SnCl_2$ → Angular, polar.

I_3^+ → Angular, polar.

NH_2^- → Angular, polar.

$IF_3 \longrightarrow$



T-shaped, polar

All of the above are planar

Sol 25: (B) P are more energetic than S.

(higher ℓ value for P).

∴ More is % of P, more is energy.

$sp < sp^2 < sp^3$.

Sol 26: (D) Generally, as s-character increases, the bond-angle increases. But few hybridizations have multiple bond-angles, where this rule becomes false.

Sol 27: (C) 1S sp, sp is more circular compared to sp^2,sp^3. So, overlap will be stronger.

Sol 28: (C) $SF_4 \rightarrow sp^3d$ $BCl_3 \rightarrow sp^2$

$CF_3H - sp^3$, $CCl_4 \rightarrow sp^3$

Sol 29: (i) False. Low IP → metals

High EA → Non-metals.

They tend to form Ionic bonds

(ii) True.

(iii) True.

(iv) False. Ionic interactions are non-directional.

Sol 30: (i) False. E.g. HCl.

(ii) False. E.g. CCl_4. C-Cl is polar, CCl_4 is non-polar.

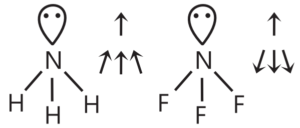
(iii) False. Net Dipole moment depends on both BP & LP.

(iv) False. CH_2Cl_2 is polar because of H it's tetrahedral structure. It can't be planar.

(v) False. Net dipole moment is due to BP and LP also

(vi) True. SO_2 is angular, CO_2 is linear

(vii) False.



DM of NH_3 = NF_3

(viii) True. As the amount of charges on adjacent atoms decrease, the dipole moment also decrease.

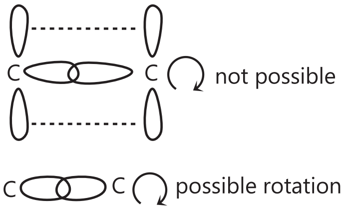
E.g. $A^+ + B^- \Leftrightarrow \overset{\delta+}{A} = :\overset{\delta-}{B}$

Sol 31: (i) π–bond → between 2p orbitals

(ii) Sigma bond.

If there are both σ & π bond, the due to the formation of π – bond, the 2 atoms become rigid.

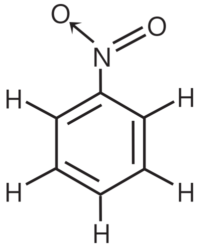
E.g.



(iii) 1. 2 atoms can't form 2 sigma bonds between each other because σ bond is formed along the inter-nuclear axis.

(iv) Repulsions between LP – LP > LP – BP > BP – BP. Because LP are closer to atom then BPs.

(v)



bond pairs so 36 bonded e^-

Sol 32: (B, C, D) Lattice energy $\propto \frac{q_1 q_2}{r_+ + r_-}$

$\therefore$ LE of MgO > CaO > SrO > BaO

LiF > LiCl > LiBr > LiI

$MgO > MgF_2 > LiF > NaF$ and

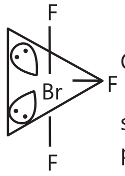
LiF > NaF > KF > RbF > CsF.

Sol 33: (A, C) Cation can attract more than 1 anion at a time (Ex. $MgCl_2$) Brittleness is due to repulsions between same charges. They don't conduct electricity in solid state (no charge movement).

Match the Columns

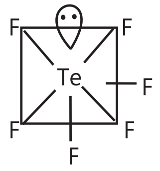
Sol 34: A → p, s; B → p, q, r, s; C → p, r; D → p, q

(A) BrF_3



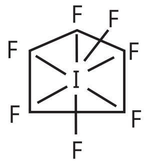
One angle
≤90°
sp^3d, planar,
polar

(B) TeF_5^-



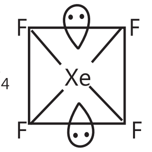
One angle
≤ 90°
polar sp^3d^2,
non-planar

(C) IF_7



angle ≤ 90°
non-polar,
non-planar
sp^3d^3

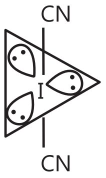
(D) XeF_4



1 angle ≤ 90°
non-polar,
planar sp^3d^2

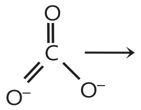
Sol 35: A → p, r, s; B → p, r; C → q, s; D → q, s

(A) $I(CN)_2^-$



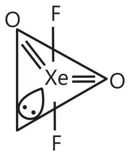
sp^3d, planar
$p\pi$-$p\pi$ in CN^-
$\mu_0 = 0$

(B) CO_3^{2-}



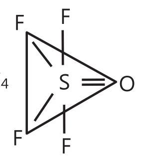
Planar
$p\pi$-$p\pi$
$\mu_D = 0$

(C) XeO_2F_2



sp^3d
$p\pi$-$d\pi$
bonding
$\mu_D \neq 0$

(D) SOF_4



sp^3d
$p\pi$-$d\pi$
bonding
$\mu_D \neq 0$

Sol 36: A → p, r, s; B → p, q, s; C → p, r, s; D → p, q, s

(A) $H_2S_2O_5$

O. S. of S →+4

So, M-O-M might not be present, s-sp^3, non polar

(B) $H_6B_2O_6^{2-}$ O. S. of B = $\frac{12-6}{2} = +3$ So, there must be M–O–M present, B → sp^3 non-polar

(C) $H_2P_2O_6$ M-O-M is absent, sp^3, non-polar

(D) $H_6Si_2O_7$ M-O-M is present, sp^3, non-polar

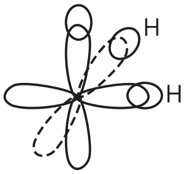
Assertion Reasoning Type

Sol 37: (A) As lattice energy is evolved during the formation of ionic bond, more is the lattice energy, more is the stability of the compound.

Sol 38: (D) When the atoms of opposite sign comes too close, their nucleus-nucleus repulsions & inter-electronic repulsions also increase. So, lattice energy cannot tend to Infinity.

Sol 39: (B) Direction of Bond moment is from positive pole towards negative pole. But it is not the reason for statement-I which is Symmetries molecular has no polarity.

Sol 40: (D) Statement-I is false because some acceptors accept e$^-$ pairs when there are empty d-orbitals. Ex. Complexes.

Sol 41: (A) 

All bond angles with 90° as angle b/w p orbitals is 90°.

Sol 42: (A) Repulsions of $\angle LP - \angle LP > \angle LP - BP$, because both ∠LP'S on single atom are close to each whereas BP will be shared by two atoms.

Sol 43: (A) The size of 3p orbitals is large compared to 2p. So, triple bond in P will be weaker compared to N. So, P_2 is not possible.

Sol 44: (C) d_{c-c} in benzene is not greater than

d_{B-N}

d_{c-c} = 1. 39 A°

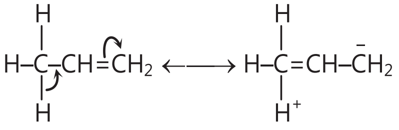
d_{B-N} = 1. 43 A° (factual knowledge).

Sol 45: (A) Most of the compared having layered structure have Vander waal's forces acting between the layers.

Previous Years' Questions

Sol 1: (A) The bond order of CO=3. NO$^+$, CN$^-$ and N_2 are isoelectronic with CO, have the same bond orders as CO. NO$^-$ (16e$^-$) has bond order of 2.

Sol 2: (B)



(I) (II)

I and II are hyperconjugating structures of propene and involves σ-electrons of C–H bond and p-orbitals of pi bond in delocalization.

Sol 3: (A) For molecules lighter than O_2, the increasing order of energies of molecular orbitals is:

$$\sigma 1s\, \overset{*}{\sigma}\, 1s \sigma\ 2s \overset{*}{\sigma} 2s \begin{bmatrix} \pi 2p_y \\ \pi 2p_z \end{bmatrix} \sigma 2p_x\, \overset{*}{\sigma}\, 2p_x \begin{bmatrix} \overset{*}{\pi} 2p_y \\ \overset{*}{\pi} 2p_z \end{bmatrix} \ldots\ldots\ldots$$

Where, $\pi 2p_y$ and $\pi 2p_z$ are degenerate molecular orbitals, first singly occupied and then pairing starts if Hund's rule is obeyed. If Hund's rule is violated in B_2, electronic arrangement would be:

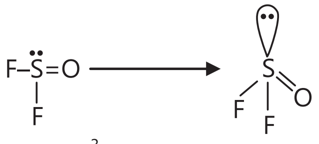
$$\sigma 1s^2\, \overset{*}{\sigma}\, 1s^2 \sigma\ 2s^2\, \overset{*}{\sigma} 2s^2 \begin{bmatrix} \pi 2p^2_y \\ \pi 2p_z \end{bmatrix} \ldots\ldots\ldots$$

No unpaired electron-diamagnetic.

Bond-order

$$= \frac{\text{bonding electrons} - \text{anit bonding electrons}}{2}$$

$$= \frac{6-4}{2} = 1$$

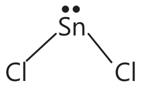
Sol 4: (D) 

S is sp^3 hybridised

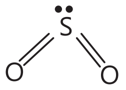
Pyramidal

SO_3 is planar (S is sp^2 hybridised), BrF_3 is T-shaped and SiO_3^{2-} is planar (Si is sp^{2}hybridised)

Sol 5: (B, C, D) $S=C=S$ Linear $\quad O=\overset{+}{N}=O$ Linear $\quad \overset{-}{O}-N\equiv O$ Linear



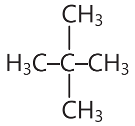
Bent



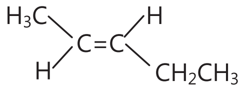
Bent

Sol 6: (A, C) CN^- and NO^+ are isoelectronic, have the same bond orders of 3

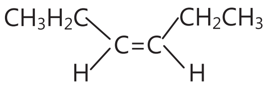
Sol 7: (B, C)



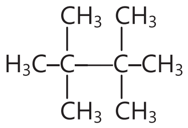
Symmetric, Non-polar



Polar



Polar



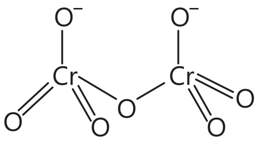
Symmetric, Non-polar

Sol 8: A → p, s; B → r; C → p, q; D → p

(A) In the reaction: $O_2^- \longrightarrow O_2 + O_2^{2-}$

Oxygen on reactant side is in $-\frac{1}{2}$ oxidation state. In product side, one of the oxygen is in zero oxidation state, ie, oxidized while the other oxygen is in –1 oxidation state, ie. reduced, Hence, in the above reaction, oxygen ($O^{-1/2}$) is simultaneously oxidized and reduced disproportionated.

(B) In acid medium, CrO_4^{2-} is converted into $Cr_2O_7^{2-}$ which is a dimeric, bridged tetrahedral:



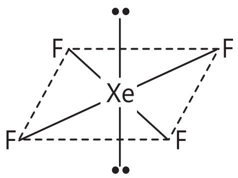
(C) $MnO_4^- + NO_2^- + H^+ \longrightarrow Mn^{2+} + NO_3^-$

The above is a redox reaction and a product NO_3^- has trigonal planar structure.

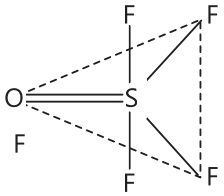
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \longrightarrow Fe^+ + NO$

The above is a redox reaction.

Sol 9:



Square planar



Trigonal bipyramidal

Sol 10: Bond orders : $O_2^- = 1.5$, $O_2 = 2$, $O_2^+ = 2.5$

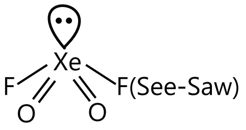
Bond lengths : $O_2^+ < O_2 < O_2^-$

Sol 11: No, (i) NMe_3 is pyramidal while (ii) $N(SiMe_3)_3$ is planar. In the later case, pπ — dπ back bonding between N and Si makes N sp^2hybridised.

Sol 12: (D) Shape of XeO_2F_2 is

Hybridisation $H = \frac{1}{2}V + M - C + A$

$$= \frac{1}{2}8 + 2 - 0 + 0 = 5(sp^3d)$$



Sol 13: (A, C)

(A) True.

(B) O_2^{2+} (Bond order = 3) O_2 (Bond order = 2)

Bond length: $O_2 > O_2^{2+}$.

(C) True.