

DAY FOUR

Chemical Bonding and Molecular Structure

Learning & Revision for the Day

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| <ul style="list-style-type: none">• Lewis Structure• Ionic Bond• Covalent Bond | <ul style="list-style-type: none">• Resonance• Valence Bond Theory (VBT)• Shapes of Molecules or VSEPR Theory | <ul style="list-style-type: none">• Molecular Orbital Theory of Homonuclear Diatomic Molecules• Metallic Bonding• Hydrogen Bonding |
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A **chemical bond** involves either the sharing or transfer of electrons to achieve a state of lower energy. The different types of chemical bonds formed between atoms are as follows:

- | | | |
|--------------------|--------------------|-----------------------|
| (i) Ionic bond | (ii) Covalent bond | (iii) Coordinate bond |
| (iv) Metallic bond | (v) Hydrogen bond | |

Kossel-Lewis Approach (Octet Rule)

- According to this approach, the atoms of different elements take part in chemical combination in order to complete their octet (to have eight electrons in the outermost or valence shell) or duplet (to have two valence electrons in some cases such as H, Li, Be etc.,) or to attain the nearest noble gas configuration.
- Limitations of octet rule is that it fails to predict the shape of the molecule and to explain the relative stability of molecules.

Exceptions of Octet Rule

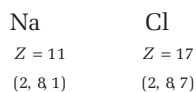
- Electron deficient compounds : BeCl_2 , BF_3 , AlCl_3 , etc.
- Hypervalent compounds : PCl_5 , SF_6 , IF_7 , H_2SO_4 , etc.
- Compounds of noble gases : XeF_2 , XeF_6 , XeF_4 , KrF_2 , etc.
- Odd electron molecules: NO , NO_2 , O_2 , O_3 , etc.

H_2^+ , He_2^+ , O_2 , NO , NO_2 , ClO_2 are some of the examples of stable molecules having odd electron bonds (bonds formed by sharing of usually one or three electrons).

Lewis Structure

This structure is also known as **Lewis dot structure** and it is used to represent the valence electrons.

- In this structure, only the outer shell electrons are involved and they are known as **valence electrons**.
- It may be represented by dot, cross or any other symbol.



Electron dot structure- Na^\bullet , $\times \text{Cl} \times$

- The molecules in which central atom has less than 8 electrons in their valence shell are known as **electron deficient** or **Lewis acids**. e.g. AlCl_3 , BF_3 etc.
- The molecules in which central atom has more than 8 electrons in their valence shell are known as **electron rich** or **Lewis bases**. e.g. PCl_5 , IF_7 , H_2SO_4 etc.

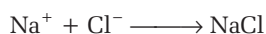
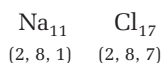
Formal charge (FC) on an atom in a **Lewis structure**

$$= \left[\begin{array}{l} \text{Total number of} \\ \text{valence electrons} \\ \text{in the free atom} \end{array} \right] - \left[\begin{array}{l} \text{Total number of} \\ \text{non - bonding} \\ \text{electrons} \end{array} \right] - \frac{1}{2} \left[\begin{array}{l} \text{Total number of} \\ \text{bonding electrons} \end{array} \right]$$

Ionic Bond

The attractive forces of **ionic bond** (i.e. electrostatic force of attraction) are developed between an electropositive atom (i.e. an atom with tendency to loose electron and convert into a cation) and an electronegative atom (i.e. an atom with tendency to gain electron and convert into an anion) due to complete transfer of electrons from former to later.

- Ionic bond is generally formed between the atoms having large difference in their electronegativity.
- Ionic bond is formed by the complete transfer of electron(s) from one atom to the other. e.g.



- Ionic bonds are just like electrostatic forces. These bonds are non-directional and also known as electrovalent bonds or polar bonds.
- Elements of group 1 and 2 on combining with halogens, oxygen and sulphur generally form ionic bonds.
- Bonding in compounds of transition metals (in lower oxidation state) is ionic with partial covalent character.

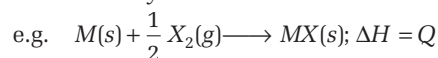
- The polar solvents like water have high value of dielectric constant. Due to this ions, get separated and solvated by solvent molecules. Non-polar solvents have very low dielectric constant.
- A number of ionic solids are almost insoluble in water because hydration energy is smaller than their lattice energy. Examples of water insoluble salts are AgCl , AgBr , AgI , Ag_2CrO_4 , PbSO_4 , BaSO_4 , CaCO_3 .

Various factors which favour the formation of ionic bonds are :

- Low ionisation energy of the electropositive element.
- High electron affinity of electronegative element.
- High lattice enthalpy

$$\text{Lattice enthalpy} \propto \frac{\text{charge on ions}}{\text{size of ions}}$$

- Calculation of Lattice Enthalpy** is carried out by Born-Haber cycle.



Here, ΔH = enthalpy change of the reaction

Q = heat of the reaction.

The above reaction includes the various steps:

- $M(s) \longrightarrow M(g); \Delta H_1 = S$ (S = Sublimation energy)
- $M(g) \longrightarrow M^+(g) + e^-; \Delta H_2 = I$ (I = Ionisation energy)
- $\frac{1}{2} X_2(g) \longrightarrow X(g); \Delta H_3 = \frac{D}{2}$ (D = Dissociation energy)
- $X(g) + e^- \longrightarrow X^-(g); \Delta H_4 = -E$ (E = Electron affinity)
- $M^+(g) + X^-(g) \longrightarrow MX(s); \Delta H_5 = -U$ (U = Lattice enthalpy)

Overall enthalpy change of the reaction is given by $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

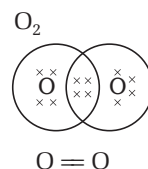
or alternatively, the above equation can be written as:

$$\Delta H = S + I + \frac{D}{2} - E - U \text{ or } U = S + I + \frac{D}{2} - E - \Delta H$$

- NOTE**
- Both lattice energy and hydration energy decreases with increase in ionic size.
 - If both anions and cations are of comparable size, the cationic radius will influence the lattice energy.

Covalent Bond

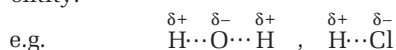
The bond formed by mutual sharing of equal electrons between two atoms of comparable electronegativity is known as covalent bond. e.g. formation of oxygen molecule O_2 , 2,6



The covalent bond can be divided into two types:

- (i) **Non-polar covalent bond** is formed between two homonuclear atoms, i.e. between atoms of exactly equal electronegativity. e.g. $\text{H}_2, \text{Cl}_2, \text{F}_2, \text{Br}_2$, etc.
- (ii) **Polar covalent bond** is formed between heteronuclear or with different electronegativity.

- The bond formed has partial ionic character as the electron pair is attracted by more electronegative entity.



- The greater the difference in electronegativity, higher is the polar nature. The relative order of electronegativity of some important elements is

	F	> O	> Cl	≈ N	> Br	> S	≈ C	≈ I	> H
Max. of all the elements known	4.0	3.5	3.0	2.8	2.5	2.1			

Polar Character of Covalent Bond

- Electronegativity difference between combining atoms = 1.7, then bond is 50% ionic and 50% covalent.
- Electronegativity difference > 1.7, ionic character in bond is more than 50%.
- Electronegativity difference < 1.7, ionic character in bond is less than 50%.
- Calculation of % ionic characters** is done by the following ways:

(i) Pauling equation

$$\% \text{ ionic character} = 18 (X_A - X_B)^{1.4}$$

(ii) Hannay and Smith equation

$$\% \text{ ionic character} = 16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

where, $(X_A - X_B)$ = electronegativity difference.

- Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character which is assessed on the basis of **Fajan's rule**. According to Fajan's rule,

(i) The magnitude of covalent character in an ionic bond depends upon the polarising power.

(ii) Higher the polarising power, more will be the covalent character. In general,

$$\text{Polarising power} \propto \frac{1}{\text{size of cation}} \propto \text{size of anion} \propto \text{charge on ions}$$

e.g. In between NaI and NaCl, NaI due to larger size of I^- ion has more covalent character.

FeCl_2 is less covalent than FeCl_3 because polarising power of Fe^{2+} is less than that of Fe^{3+} ion having smaller size and higher oxidation state.

- (iii) Cation with pseudo noble gas configuration has greater polarising power than the other noble gas configuration cation.

Bond Parameters

The covalent bonds are characterised by the some parameters which are as follows:

- (i) **Bond length** is the average distance between the centre of nuclei of the two bonded atoms in a molecule. It depends upon the size of atoms, hybridisation, steric effect, resonance, etc. Usually bond length of polar bond is smaller as compared to a non-polar bond. Bond length increases as the size of atom or orbital increases.

- (ii) **Bond order** is just like number of bond(s) between two atoms.

$$\text{Bond order} \propto \frac{1}{\text{bond length}}$$

Bond order \propto bond strength (stronger the bond, larger will be the bond dissociation energy and bond enthalpy.) e.g. CO_3^{2-} .

$$\text{Bond order} = 1 + \frac{\text{number of double bonds}}{\text{number of delocalisation position}}$$

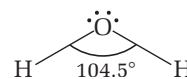
$$\text{CO}_3^{2-}, 1 + \frac{1}{3} = 1.33; \text{O}_3, 1 + \frac{1}{2} = 1.5; \text{SO}_4^{2-}, 1 + \frac{2}{4} = 1.5$$

- (iii) **Bond enthalpy** is the amount of energy required to break a particular bond in one mole of gaseous molecule.

Bond enthalpy \propto electronegativity

$$\propto \frac{1}{\text{size of atoms}} \propto \frac{1}{\text{number of lone pair of electrons}}$$

- (iv) **Bond angle** is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule or complex ion.



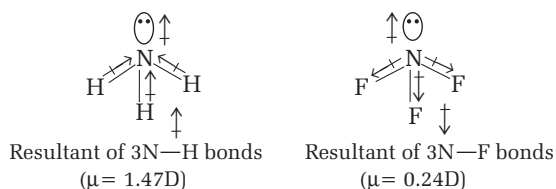
NOTE As the number of lone pair of electrons, on central atom increases, the repulsions between those of lone pair of electrons increases and therefore bond angle decreases.

- (v) **Dipole moment (μ)** is defined as the product of charge (q) and distance between the charges (d).

$$\mu = q \times d$$

Its unit in CGS system is Debye (D).

- Dipole moment is usually indicated by an arrow, having positive sign on the tail.
- A molecule is said to be polar, if the net dipole moment of the molecule is not equal to zero. e.g. NF_3 has lower dipole moment than NH_3 because resulting vector is towards the lone pair in NH_3 but in NF_3 it is opposite of lone pair.



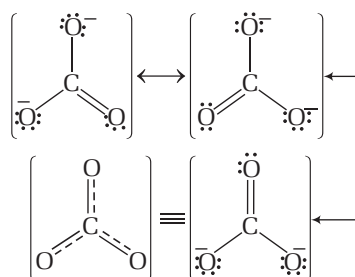
- Dipole moment is used to calculate the percentage ionic character of any molecule.

$$\% \text{ ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

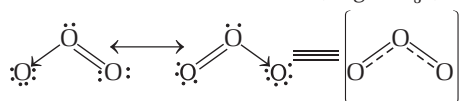
$$\text{where, } \mu_{\text{ionic}} = q \times d \quad [q = 4.8 \times 10^{-10} \text{ esu}]$$

Resonance

- There are certain molecules (benzene, ozone, nitric acid and many more), whose all the properties cannot be explained by a single structure it explain by two or more structures, called **resonating structures** and the phenomenon is called resonance .
- These structures are required to explain all the properties and the actual structure is intermediate of these structures.

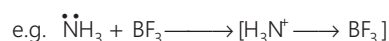


- The intermediate structure is called resonance hybrid and this phenomenon is called resonance, e.g. CO_3^{2-} , O_3 , etc.



- Resonance is shown by only those molecules which possess conjugate single and multiple bonds.
- It imparts stability to the molecule and hence, decreases its reactivity.
- Since, the electrons are not localised between any particular atoms and are uniformly distributed in the resonance hybrid.
- All the bonds are similar and are of equal bond lengths.
- The difference in the energy of a resonance hybrid and most stable structure (with least energy) is called **resonance energy**.

NOTE A type of covalent bond in which the shared pair of electrons are supplied by one atom (donor) and shared by both the atoms.



Donor Acceptor Complex

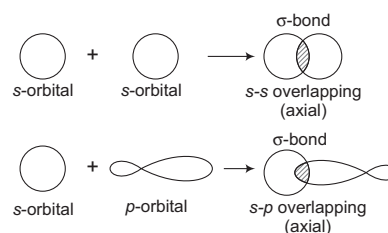
This bond is also called dative bond.

Valence Bond Theory (VBT) (Given by Heitler and London)

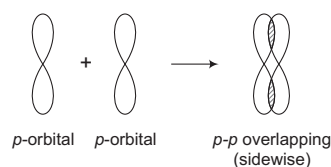
It explains bond formation in terms of overlapping of orbitals, e.g. the formation of H_2 molecule from two hydrogen atoms involves the overlapping of 1s-orbital of the two H-atoms, which are singly occupied. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer.

The overlapping of orbitals may results in two types of bonds given ahead.

- Sigma (σ) Bond** is the result of end to end overlapping or axial overlapping between s - s , p - p , s - p orbitals. Single bond is always sigma bond. The electron density accumulates between the centres of the atoms being bonded.



- Pi (π) Bond** is formed by incomplete overlapping of orbitals or in other words sidewise or parallel overlapping of p - p orbitals results in π -bond formation.



- Double bond has one σ -bond and one π -bond.
- Triple bond has two π -bonds and one σ -bond.

Concept of Hybridisation Involving s , p and d -orbitals

- It is defined as intermixing of atomic orbitals of nearly the same energy and resulting in the formation of new atomic orbitals same in number and identical in all respects (shape, energy and size).
- There are various types of hybridisation involving s , p and d orbitals, e.g. sp , sp^2 , sp^3 , sp^3d , etc.
- The hybridisation of the central atom of the molecule can be determined by $H = \frac{1}{2} [V + Y - C + A]$

Here, V = Number of valence shell electrons of the central metal

Y = Number of monovalent atom

C = Charge on cation

A = Charge on anion

NOTE

- (i) The d -orbital taking part in dsp^2 -hybridisation is $d_{x^2-y^2}$, while in sp^3d it is d_{z^2} and in sp^3d^2 , the two d -orbitals are d_{z^2} and $d_{x^2-y^2}$.
- (ii) In dsp^3 , if d_{z^2} is used, the shape is trigonal bipyramidal. If in dsp^3 , $d_{x^2-y^2}$ is used, the shape is square pyramidal.

Shapes of Molecules or VSEPR Theory

- According to this theory all valence shell electron pairs surrounding the central atom and arrange themselves in such a manner, so that they are as far away from each other as possible.
- If the central atom is surrounded by bond pairs of electrons only, the molecule is symmetrical or regular geometry.
- There are two types of electron pairs around the central atom; bonding electron pair (bp) and non-bonding electron pairs (lp). The strength of repulsion between the electron pairs varies as:

$$lp-lp > lp-bp > bp-bp$$

- The VSEPR theory is able to predict geometry of a large number of molecules.

Shapes (Geometry) of some simple molecules

Number of electron pairs	Geometry	Bond angle	Hybridisation	Example
2 bp	Linear	180°	sp	BeCl_2
3 bp	Trigonal planar	120°	sp^2	BF_3
2 $bp+1lp$	Angular	119.5°	sp^2	SO_2
4 bp	Tetrahedral	109° 28'	sp^3	CH_4
3 $bp+1lp$	Pyramidal	107° 48' and 102° 35'	sp^3, sp^3	NH_3, NF_3
2 $bp+2lp$	Angular or bent	≈ 104° 27' and ≈ 90°	sp^3, sp^3	$\text{H}_2\ddot{\text{O}}, \text{H}_2\ddot{\text{S}}$
5 bp	Trigonal bipyramidal	120° and 90°	sp^3d	PCl_5
4 $bp+1lp$	See-Saw	101° 36' and 86° 33'	sp^3d	$:\text{SF}_4, \text{IF}_4^+$
3 $bp+2lp$	T-shaped	87° 40'	sp^3d	$:\ddot{\text{Cl}}\text{F}_3$
2 $bp+3lp$	Linear	180°	sp^3d	$:\ddot{\text{X}}\text{eF}_2, \text{I}_3^-$
6 bp	Octahedral	90°	sp^3d^2	SF_6
5 $bp+1lp$	Square pyramidal	84° 30'	sp^3d^2	$:\text{XeOF}_4, \text{BrF}_5$
4 $bp+2lp$	Square planar	90°	sp^3d^2	$:\ddot{\text{X}}\text{Cl}_4^-, \ddot{\text{X}}\text{eF}_4$
7 bp	Pentagonal bipyramidal	72°, 90°	sp^3d^3	IF_7

Molecular Orbital Theory of Homonuclear Diatomic Molecules (Given by Hund and Mulliken)

- This theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.
- Formation of molecular orbitals involve linear combination of atomic orbitals. Molecular orbitals formed are of two types:
 - Bonding MO which are of lower energy are represented as σ or π . These make bond stronger.
 - Antibonding MO which are of higher energy, are represented as σ^* or π^* . These reduces the stability of molecules.
- The electronic configuration of molecular orbitals (MO) is written in the following manner.

- (i) For electrons greater than 14, e.g. O_2, F_2 , etc.

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, (\pi 2p_x \approx \pi 2p_y), (\pi^* 2p_x \approx \pi^* 2p_y), \sigma^* 2p_z$$

- (ii) For electrons less than or equal to 14, e.g. $\text{B}_2, \text{C}_2, \text{N}_2$, etc.

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, (\pi 2p_x \approx \pi 2p_y), \sigma 2p_z, (\pi^* 2p_x \approx \pi^* 2p_y), \sigma^* 2p_z$$

- Bond order for diatomic molecule or ions,

$$\text{BO} = \frac{N_b - N_a}{2}$$

N_b = number of bonding electrons

N_a = number of antibonding electrons

- The molecule is stable if $N_b > N_a$, i.e. if bond order is positive.
- The molecule is unstable if $N_b < N_a$ or $N_b = N_a$, i.e. if the bond order is negative or zero.
- Magnetic behaviour of a molecule can also be conveyed from its electronic configuration. If any unpaired electron is present in electronic configuration the molecule is paramagnetic and in opposite conditions, molecule is diamagnetic.

$$\text{Magnetic moment} = \sqrt{n(n+2)} \text{ BM}$$

where, n = number of unpaired electrons

(BM = Bohr Magnetron)

Metallic Bonding

The attractive force which hold together the constituent particles in a metal is known as **metallic bonding**. The electron sea model and band model have been proposed to explain metallic bonding.

- (i) **According to electron sea model**, metallic crystal consists of positive kernels packed together as closely as possible in a regular geometric pattern and immersed in a sea of mobile electrons.
- (ii) **According to band model** is based on molecular, orbital theory. Atomic orbitals of atoms with same energy and same symmetry overlap to form energy bands.

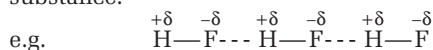
The highest occupied energy band is valence band and lowest unoccupied energy band is conduction band. The gap between the top of the valence band and the bottom of the conduction band is called energy gap.

Hydrogen Bonding

It can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. Cl has same electronegativity as nitrogen but it does not form strong H-bonds due to its larger size. Strongest H-bond exist in KHF_2 . It is of two types:

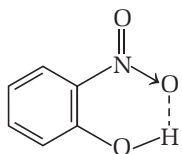
There are two types of H-bonds.

- (i) **Intermolecular hydrogen bonding** is formed between the different molecules of same substance or different substance.



Intermolecular H-bonding decreases the volatility increases the boiling point and increases the viscosity and surface tension of a substance.

- (ii) **Intramolecular hydrogen bonding** is formed within the same molecule. e.g. intramolecular H-bonding increases the volatility (decreases the boiling point) of the compound and also decreases its solubility in water.



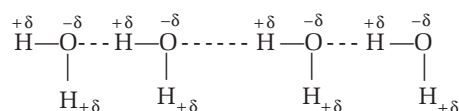
Intramolecular H-bonding in *o*-nitrophenol

- Boiling point of H_2O is more than that of HF because number of H-bonds formed by H_2O is more than that by HF.
- Hydrogen bonding is strongest when the bonded structure is stabilised through resonance.

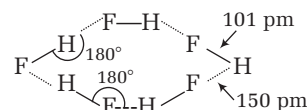
Effects of H-Bonding

The characteristics of H-bonding in a particular matter. Some of the matters on which there is some effects of hydrogen bonding are given below:

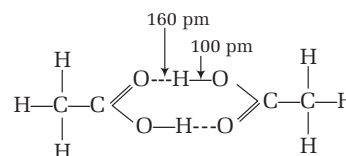
- Due to polar nature of H_2O , there is association of water molecules giving a liquid state of abnormally high boiling point.



- When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). Due to this, volume of ice is greater than liquid water and thus, ice is lighter than water.
- In the gaseous state, several polymeric forms of HF molecules exist in which the monomers are held to gether through H-bonding. e.g.,



- Carboxylic acid dimerises in gaseous state due to H-bonding. The dimerisation of carboxylic acids is given below:



DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

- 1 Which of the following compounds does the central atom follow the octet rule?
 (a) SCl_2 (b) XeOF_2
 (c) XeF_4 (d) AlCl_3
- 2 In the Lewis dot structure, the electrons which complete an octet but are not located between two atoms are referred to as
 (a) lone pairs (b) excess electrons
 (c) bonding pairs (d) delta minus electrons
- 3 Which of the following is least likely to behave as Lewis base?
 → CBSE-AIPMT 2011
 (a) NH_3 (b) BF_3
 (c) OH^- (d) H_2O
- 4 In which of the following sets do all the compounds have ionic bonds only?
 (a) CsBr , BaBr_2 , SrO (b) CsF , BF_3 , NH_3
 (c) Al_2O_3 , CaO , SO_2 (d) NaCl , NCl_3 , CCl_4
- 5 An ionic compound M^+X^- is most likely to be formed from A and B when
 (a) electronegativity of X is low
 (b) ionisation energy of M is low
 (c) ionisation energy of B is low
 (d) electron gain enthalpy of B is low
- 6 Which of the following elements forms predominantly covalent compounds as compared to other elements which form ionic compounds?
 (a) Mg (b) Ca
 (c) Be (d) Sr
- 7 I_4O_9 is a/an
 (a) ionic compound (b) covalent compound
 (c) coordinate compound (d) double salt
- 8 The correct statement for the molecule, CsI_3 is
 (a) It is a covalent molecule
 (b) It contains Cs^+ and I_3^- ions
 (c) It contains Cs^+ and I^- ions
 (d) It contains Cs^+ , I^- and lattice I_2 molecule
- 9 Which contains both polar and non-polar covalent bonds?
 (a) NH_4Cl (b) H_2O_2
 (c) HCN (d) CH_4
- 10 Which among the following are non-polar molecules?
 I. NCl_3 II. SO_3 III. PCl_5
 (a) Only I (b) Only II
 (c) Both I and II (d) Both II and III
- 11 NF_3 and BF_3 are both covalent compounds, but NF_3 is polar whereas BF_3 is non-polar. This is due to the reason
 (a) BF_3 is planar but NF_3 is pyramidal
 (b) B—F bonds are non-polar, while N—F bonds are polar
 (c) B is a metal while nitrogen is a gas in uncombined state
 (d) atomic size of boron is larger than that of nitrogen
- 12 The covalent bond forms when the difference in the value of electronegativities should be
 (a) more than 1.7
 (b) 1.7 or more
 (c) equal to or less than 1.7
 (d) None of the above
- 13 The formal charge of the O-atoms in the ion
 $[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^+$ is
 (a) -2 (b) -1 (c) 0 (d) +1
- 14 Among CaH_2 , BeH_2 , BaH_2 , the order of ionic character is
 (a) $\text{BeH}_2 < \text{BaH}_2 < \text{CaH}_2$ (b) $\text{CaH}_2 < \text{BeH}_2 < \text{BaH}_2$
 (c) $\text{BeH}_2 < \text{CaH}_2 < \text{BaH}_2$ (d) $\text{BaH}_2 < \text{BeH}_2 < \text{CaH}_2$
- 15 In the case of alkali metals, the covalent character decreases in the order
 → CBSE-AIPMT 2009
 (a) $\text{MCl} > \text{MI} > \text{MBr} > \text{MF}$ (b) $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$
 (c) $\text{MF} > \text{MCl} > \text{MI} > \text{MBr}$ (d) $\text{MI} > \text{MBr} > \text{MCl} > \text{MF}$
- 16 Among the following is maximum covalent character is shown by which of the following the compound?
 (a) FeCl_2 (b) SnCl_2 (c) AlCl_3 (d) MgCl_2
- 17 The covalent bond length is shortest in which of the following bonds?
 (a) $\text{C}—\text{O}$ (b) $\text{C}—\text{C}$
 (c) $\text{C} \equiv \text{N}$ (d) $\text{O}—\text{H}$
- 18 The correct order of increasing bond length of $\text{C}—\text{H}$, $\text{C}—\text{O}$, $\text{C}—\text{C}$ and $\text{C}=\text{C}$ is
 → CBSE-AIPMT 2011
 (a) $\text{C}—\text{C} < \text{C}=\text{C} < \text{C}—\text{O} < \text{C}—\text{H}$
 (b) $\text{C}—\text{O} < \text{C}—\text{H} < \text{C}—\text{C} < \text{C}=\text{C}$
 (c) $\text{C}—\text{H} < \text{C}—\text{O} < \text{C}—\text{C} < \text{C}=\text{C}$
 (d) $\text{C}—\text{H} < \text{C}=\text{C} < \text{C}—\text{O} < \text{C}—\text{C}$
- 19 The correct order in which the O—O bond length increases in the following is
 (a) $\text{H}_2\text{O}_2 < \text{O}_2 < \text{O}_3$ (b) $\text{O}_3 < \text{H}_2\text{O}_2 < \text{O}_2$
 (c) $\text{O}_2 < \text{O}_3 < \text{H}_2\text{O}_2$ (d) $\text{O}_2 < \text{H}_2\text{O}_2 < \text{O}_3$
- 20 The correct order of $\text{C}—\text{O}$ bond length among CO , CO_3^{2-} , CO_2 is
 (a) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$ (b) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$
 (c) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$ (d) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$



21 Maximum bond angle at nitrogen is present in which of the following? → CBSE-AIPMT 2015

- (a) NO_2 (b) NO_2^- (c) NO_2^+ (d) NO_3^-

22 The correct order of increasing bond angles in the following species is → CBSE-AIPMT 2010

- (a) $\text{Cl}_2\text{O} < \text{ClO}_2 < \text{ClO}_2^-$ (b) $\text{ClO}_2 < \text{Cl}_2\text{O} < \text{ClO}_2^-$
(c) $\text{Cl}_2\text{O} < \text{ClO}_2^- < \text{ClO}_2$ (d) $\text{ClO}_2^- < \text{Cl}_2\text{O} < \text{ClO}_2$

23 Consider the molecules CH_4 , NH_3 and H_2O . Which of the given statements is false? → NEET 2016, Phase I

- (a) The $\text{H}-\text{O}-\text{H}$ bond angle in H_2O is larger than $\text{H}-\text{C}-\text{H}$ bond angle in CH_4
(b) The $\text{H}-\text{O}-\text{H}$ bond angle in H_2O is smaller than the $\text{H}-\text{N}-\text{H}$ bond angle in NH_3
(c) The $\text{H}-\text{C}-\text{H}$ bond angle in CH_4 is smaller than the $\text{H}-\text{N}-\text{H}$ bond angle in NH_3
(d) The $\text{H}-\text{C}-\text{N}$ bond angle in CH_4 , the $\text{H}-\text{N}-\text{H}$ bond angle in NH_3 and the $\text{H}-\text{O}-\text{H}$ bond in H_2O are all greater than 90°

24 The correct decreasing order of dipole moment in CH_3Cl , CH_3Br and CH_3F is

- (a) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br}$ (b) $\text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$
(c) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br}$ (d) $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{F}$

25 Which of the following molecules has the maximum dipole moment? → CBSE-AIPMT 2014

- (a) CO_2 (b) CH_4 (c) NH_3 (d) NF_3

26 The correct order of increasing bond angles in the following triatomic species is → CBSE-AIPMT 2014

- (a) $\text{NO}_2^- < \text{NO}_2^+ < \text{NO}_2$ (b) $\text{NO}_2^- < \text{NO}_2 < \text{NO}^+2$
(c) $\text{NO}_2^+ < \text{NO}_2 < \text{NO}_2^-$ (d) $\text{NO}_2^+ < \text{NO}_2^- < \text{NO}_2$

27 Which combination is best explained by the coordinate covalent bond?

- (a) $\text{H}^+ + \text{H}_2\text{O}$ (b) $\text{Cl} + \text{Cl}$ (c) $\text{Mg} + \frac{1}{2} \text{O}_2$ (d) $\text{H}_2 + \text{I}_2$

28 What is the nature of the bond between B and O in $(\text{C}_2\text{H}_5)_2\text{OBH}_3$?

- (a) Covalent (b) Coordinate covalent
(c) Ionic bond (d) Banana shaped bond

29 The compound containing coordinate bond is

- (a) SO_3 (b) SO_2
(c) H_2SO_4 (d) All of these

30 In which of the following compounds resonance does not occur?

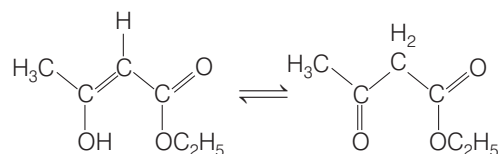
- (I) H_2O (II) SiO_2 (III) SO_3 (IV) CO_2
The correct answer.

- (a) Both I and IV (b) Both I and II
(c) Both III and IV (d) I, II and IV

31 Which of the following species contains equal number of σ and π bond? → CBSE-AIPMT 2015

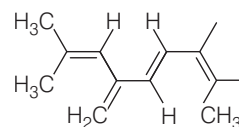
- (a) HCO_3^- (b) XeO_4
(c) $(\text{CN})_2$ (d) $\text{CH}_2(\text{CN})_2$

32 The enolic form of ethyl acetoacetate as below has



- (a) 18 σ bonds and 2 π bonds
(b) 16 σ bonds and 1 π bond
(c) 9 σ bonds and 2 π bonds
(d) 9 σ bonds and 1 π bond

33 The total number of π bond electrons in the following structure is



- (a) 4 (b) 8
(c) 12 (d) 16

34 Which one of the following molecules contains no π -bond? → NEET 2013

- (a) H_2O (b) SO_2 (c) NO_2 (d) CO_2

35 The hybridisation scheme for the central atom includes a d -orbital contribution in

- (a) I_3^- (b) PCl_3
(c) NO_3^- (d) H_2Se

36 The hybridisations of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ respectively are → NEET 2016, Phase II

- (a) sp, sp^3 and sp^2 (b) sp^2, sp^3 and sp
(c) sp, sp^2 and sp^3 (d) sp^2, sp and sp^3

37 In which one of the following species, the central atom has the type of hybridisation which is not the same as that present in the other three? → CBSE AIPMT 2010

- (a) SF_4 (b) I_3^- (c) SbCl_5^{2-} (d) PCl_5

38 Which one of the following pairs is isostructural (i.e. having the same shape and hybridisation)?

→ CBSE-AIPMT 2012

- (a) BCl_3 and BrCl_3 (b) NH_3 and NO_3^-
(c) NF_3 and BF_3 (d) BF_4^- and NH_4^+

39 In the structure of ClF_3 , the number of lone pairs of electrons on central atom Cl is → NEET 2018

- (a) four (b) two (c) one (d) three

40 Which of the following pairs of ions is isoelectronic and isostructural? → NEET 2016, Phase II

- (a) $\text{CO}_3^{2-}, \text{NO}_3^-$ (b) $\text{ClO}_3^-, \text{CO}_3^{2-}$
(c) $\text{SO}_3^{2-}, \text{NO}_3^-$ (d) $\text{ClO}_3^-, \text{SO}_3^{2-}$

41 Which of the following pairs of ions are isoelectronic and isostructural? → CBSE-AIPMT 2015

- (a) $\text{CO}_3^{2-}, \text{SO}_3^{2-}$ (b) $\text{ClO}_3^-, \text{CO}_3^{2-}$
(c) $\text{SO}_3^{2-}, \text{NO}_3^-$ (d) $\text{ClO}_3^-, \text{SO}_3^{2-}$



42 Predict the correct order among the following.

→ NEET 2016, Phase I

- (a) lone pair-long pair > bond pair-bond pair > lone pair-bond pair
(b) bond pair-bond pair > long pair-bond pair > lone pair-lone pair
(c) lone pair-bond pair > bond pair-bond pair > lone pair-lone pair
(d) lone pair-long pair > lone pair-bond pair > bond pair-bond pair

43 The correct bond order in the following species is

→ CBSE-AIPMT 2015

- (a) $O_2^{2+} < O_2^+ < O_2^-$ (b) $O_2^{2+} < O_2^- < O_2^+$
(c) $O_2^{2+} < O_2^- < O_2^{2+}$ (d) $O_2^- < O_2^+ < O_2^{2+}$

44 Which of the following has a bond order 1.75?

- (a) ClO_3^- (b) ClO_4^- (c) NO_3^- (d) CO_3^{2-}

45 The pair of species with the same bond order is

→ CBSE-AIPMT 2012

- (a) O_2^{2-} , B_2 (b) O_2^+ , NO^+ (c) NO , CO (d) N_2 , O_2

46 Bond order of 1.5 is shown by

→ CBSE-AIPMT 2012

- (a) O_2^+ (b) O_2^- (c) O_2^{2-} (d) O_2

47 Which of the following order of energies of molecules orbitals of N_2 is correct ?

- (a) $(\pi 2p_y) < (\sigma 2p_z) < (\pi 2p_x) \approx (\pi 2p_y)$
(b) $(\pi 2p_y) > (\sigma 2p_z) > (\pi 2p_x) \approx (\pi 2p_y)$
(c) $(\pi 2p_y) < (\sigma 2p_z) > (\pi 2p_x) \approx (\pi 2p_y)$
(d) $(\pi 2p_y) > (\sigma 2p_z) < (\pi 2p_x) \approx (\pi 2p_y)$

48 The boiling point of ethanol is higher than that of dimethyl ether due to presence of

- (a) hydrogen bonding in ethanol
(b) hydrogen bonding in dimethyl ether
(c) CH_3 group in ethanol
(d) CH_3 group in dimethyl ether

Direction (Q. Nos. 49-50) Each of these questions contains two statements : Assertion and Reasons. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

- (a) Assertion is true, Reason is true; Reason is the correct explanation for Assertion
(b) Assertion is true, Reason is true; Reason is not a correct explanation for Assertion
(c) Assertion is true, Reason is false
(d) Both Assertion and Reason are false

49 **Assertion (A)** All F—S—F angle in SF_4 is greater than 90° but less than 180° .

Reason (R) The lone pair-bond pair repulsion is weaker than bond pair-bond pair repulsion.

50 **Assertion (A)** Among the two H — O bonds in H_2O molecule, the energy required to break the first O — H bond and the other O — H bond is the same.

Reason (R) This is because the electronic environment around oxygen is the same even after breakage of one O — H bond.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Atoms combine with each other such that outermost shell acquires stable configuration of electrons. If stability were attained with 6 electrons rather than 8, what would be the formula of stable fluoride ions?

- (a) F^{2+} (b) F^+
(c) F^{3+} (d) F^-

2 The two species NO_3^- and H_3O^+ shows some of the following written properties. Which one of them is correct?

- (a) Isostructural with same hybridisation for the central atom
(b) Dissimilar in hybridisation for the central atom with different structures
(c) Similar in hybridisation for the central atom with different structures
(d) Isostructural with different hybridisation for the central atom

3 The dipole moment of KCl is 3.336×10^{-29} cm, which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. What is the percentage ionic character of KCl?

- (a) 80% (b) 85%
(c) 90% (d) 95%

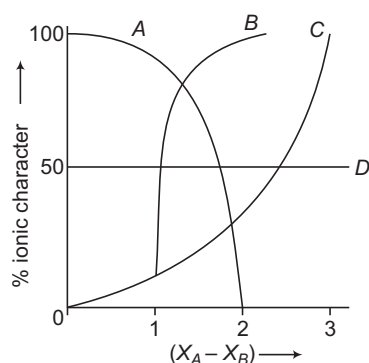
4 The charge/size ratio of cation determines its polarising power. Which one of the following sequence represents the increasing order of the polarising power of the cationic species, K^+ , Ca^{2+} , Mg^{2+} , Be^{2+} ?

- (a) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
(d) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$

- 5 The correct order of hybridisation of the central atom in the following species.

NH_3 , $[\text{PtCl}_4]^{2-}$, PCl_5 and BCl_3 are respectively.

- (a) sp^3 , dsp^2 , dsp^3 , sp^2 (b) dsp^2 , sp^2 , sp^3 , dsp^3
 (c) dsp^2 , sp^3 , sp^2 , dsp^3 (d) sp^3 , dsp^3 , sp^2 and sp^3
- 6 The nitrogen atoms in NH_3 , NH_2^- and NH_4^+ are all surrounded by eight electrons. When these species are arranged in the increasing order of $\text{H}-\text{N}-\text{H}$ bond angle, correct order is
- (a) NH_4^+ , NH_2^- , NH_3 (b) NH_3 , NH_2^- , NH_4^+
 (c) NH_3 , NH_4^+ , NH_2^- (d) NH_2^- , NH_3 , NH_4^+
- 7 In BF_3 , the bond dissociation energy of $\text{B}-\text{F}$ is 646 kJ mol^{-1} while that of $\text{C}-\text{F}$ in CF_4 is 515 kJ mol^{-1} . The correct reason for higher $\text{B}-\text{F}$ bond dissociation energy as compared to that of $\text{C}-\text{F}$ is
- (a) significant $p\pi-p\pi$ interaction between B and F in BF_3 while no such possibility of interaction between C and F in CF_4 .
 (b) smaller size of B-atom as compared to that of C-atom
 (c) lower degree of $p\pi-p\pi$ interaction between B and F in BF_3 than that C and F in CF_4
 (d) stronger σ - bond between B and F in BF_3 as compared to that between C and F in CF_4
- 8 Which of the following is not correct regarding the structure of POCl_3 ?
- (a) Lewis structure violates octet rule
 (b) It has irregular tetrahedral geometry
 (c) $\text{P}=\text{O}$ bond and $\text{P}-\text{Cl}$ bond repulsion is greater than $\text{P}-\text{Cl}$ and $\text{P}-\text{Cl}$ bond repulsion
 (d) $\text{Cl}-\text{P}=\text{O}$ bond angle is lesser than $\text{Cl}-\text{P}-\text{Cl}$ bond angle
- 9 For AB bond, if per cent ionic character is plotted against electronegativity difference ($X_A - X_B$), the shape of the curve would look like as.



The correct curve is

- (a) A (b) B (c) C (d) D
- 10 Polarity in a molecule and hence, the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has highest dipole moment?
- (a) CO_2 (b) HI (c) H_2O (d) SO_2

- 11 The bond order of NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these 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 in NO^+ is greater than in NO
 (d) Bond length is unpredictable

- 12 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

- 13 Among the following, the species having square planar geometry for central atom are

I. XeF_4 II. SF_4 III. $[\text{NiCl}_4]^{2-}$ IV. $[\text{PtCl}_4]^{2-}$
 (a) I and IV (b) I and II
 (c) II and III (d) III and IV

- 14 The Molecular shape of SF_6 , CCl_4 and XeF_4

(a) the same, with 0, 0 and 1 lone pair of electrons
 (b) different, with 2, 0 and 2 lone pair of electrons
 (c) different, with 0, 0 and 2 lone pairs of electrons
 (d) the same with 1, 0 and 1 lone pair of electrons

- 15 Arrange the following compounds in order of increasing dipole moment,

I. toluene II. *o*-dichlorobenzene
 III. *m*-dichlorobenzene IV. *p*-dichlorobenzene
 (a) $\text{I} < \text{IV} < \text{III} < \text{II}$ (b) $\text{IV} < \text{I} < \text{III} < \text{II}$
 (c) $\text{IV} < \text{I} < \text{II} < \text{III}$ (d) $\text{IV} < \text{III} < \text{II} < \text{I}$

- 16 The difference of electronegativities between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5D) is larger than that of NF_3 (0.2D). The correct reason for this is

(a) in NH_3 , the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions
 (b) in NH_3 as well as in NF_3 , the atomic dipole and bond dipole are in opposite directions
 (c) in NH_3 , the atomic dipole and bond dipole are in the opposite direction whereas in NF_3 these are in the same directions
 (d) in NH_3 as well as in NF_3 , the atomic dipole and bond dipole are in the same direction

- 17 The incorrect statement for σ and π -bonds formed between two carbon atoms is

(a) sigma bond is stronger than a π -bond
 (b) bond energies of sigma and π -bonds are of the order of 24 kJ/mol , 347 kJ/mol respectively
 (c) sigma bond determines the direction between carbon atoms but a π -bond has no primary effect in this regard
 (d) Free rotation of atoms about a sigma bond is allowed but not in case of π -bond

- 18** The dipole moment of KCl is 3.336×10^{-29} C-m, which indicates that it is highly polar molecule. The inter atomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. The percentage ionic character of KCl is
(a) 70% (b) 70.5% (c) 80.2% (d) 80.7%

- 19** The dielectric constant of H_2O is 80. The electrostatic force of attraction between Na^+ and Cl^- will be
(a) reduced to $\frac{1}{40}$ in water than in air
(b) reduced to $\frac{1}{80}$ in water than in air

- (c) will be increased to 80 in water than in air
(d) will remain unchanged

- 20** The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because
(a) NO_2 group at *p*-position behave in a different way from that at *o*-position
(b) intramolecular hydrogen bonding exists in *p*-nitrophenol
(c) there is intermolecular hydrogen bonding in *p*-nitrophenol
(d) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol

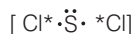
ANSWERS

SESSION 1	1 (a)	2 (a)	3 (b)	4 (a)	5 (b)	6 (c)	7 (a)	8 (b)	9 (b)	10 (b)
	11 (a)	12 (c)	13 (c)	14 (c)	15 (d)	16 (c)	17 (d)	18 (d)	19 (c)	20 (d)
	21 (c)	22 (d)	23 (a)	24 (c)	25 (c)	26 (b)	27 (a)	28 (b)	29 (d)	30 (c)
	31 (b)	32 (a)	33 (b)	34 (a)	35 (a)	36 (c)	37 (c)	38 (d)	39 (b)	40 (a,d)
	41 (d)	42 (d)	43 (d)	44 (b)	45 (a)	46 (b)	47 (a)	48 (a)	49 (c)	50 (c)
SESSION 2	1 (b)	2 (b)	3 (a)	4 (c)	5 (a)	6 (d)	7 (a)	8 (d)	9 (c)	10 (c)
	11 (b)	12 (c)	13 (a)	14 (c)	15 (b)	16 (a)	17 (b)	18 (c)	19 (b)	20 (c)

Hints and Explanations

SESSION 1

- 1** In SCl_2 , the central atom follow the octet rule, others not.



- 2** In Lewis dot structure, the electrons which are not located between two atoms and complete an octet is known as lone pair.

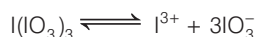
- 3** BF_3 is an electron deficient species, thus behave like a Lewis acid.

- 4** **Ionic** **Covalent**
(a) NaCl $NaCl_3, CCl_4$
(b) CsBr, $BaBr_2, SrO$ —
(c) CsF BF_3, NH_3
(d) Al_2O_3, CaO SO_2

- 5** Due to low ionisation energy of *M*, it loses its electrons easily and are gained by *X*. Thus, ionic bond gets form.

- 6** Smaller the size of the cation, more is the covalent character.

- 7** I_4O_9 is actually $I(IO_3)_3$. It is an ionic compound.



- 8** CsI_3 is an ionic compound. It consists of Cs^+ (cation) and I_3^- (anion) ions. I_3^- ion is made up of I_2 and I^- which is linear in shape.

- 9** In H_2O_2 , $O-O$ bond is non-polar, while $O-H$ bond is polar.

- 10** SO_3 is non-polar molecule due to symmetry.

- 11** In NF_3 , the direction of dipole moment do not cancel out, but in BF_3 due to symmetry, the direction of dipole moment gets cancel out. Thus, net dipole moment in BF_3 is zero but not NF_3 .

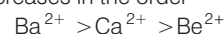
- 12** The covalent bond forms when the electronegativity difference between the two atoms is equal to or less than 1.7.

- 13** Formal charge $= v - \frac{s}{2} - u = 0$

Where, $v = 6, s = 4, u = 4$

- 14** According to Fajan's rule, compounds with small cation, large anion, more charge on cation or anion shows more covalent character. As the above condition opposes, it shows ionic

character. Since, size of cation decreases in the order



\therefore Ionic character have an order,



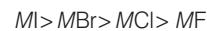
- 15** According to Fajan's rule,

$$\text{Covalent character} \propto \frac{1}{\text{Size of cation} \times \text{Size of anion}}$$

In the given options, cation is same but anions are different. Among halogens the order of size is

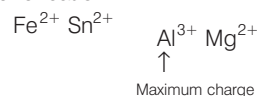


\therefore Order of covalent character is



- 16** According to Fajan's rule, the polarising power and covalent character depends on large charge on ions:

(i) smaller size of cation (ii) larger size of anion. Here all anions are same, i.e. Cl^- anion hence, the covalent character will be decided by polarising power of cation.



Out of the above Al^{3+} has maximum charge and polarising power, hence maximum covalent character.

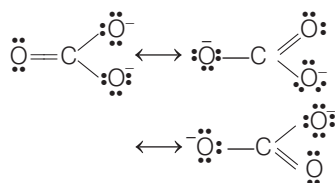
- 17** $\text{C} \equiv \text{N}$ bond length is very short among the given set. Due to presence of triple bond between N and C atoms, but $\text{O}-\text{H}$ bond is smallest due to small size of H-atom.



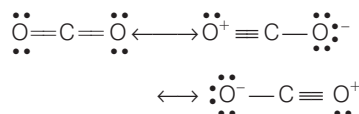
- 18** $\text{C}-\text{H}$ bond length = 0.109 nm
 $\text{C}=\text{C}$; bond length = 0.134 nm
 $\text{C}-\text{O}$; bond length = 0.143 nm
 $\text{C}-\text{C}$; bond length = 0.154 nm
 \therefore Correct order of bond length is
 $\text{C}-\text{H} < \text{C}=\text{C} < \text{C}-\text{O} < \text{C}-\text{C}$

- 19** Bond length of $\text{O}-\text{O}$ in $\text{O}_2 = 1.21 \text{ \AA}$
Bond length of $\text{O}-\text{O}$ in $\text{O}_3 = 1.278 \text{ \AA}$
Bond length of $\text{O}-\text{O}$ in $\text{H}_2\text{O}_2 = 1.49 \text{ \AA}$
Therefore, correct order of $\text{O}-\text{O}$ bond length is $\text{O}_2 < \text{O}_3 < \text{H}_2\text{O}_2$.

- 20** A multiple bond is always shorter than the corresponding single bond. The C-atom in CO_3^{2-} is sp^2 -hybridised as shown.



The C-atom in CO_2 is sp -hybridised with bond distance of carbon-oxygen is 122 pm.

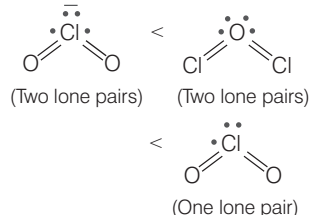


The C-atom in CO is sp -hybridised with $\text{C}-\text{O}$ bond distance 110 pm : $\text{C} \equiv \text{O}$
So, the correct order is
 $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$.

- 21** Species NO_3^- NO_2 NO_2^- NO_2^+
Hybridisation sp^2 sp^2 sp^2 sp
(linear)
Bond angle $120^\circ < 120^\circ < 120^\circ < 180^\circ$
So, NO_2^+ has maximum bond angle.
- 22** As the number of lone pairs of electrons increases, bond angle decreases due to repulsion between $lp-lp$. Moreover, as

the electronegativity of central atom decreases, bond angle decreases.

Hence, the order of bond angle is



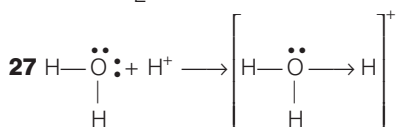
- 23** As the number of lone pair of electrons on central element increases, repulsion between those lone pair of electrons increases and therefore, bond angle decreases.

Molecules	Bond	angle
CH_4 (no lone pair of electrons)		109.5°
NH_3 (one lone pair of electrons)		107.5°
H_2O (two lone pair of electrons)		104.45°

- 24** $\text{C}-\text{F}$ bond length is smaller than $\text{C}-\text{Cl}$ bond length, hence CH_3F dipole moment is less than CH_3Cl .

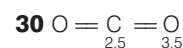
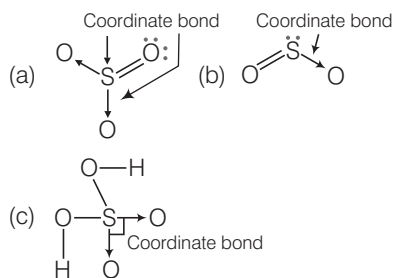
- 25** NH_3 has maximum dipole moment.
Dipole moment in $\text{NH}_3 = 4.90 \times 10^{-30} \text{ cm}$

- 26** $\text{NO}_2^+ = \frac{5-1}{2} = 2 - sp = 180^\circ$
 $\text{NO}_2 = \frac{5}{2} = 2.5 - sp^2 = 120^\circ$
 $\text{NO}_2^- = \frac{5+1}{2} = 3 - sp^2 = 120^\circ$



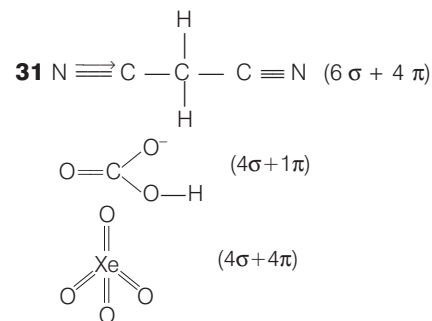
- 28** In $(\text{C}_2\text{H}_5)_2\text{OBH}_3$ coordinate bond is formed in between B and O.
 $(\text{C}_2\text{H}_5)_2\text{O} \longrightarrow \text{BH}_3$
 $(\text{C}_2\text{H}_5)_2\text{O}$ gives one lone pair of electron to BH_3 . So, it is called electron pair donor and BH_3 is called electron pair acceptor.

- 29** The structures of the given compounds are as:



$\text{C}-\text{O}$ bond is polar due to (EN) difference, but molecule is non-polar due to the fact that molecules is linear and $\mu = 0$.

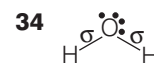
While in SO_3 , due to symmetry in structure. The dipole moment is zero.



In XeO_4 , equal number of σ and π bonds, i.e. four.

- 32** The enolic form of ethyl acetate has 18 single bond (16 sigma bond) and 2 double bond (2 sigma and 2 Pi bonds).

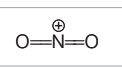
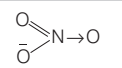
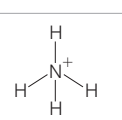
- 33** These are 4π bonds, hence total π electrons are 8.



It contains only two σ -bonds.

- 35** (a) I_3^- , sp^3d (b) PCl_3 , sp^3
(c) NO_3^- , sp^2 (d) H_2Se , sp^3

36

Ion	Structure	Hybridisation
NO_2^+		sp
NO_3^-		sp^2
NH_4^+		sp^3

Thus option (c) is correct.

- 37** Molecules having the same number of hybrid orbitals, have same hybridisation and number of hybrid orbitals.

$$H = \frac{1}{2}[V + Y - C + A]$$

where, V = number of valence electrons of central atom

Y = number of monovalent atoms

C = charge on cation

A = charge on anion

$$(a) \text{ In SF}_4, \quad H = \frac{1}{2}[6 + 4 - 0 + 0] = 5$$

$$(b) \text{ In I}_3^-, \quad H = \frac{1}{2}[7 + 2 + 1] = 5$$

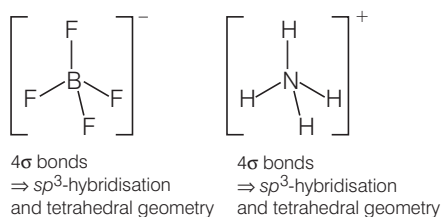
$$(c) \text{ In SbCl}_5^{2-}, \quad H = \frac{1}{2}[5 + 5 + 2] = 6$$

$$(d) \text{ In PCl}_5, \quad H = \frac{1}{2}[5 + 5 + 0 - 0] = 5$$

Since, only SbCl_5^{2-} has different number of hybrid orbitals (i.e. 6) from the other given species, its hybridisation is different from the others, i.e. sp^3d^2 .

(The hybridisation of other species is sp^3d).

38 BF_4^- and NH_4^+

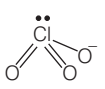
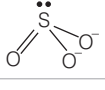
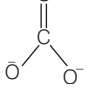
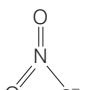


Thus, BF_4^- and NH_4^+ are isostructural.

39 The central atom Cl has seven electrons in the valence shell. Three of these will form electron pair bonds with three fluorine atom leaving behind four electrons.

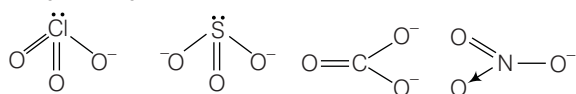


40

Species	Total number of electrons	Structure	Shape
ClO_3^-	42		Pyramidal
SO_3^{2-}	42		Pyramidal
CO_3^{2-}	32		Trigonal planar
NO_3^-	32		Trigonal planar

Hence, both options (a) and (d) are correct.

41 ClO_3^- , SO_3^{2-}



Number of electrons

$$\text{CO}_3^{2-} = 6 + 2 + 24 = 32$$

$$\text{SO}_3^{2-} = 16 + 2 + 24 = 42$$

$$\text{ClO}_3^- = 4 + 24 + 1 = 29$$

$$\text{NO}_3^- = 7 + 2 + 24 = 33$$

Hence, ClO_3^- and SO_3^{2-} are isoelectronic and are pyramidal in shape.

42 According to the postulate of VSEPR theory, a lone pair occupies more space than a bonding pair, since it lies closer to the central atom. This means that the repulsion between the different electron pairs follow the order.

$$lp-lp > lp-bp > bp-bp$$

$$\text{43 } \text{O}_2^- \Rightarrow \text{bond order} = \frac{10-7}{2} \Rightarrow 3/2 = 1.5$$

$$\text{O}_2^+ \rightarrow \text{bond order} = \frac{10-5}{2} = 5/2 = 2.5$$

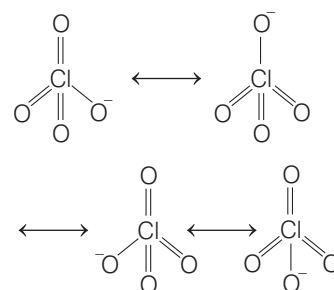
$$\text{O}_2^{2+} \rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2, (\pi 2p_x^2 \approx \pi 2p_y^2)$$

$$(\pi^* 2p_x^0 \approx \pi^* 2p_y^0)$$

$$\text{Bond order} = \frac{10-4}{2} = \frac{6}{2} = 3$$

Correct bond order is $\text{O}_2^{2+} > \text{O}_2^+ > \text{O}_2^-$.

44



Bond order

$$= 1 + \frac{\text{total number of double bond between Cl and O}}{\text{total number of bonds at delocalisation position}}$$

$$= 1 + \frac{3}{4} = \frac{7}{4} = 1.75$$

$$\text{45 } \text{O}_2^{2-} (8 + 8 + 2 = 18) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2$$

$$\pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^2 \approx \pi^* 2p_y^2$$

$$\text{Bond order (BO)} = \frac{N_b - N_a}{2} = \frac{10-8}{2} = 1$$

$$\text{B}_2 (5 + 5 = 10) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi 2p_y^1$$

$$\text{BO} = \frac{6-4}{2} = 1$$

Thus, O_2^{2-} and B_2 have the same bond order.

Note BO of $\text{O}_2^+ = 2.5$, $\text{NO}^+ = 3$, $\text{NO} = 2.5$, $\text{CO} = 3$,

$\text{N}_2 = 3$ and $\text{O}_2 = 2$

- 46 (a) MO configuration of O_2^+

$$(8 + 8 - 1 = 15)$$

$$BO = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = 2.5$$

Similarly,

- (b) O_2^- ($8 + 8 + 1 = 17$)

$$\text{So, } BO = \frac{N_b - N_a}{2} = \frac{10 - 7}{2} = 1.5$$

- (c) O_2^{2-} ($8 + 8 + 2 = 18$)

$$\text{So, } BO = \frac{N_b - N_a}{2} = \frac{10 - 8}{2} = 1$$

- (d) O_2 ($8 + 8 = 16$)

$$BO = \frac{10 - 6}{2} = 2$$

Thus, O_2^- shows the bond order 1.5.

- 47 Electronic configuration of N is

$$1s^2 2s^2 2p^3.$$

In N_2 molecule, there are 14 electrons. Therefore, its electronic configuration is

$$N_2 : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2, \sigma^* 2s^2,$$

$$\sigma 2p^2_z, \pi 2p^2_x \equiv \pi 2p^2_y.$$

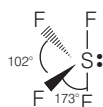
Hence, option (a) is correct.

- 48 Ethanol have hydrogen bonding so its boiling point is higher than its isomer dimethyl ether.

- 49 SF_4 has see-saw shape. It has non-planar structure. In this structure, bond angles are different between different S—F atoms.

According to VSEPR theory,

$$lp - lp > lp - bp > bp - bp.$$



- 50 The bond enthalpies of the two O—H bonds in H_2O are not equal because the electronic environment around O is not the same after the breaking of one O—H bond.

SESSION 2

- 1 The formula of the stable fluoride ion will be F^- .

2 NO_3^- hybridization = $\frac{5 + 1}{2} = 3$

$$= sp^2 \text{ trigonal planar}$$

H_3O^+ hybridisation

$$= \frac{6 + 3 - 1}{2} = 4 = sp^3$$

Tetrahedral dissimilar in hybridisation with different structure.

- 3 Dipole moment $\mu = q \times d$

$$\therefore 3.336 \times 10^{-29} = q \times 2.6 \times 10^{-10}$$

$$\therefore q = \frac{3.336 \times 10^{-29}}{2.6 \times 10^{-10}} = 1.283 \times 10^{-19} \text{ C}$$

If 1.602×10^{-19} C charge on each, then % ionic character = 100

$$\therefore 1.283 \times 10^{-19} \text{ C charge on each, then \% ionic character}$$

$$= \frac{1.283 \times 10^{-19}}{1.602 \times 10^{-19}} \times 100 = 80.09\% (\approx 80\%)$$

- 4 Polarising power of metals decreases with increasing size of metals.

$$K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$$

- 5 (i) $NH_3 = \frac{5 + 3}{2} = sp^3$

(ii) $[PtCl_4]^{2-} = \frac{8}{2} = 4 = dsp^2$

(iii) $PCl_5 = \frac{5 + 5}{2} = 5 = sp^3d$

(iv) $BCl_3 = \frac{3 + 3}{3} = 3 = sp^2$

- 6 $NH_3 = \frac{5 + 3}{2} = sp^3 = 107^\circ$ one lone pair

$$NH_2^- = \frac{5 + 2 + 1}{2} = sp^3 = 105^\circ$$

with two lone pairs

$$NH_4^+ = \frac{5 + 4 - 1}{2} = sp^3 = 109^\circ 28'$$

without lone pair

- 7 B—F has high bond dissociation energy due to $p\pi - p\pi$ interaction in between B and F. But there is no such type of possibility in between C and F.

- 8 $POCl_3$ is a Lewis structure which violates the octet rule. It has irregular tetrahedral geometry and P=O bond and P—Cl bond repulsion is greater than P—Cl and P—Cl bond repulsion.

- 9 The shape of the curve would look like a parabolic i.e. (c).

- 10 (i) $O=C=O$ is linear having zero dipole moment.

(ii) is bent or V-shaped with the highest dipole moment in these four.

11 Bond length $\propto \frac{1}{\text{Bond order}}$

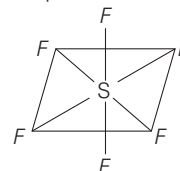
- 12 More the charge on the cation, more is the covalent nature of the compound. Hence MCl_2 is more ionic than MCl_4 .

- 13 XeF_4 and $[PtCl_4]^{2-}$ have planar geometry.

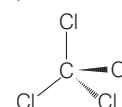
SF_4 has see-saw geometry.

$[NiCl_4]^{2-}$ has tetrahedral geometry.

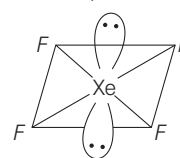
- 14 (i) SF_6 has octahedral geometry with 0 lone pairs



- (ii) CCl_4 has tetrahedral geometry with 0 lone pairs.



- (iii) XeF_4 has square planar geometry with 2 lone pairs.



- 15 Increasing order of dipole moment.

p -dichlorobenzene < toluene
< m -dichlorobenzene
< o -dichlorobenzene.

- 16 In NH_3 , the atomic dipole and bond dipole are in the same direction, whereas in NF_3 , the atomic dipole and bond dipole are in the opposite direction.

- 17 A sigma bond is stronger than a π -bond. A sigma bond determines the direction between carbon atoms, but a π -bond has no primary effect in this regard as well as free rotation of atoms about a sigma bond is allowed but not in the case of a π -bond.

- 18 Dipole moment is calculated as,
- $$\mu = q \cdot d = 1.6 \times 10^{-19} \times 2.6 \times 10^{-10}$$
- $$= 4.6 \times 10^{-29} \text{ m}$$

$$\% \text{ ionic character} = \frac{\mu_{\text{Obs.}}}{\mu_{\text{Theo.}}} \times 100$$

$$= \frac{3.336 \times 10^{-29}}{4.16 \times 10^{-29}} \times 100 = 80.2\%$$

- 19 The electrostatic force of attraction between Na^+ and Cl^- will be reduced to $\frac{1}{80}$ in water than in air.

- 20 p -nitrophenol has intermolecular H-bonding, whereas o -nitrophenol has intramolecular H-bonding due to this p -nitrophenol has a higher boiling point than o -nitrophenol.