DAY FOUR

Chemical Bonding & Molecular Structure

Learning & Revision for the Day

- Ionic or Electrovalent Bond
- Covalent Bond
- Bond Parameters
- Resonance
- Coordinate Bonding
- Valence Bond Theory
- Concept of Hybridisation Involving s, ***p*** and ***d***-orbital
- VSEPR Theory
- Molecular orbital Theory
- Hydrogen Bonding
- Metallic Bonding

A **chemical bond** is the attractive force which holds the various constituents (atoms, ions etc.) together in different chemical species.

The different types of chemical bonds formed between atoms are as follows:

(i) Ionic bond (ii) Covalent bond (iii) Coordinate 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 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. This is known as octet rule.
- In Lewis symbol, the number of dots around the symbol represents the number of valence electrons. The number of electrons helps to calculate the common valency of the element.

Limitations of Octet Rule

In accordance to this rule, the shape of the molecule cannot be predicted. The relative stability of molecule cannot be known by this rule.

However, the octet rule is violated in a significant number of cases. These are:

(i) Electron deficient compounds : $BeCl_2$, BF_3, $AlCl_3$ etc.
(ii) Hypervalent compounds : PCl_5, SF_6, IF_7, H_2SO_4 etc.
(iii) Compounds of noble gases : XeF_2, XeF_6, XeF_4, KrF_2 etc.
(iv) 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).

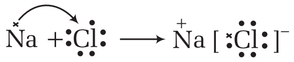
Ionic or Electrovalent Bond

The attractive forces of ionic bond (i.e. electrostatic force of attraction) are developed between an electropositive atom and an electronegative atom due to complete transfer of electrons from former to later. It is generally formed between the atoms having large difference in their electronegativity.

Formation of Ionic Bond

- Ionic bond is formed by the complete transfer of electron(s) from one atom to the other.

  e.g. $_{11}\text{Na}$ (2, 8, 1) $_{17}\text{Cl}$ (2, 8, 7)



$$\text{Na}^+ + \text{Cl}^- \longrightarrow \text{NaCl}$$

- Ionic bonds are non-directional and also known as electrovalent bonds or polar bonds.

Factors Affecting the Formation of Ionic Bonds

The formation of an ionic bond is related to cation and anions which depends upon the following factors:

(i) Low ionisation energy of the electropositive element.
(ii) High electron affinity of electronegative element.
(iii) High lattice enthalpy

$$\left(\text{Lattice enthalpy} \propto \frac{\text{charge on ions}}{\text{size of ion}}\right)$$

NOTE
- Elements of group 1 and group 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.

Lattice Enthalpy and Its Calculation

The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. This energy is calculated by **Born-Haber cycle**.

Born-Haber cycle includes

(i) vaporisation of reactants into gaseous state
(ii) conversion of gaseous atoms into ions
(iii) combination of gaseous ions to form ionic lattice of molecules

e.g. $M(s) + \frac{1}{2}X_2(g) \longrightarrow MX(s),\ \Delta H = Q$

Here, ΔH = enthalpy change of the reaction
Q = heat of the reaction.

The above reaction includes the various steps:

(a) $M(s) \longrightarrow M(g);\ \Delta H_1 = S$ (S = sublimation energy)
(b) $M(g) \longrightarrow M^+(g) + e^-;\ \Delta H_2 = I$ (I = ionisation energy)
(c) $\frac{1}{2}X_2(g) \longrightarrow X(g);\ \Delta H_3 = \frac{D}{2}$ (D = dissociation energy)
(d) $X(g) + e^- \longrightarrow X^-(g);\ \Delta H_4 = -E$ (E = electron affinity)
(e) $M^+(g) + X^-(g) \longrightarrow MX(s);\ \Delta H_5 = -U$ (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:

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

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

NOTE
- 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, $PbSO_4$, $BaSO_4$, $CaCO_3$.
- Both lattice energy and hydration energy decreases with increase in ionic size.
- If both anion and cation are of comparable size, the cationic radius will influence the lattice energy.

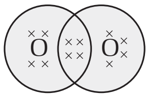
Covalent Bond

The chemical bonds that are formed by sharing of electrons between the elements of almost same electronegativity or between the elements having less difference in electronegativity are called covalent bonds.

e.g. Formation of O_2 molecule.

$$_8\text{O} = 2, 6$$

O=O Or



The covalent bond can be of the following two types:

1. **Non-polar Covalent Bond** If the covalent bond is formed between two homonuclear atoms, i.e. between atoms of exactly equal electronegativity, the electron pair is equally shared between them. e.g. H_2, Cl_2, F_2, Br_2 etc.
2. **Polar Covalent Bond** If the bond forming entities are dissimilar, i.e. heteronuclear or with different electronegativity, the bond formed has partial ionic character as the electron pair is attracted by more electronegative entity.

$$\overset{\delta+}{\text{H}}\cdots\overset{\delta-}{\text{O}}\cdots\overset{\delta+}{\text{H}} \qquad \overset{\delta+}{\text{H}}\cdots\overset{\delta-}{\text{Cl}}$$

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

$$\boxed{\underset{4.0}{\text{F}}} > \underset{3.5}{\text{O}} > \underset{3.0}{\text{Cl}} \approx \text{N} > \underset{2.8}{\text{Br}} > \underset{2.5}{\text{S}} \approx \text{C} \approx \underset{2.1}{\text{I}} > \text{H}$$

Calculation of Percentage Ionic Character

The ionic character in polar bond can be calculated by the following methods:

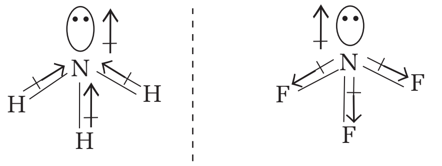
1. **Pauling equation**
   Percentage ionic character = $18\ (\chi_A - \chi_B)^{1.4}$
2. **Hannay and Smith equation**
   Percentage ionic character = $16\ (\chi_A - \chi_B) + 3.5\ (\chi_A - \chi_B)^2$
   where, $(\chi_A - \chi_B)$ = electronegativity difference.

Dipole Moment (μ)

- It is defined as the product of the magnitude of charge (q) and distance (d) separating the centres of positive and negative charges.
- Its direction is from positive end to negative end,

$$\mu = q \times d$$

- Its unit in CGS system is debye (D).
- 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, which cancels the resultant moment.



Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ cm | Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ cm

A comparison dipole moments of NH_2 and NF_3

- Percentage ionic character of any molecule can be calculated by dipole moment (μ).

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

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

Partial Ionic Character of Covalent Bond

On the basis of electronegativity difference, partial ionic character of covalent bond can be summarised as :

(i) Electronegativity difference between combining atoms = 1.7, then bond is 50% ionic and 50% covalent.
(ii) Electronegativity difference > 1.7, ionic character in bond is more than 50%.
(iii) Electronegativity difference < 1.7, ionic character is less than 50%.

Fajan's Rule

- It states that the magnitude of covalent character in an ionic bond depends upon the polarising power. 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.

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

Formal Charge

It is 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 in the Lewis structure.

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

$$= \begin{bmatrix}\text{Total number of} \\ \text{valence electrons} \\ \text{in the free atom}\end{bmatrix} - \begin{bmatrix}\text{Total number of} \\ \text{non-bonding (lone pair)} \\ \text{electrons}\end{bmatrix} - \frac{1}{2}\begin{bmatrix}\text{Total number of} \\ \text{bonding (shared) electrons}\end{bmatrix}$$

Bond Parameters

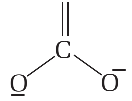
The covalent bonds are characterised by the some parameters which are as follows:

1. **Bond Length** In general the average distance between the centre of nuclei of the two bonded atoms in a molecule is known as bond length. 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.
2. **Bond Enthalpy** It is the amount of energy required to break one mole of bonds of a particular type between two atoms in gaseous state.
   Bond enthalpy ∝ electronegativity

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

3. **Bond Order** Bond order is just like number of bond(s) between two atoms in a molecule.

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

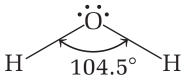


Bond order ∝ bond strength (stronger the bond, larger will be the bond dissociation energy and bond enthalpy) e.g. CO_3^{2-}.

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

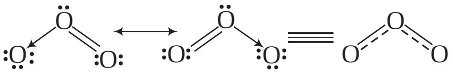
$$\text{For } O_3, \left(1+\frac{1}{2}\right) = 1.5, \quad SO_4^{2-}, \left(1+\frac{2}{4}\right) = 1.5$$

4. **Bond Angle** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule or complex ion.



Resonance

There are certain molecules (benzene, ozone, nitric acid and many more), whose all the properties cannot be explained by a single structure, then two or more structures, called **resonating structures** are required to explain all the properties and the actual structure is intermediate of these structures. 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 (due to resonance).
- 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.
- Resonance averages the bond characteristic as a whole.
- The difference in the energy of a resonance hybrid and most stable structure (with least energy) is called **resonance energy**.

Coordinate Bonding

The bonding in which one atom furnishes a pair of electrons to the other atom, but shared by both the atoms in such a manner that both atoms achieve stability, is called coordinate bonding or dative bonding. e.g.

$$\underset{\text{Acceptor}}{H^+} + \underset{\text{Donor}}{\ddot{N}H_3} \longrightarrow \overset{+}{N}H_4$$

$$\underset{\text{Donor}}{\ddot{N}H_3} + \underset{\text{Acceptor}}{BF_3} \longrightarrow \underset{\text{Complex}}{[H_3N \longrightarrow BF_3]}$$

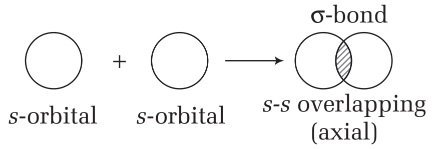
Valence Bond Theory (VBT)

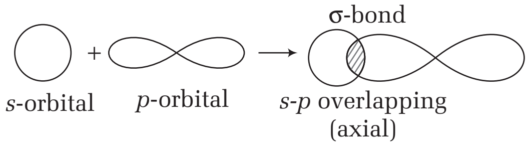
(Given by Heitler and London)

- It explains bond formation in terms of overlapping of orbitals, e.g. the formation of H_2 molecule from two hydrogen atoms involves the overlap of 1*s*-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.

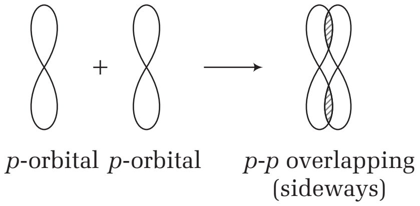
The overlapping of orbitals may results in two types of bonds given below :

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





2. **Pi (π)-Bond** It is formed by the incomplete overlapping of orbitals or in other words sidewise or parallel overlapping of *p-p* orbitals results in the 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*-orbital

- Pauling introduced the concept of hybridisation. 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).
- *sp*, sp^2, sp^3 hybridisations of atomic orbitals of Be, B, C, N and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BCl_3, CH_4, NH_3 and H_2O.

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.

- In case of 3rd period elements, the energy of 3*d*-orbitals are comparable to the energy of 3*s* and 3*p*-orbitals as well as to the energy of 4*s* and 4*p* orbitals.
- As a result of this, hybridisation involves either 3*s*, 3*p* and 3*d* or 3*d*, 4*s* and 4*p* is possible.

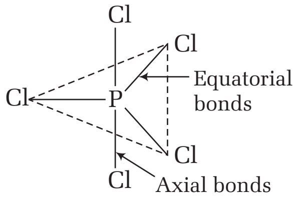
Important hybridisation schemes involving *s*, *p* and *d* orbitals are as follows:

Shape of molecules/ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d + s + p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s + p(3) + d$	PF_5, PCl_5
Square pyramidal	sp^3d^2 with one lone pair	$s + p(3) + d(2)$	BrF_5, IF_5
Octahedral	sp^3d^2, d^2sp^3	$s + p(3) + d(2)$ $d(2) + s + p(3)$	SF_6, $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$

Some important examples are :

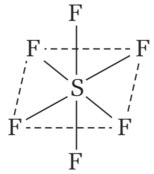
1. ***sp*^{3}*d*-hybridisation** e.g. PCl_5 molecule. In PCl_5 the two axial bonds are slightly elongated as the axial bond pairs suffer more repulsive interaction from equivalent bond pairs.

   Hence, axial bonds found to be slightly longer and weaker than equatorial bonds. Thus, PCl_5 is more reactive.



2. ***sp*^{3}*d*^{2}-hybridisation** e.g. SF_6 molecule. In SF_6, four S—F bonds are in same plane at right angles to one another and are directed towards the corner of a square. The other two F-atom lie at right angle above and below the plane of F-atoms.

SF_6 molecule is a symmetrical molecule and therefore is stable and less reactive.



The formula for predicting hybridisation of central atom and the number of hybrid orbitals (X) is given below :

$$X = \frac{1}{2}[V + M + A - C]$$

where, V = Number of valence electrons of central atom

M = Number of monovalent atoms attached

C = Cation and A = Anion

While determining the type of hybridisation on the atom, π-bonds are never taken into account, but lone pairs are always considered.

VSEPR Theory

(Given by Gillespie and Nyholm)

- VSEPR stands for Valence Shell Electron Pair Repulsion. According to this theory, all valence shell electron pairs, surrounding, the central atom arrange themselves in such a manner, so that they are as far away from each other as possible.
- 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:

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

Hybrid orbitals and molecular shapes involving *s*, *p* and *d*-orbitals

Number of electron pairs	Geometry	Hybridisation	Examples
2 *bp*	Linear	sp	BeF_2
3 *bp*	Trigonal planar	sp^2	BF_3
2*bp* + 1*lp*	Bent	sp^2	SO_2, O_3
4 *bp*	Tetrahedral	sp^3	CH_4
3*bp*+1 *lp*	Pyramidal	sp^3	$\ddot{N}H_3$
2*bp*+2 *lp*	Angular or V-shape	sp^3	$H_2\ddot{\underset{..}{O}}$
5 *bp*	Trigonal bipyramidal	sp^3d	PF_5, PCl_5
4*bp* + 1*lp*	*See-saw*	sp^3d	$:SF_4$
3*bp* + 2*lp*	T-shaped	sp^3d	$:\ddot{Cl}F_3$
6*bp*	Octahedral	sp^3d^2	SF_6
5*bp* + 1 *lp*	Square pyramidal	sp^3d^2	BrF_5
4*bp*+2*lp*	Square planar	sp^3d^2	$:XeF_4$
7*bp*	Pentagonal bipyramidal	sp^3d^3	IF_7

Molecular Orbital Theory

(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 (MO) formed are of two types :

(i) **Bonding MO** which are of lower energy, are represented as σ or π. These makes bond stronger.

(ii) **Antibonding MO** which are of higher energy, are represented as $\overset{*}{\sigma}$ or $\overset{*}{\pi}$. These reduces the stability of molecules.

The electronic configuration of molecular orbitals (MO) are written in the following manner:

(a) For species like O_2, F_2 etc.

$$\sigma 1s,\ \overset{*}{\sigma}1s, \sigma 2s,\ \overset{*}{\sigma}2s, \sigma 2p_z, (\pi\ 2p_x = \pi 2p_y),$$
$$(\overset{*}{\pi} 2p_x = \overset{*}{\pi} 2p_y),\ \overset{*}{\sigma}2p_z$$

(b) For species like $Li_2, Be_2, B_2,\ C_2,\ N_2$ etc.

$$\sigma 1s,\ \overset{*}{\sigma}\,1s, \sigma 2s,\ \overset{*}{\sigma}\,2s, (\pi\ 2p_x = \pi 2p_y), \sigma 2p_z,$$
$$(\overset{*}{\pi} 2p_x = \overset{*}{\pi} 2p_y), \overset{*}{\sigma}\,2p_z$$

Bond Order (B.O.) for diatomic molecule or ions,

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

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 case of paired electrons, molecule is diamagnetic.

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

  (BM = Bohr Magneton)

  where, n = number of unpaired electrons

Hydrogen Bonding

Hydrogen bond 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 large size. Strongest H-bond exist in KHF_2.

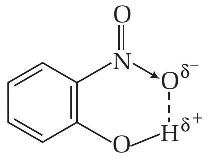
There are two types of H-bonds:

1. **Intermolecular hydrogen bonding** is a type of H-bond that is formed between the different molecules of same substance or different substance.

   e.g. $\overset{+\delta}{H}—\overset{-\delta}{F}\text{- - -}\overset{+\delta}{H}—\overset{-\delta}{F}\text{- - -}\overset{+\delta}{H}—\overset{-\delta}{F}$

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

2. **Intramolecular hydrogen bonding** is a type of H-bond that is formed within the same molecule. Intramolecular H-bonding increases the volatility, decreases the boiling point of the compound and also decreases its solubility in water.



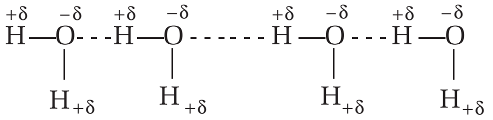
Intramolecular H-bonding in *o*-nitrophenol

- 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.

Effect of H-Bonding

Various effects arise due to H-bonding in molecules are as follows:

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

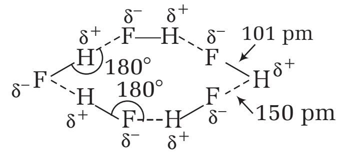
  

  $$\overset{+\delta}{H}—\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}\text{- - -}\overset{+\delta}{H}—\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}\text{- - - - - -}\overset{+\delta}{H}—\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}\text{- - -}\overset{+\delta}{H}—\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}$$

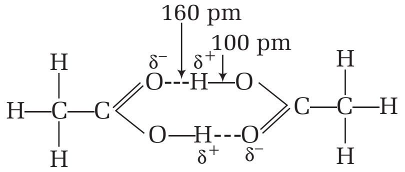
  Actually, in water, one water molecule is joined to four water molecules (two with H-atom and other two with O-atoms.)

  Thus, coordination number of water molecule in water is four.
- 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 another words, we can say that when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks, hence volume increases and hence, density decreases. Thus, water has maximum density at 4°C.

- In the gaseous state, several polymeric forms of HF molecules exist in which the monomers are held together through H-bonding. A pentagonal arrangement of H—F molecules is shown below:



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



Metallic Bonding

The attractive force which hold together the constituent particles in a metal is known as **metallic bonding**.

The two models which explain metallic bonding are :

(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**, 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 these two bands is called energy gap. In insulators, energy gap is very large while in semiconductors it is very small. On increasing temperature, electrical conductivity of semiconductors increases because some electrons move from valence band to conduction band.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Among the following, electron deficient molecule is

(a) CCl_4 (b) PCl_5
(c) BF_3 (d) SF_6

2 Sodium chloride is soluble in water but not in benzene because

(a) $\Delta H_{\text{Hydration}} < \Delta H_{\text{Lattice energy in water}}$
$\Delta H_{\text{Hydration}} > \Delta H_{\text{Lattice energy in benzene}}$
(b) $\Delta H_{\text{Hydration}} > \Delta H_{\text{Lattice energy in water}}$
$\Delta H_{\text{Hydration}} < \Delta H_{\text{Lattice energy in benzene}}$
(c) $\Delta H_{\text{Hydration}} = \Delta H_{\text{Lattice energy in water}}$
$\Delta H_{\text{Hydration}} < \Delta H_{\text{Lattice energy in benzene}}$
(d) $\Delta H_{\text{Hydration}} < \Delta H_{\text{Lattice energy in water}}$
$\Delta H_{\text{Hydration}} = \Delta H_{\text{Lattice energy in benzene}}$

3 Which of the following compounds contain(s) no covalent bond(s)? ➞ JEE Main 2018

$KCl, PH_3, O_2, B_2H_6, H_2SO_4$

(a) KCl, B_2H_6, PH_3 (b) KCl, H_2SO_4
(c) KCl (d) KCl, B_2H_6

4 The % ionic character in Cs—Cl bond present in CsCl molecule will be, if the electronegativity values for Cs and Cl are 0.8 and 3.0 respectively

(a) 62.9% (b) 60%
(c) 75% (d) 52.14%

5 Which one of the following molecule is polar? ➞ JEE Main (Online) 2013

(a) XeF_4 (b) IF_5
(c) SbF_5 (d) CF_4

6 Which of the following pairs has zero dipole moment?

(a) CH_2Cl_2 and NF_3 (b) SiF_4 and BF_3
(c) PCl_3 and ClF (d) BF_3 and NF_3

7 Bond distance in HF is 9.17×10^{-11} m. Dipole moment of HF is 6.104×10^{-30} cm. The per cent ionic character in HF will be (electron charge $= 1.60 \times 10^{-19}$ C) ➞ JEE Main (Online) 2013

(a) 61.0% (b) 38.0%
(c) 35.5% (d) 41.6%

8 Among the following the maximum covalent character is shown by the compound ➞ AIEEE 2011

(a) $FeCl_2$ (b) $SnCl_2$ (c) $AlCl_3$ (d) $MgCl_2$

9 The correct statement for the molecule, CsI_3 is ➞ JEE Main 2014

(a) it is a covalent molecule
(b) it contains Cs^+ and I_3^-
(c) It contains Cs^{3+} and I^- ions
(d) it contains Cs^+, I^- and lattice I_2 molecule

10 Bond order normally gives idea of stability of a molecular species. All the molecules *viz.* H_2, Li_2 and B_2 have the same bond order yet they are not equally stable. Their stability order is ➞ JEE Main (Online) 2013

(a) $H_2 > B_2 > Li_2$ (b) $H_2 > Li_2 > B_2$
(c) $Li_2 > B_2 > H_2$ (d) $B_2 > H_2 > Li_2$

11 Which of the following compounds has the smallest bond angle in its molecule?

(a) H_2O (b) H_2S (c) NH_3 (d) SO_2

12 Arrange the following molecules in the increasing order of bond angle.

H_2O	H_2S	H_2Se	H_2Te
I	II	III	IV

(a) I < II < III < IV
(b) IV < III < II < I
(c) I < III < II < IV
(d) IV < II < III < I

13 Consider the following iodides,

PI_3—102°, AsI_3—100.2, SbI_3—99°

The bond angle is maximum in PI_3 which is

(a) due to small size of phosphorus
(b) due to more *bp-bp* repulsion in PI_3
(c) due to less electronegativity of phosphorus
(d) None of the above

14 Bond energy of H—H, F—F and H—F bonds are 104, 38 and 135 kcal mol^{-1} respectively. The resonance energy in the H—F molecule will be

(a) 142 kcal mol^{-1}
(b) 66 kcal mol^{-1}
(c) 72.14 kcal mol^{-1}
(d) 79.26 kcal mol^{-1}

15 The species in which the N-atom is in a state of *sp*- hybridisation is ➞ JEE Main 2016

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

16 The *d*-orbital involved in sp^3d-hybridisation is

(a) d_{xy}
(b) d_{zx}
(c) d_{z^2}
(d) $d_{x^2-y^2}$

17 The hybridisation of orbitals of N-atom in NO_3^-, NO_2^+ and NH_4^+ respectively are ➞ AIEEE 2011

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

18 The states of hybridisation of boron and oxygen atoms in boric acid (H_3BO_3) are respectively

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

19 Match the following and choose the correct option.

	Column I		Column II
A.	SF_4	1.	sp^3d^2
B.	IF_5	2.	sp^3
C.	NO_2^+	3.	sp
D.	NH_4^+	4.	sp^3d

Codes

	A	B	C	D		A	B	C	D
(a)	4	1	3	2	(b)	1	3	2	4
(c)	3	2	4	1	(d)	3	1	2	4

20 Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs.

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

21 In which of the following pairs the two species are not isostructural? ➞ AIEEE 2012

(a) CO_3^{2-} and NO_3^-
(b) PCl_4^+ and $SiCl_4$
(c) PF_5 and BrF_5
(d) AlF_6^{3-} and SF_6

22 Total number of lone pair of electron in I_3^- ion is

(a) 3
(b) 6
(c) 9
(d) 2

23 In XeF_2, XeF_4 and XeF_6, the number of lone pairs of Xe respectively are

(a) 2, 3, 1
(b) 1, 2, 3
(c) 4, 1, 2
(d) 3, 2, 1

24 The structure of IF_7 is ➞ AIEEE 2010

(a) square pyramidal
(b) trigonal bipyramidal
(c) octahedral
(d) pentagonal bipyramidal

25 Which has trigonal bipyramidal shape? ➞ JEE Main (Online) 2013

(a) $XeOF_4$
(b) XeO_3
(c) XeO_3F_2
(d) $XeOF_2$

26 The shape of IF_6^- is ➞ JEE Main (Online) 2013

(a) trigonally distorted octahedron
(b) pyramidal
(c) octahedral
(d) square antiprism

27 The molecular shapes of SF_4, CF_4 and XeF_4 are

(a) different with 1, 0 and 2 lone pairs of electrons on the central atoms, respectively
(b) different with 0, 1 and 2 lone pairs of electrons on the central atoms, respectively
(c) the same with 1, 1 and 1 lone pairs of electrons on the central atoms, respectively
(d) the same with 2, 0 and 1 lone pairs of electrons on the central atoms, respectively

28 The structure of which of the following chloro species can be explained on the basis of dsp^2-hybridisation ? ➞ JEE Main (Online) 2013

(a) $PdCl_4^{2-}$
(b) $FeCl_4^{2-}$
(c) $CoCl_4^{2-}$
(d) $NiCl_4^{2-}$

29 XeO_4 molecule is tetrahedral having ➞ JEE Main (Online) 2013

(a) two $p\pi - d\pi$ bonds
(b) one $p\pi - d\pi$ bond
(c) four $p\pi - d\pi$ bonds
(d) three $p\pi - d\pi$ bonds

30 Which of the following species is not paramagnetic? ➞ JEE Main 2017

(a) NO
(b) CO
(c) O_2
(d) B_2

31 Which of the following order of energies of molecular orbitals of N_2 is correct?

(a) $\sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 \approx \pi 2p_y^2 < \sigma 2p_z^2$
(b) $\sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 \approx \pi 2p_y^2$
(c) $\sigma^* 2s^2 < \sigma 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 < \pi 2p_y^2$
(d) $\sigma 2s^2 < \sigma 2p_z^2 < \sigma 2s^2 < \pi 2p_x^2 < \pi 2p_y^2$

32 Which one of the following molecules is/are expected to exhibited diamagnetic behaviour? ➞ JEE Main 2013

(a) N_2 (b) O_2
(c) S_2 (d) C_2

33 Which of the following statement(s) is/are correct?

(a) In the formation of dioxygen from oxygen atoms 10 molecular orbitals will be formed.
(b) All the molecular orbitals in the dioxygen will be completely filled
(c) Total number of bonding molecular orbitals will not be same as total number of anti-bonding orbitals in dioxygen
(d) Number of filled bonding orbitals will be same as number of filled anti-bonding orbitals

34 In accordance to molecular theory,

(a) O_2^+ is diamagnetic and bond order is more than O_2
(b) O_2^+ is diamagnetic and bond order is less than O_2
(c) O_2^+ is paramagnetic and bond order is more than O_2
(d) O_2^+ is paramagnetic and bond order is less than O_2

35 The stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of ➞ JEE Main 2013

(a) $Li_2^- < Li_2^+ < Li_2$
(b) $Li_2 < Li_2^- < Li_2^+$
(c) $Li_2^- < Li_2 < Li_2^+$
(d) $Li_2 < Li_2^+ < Li_2^-$

36 Which of the following pairs of molecules/ions are not likely to exist? ➞ JEE Main 2013

(a) H_2^+, He_2^{2-}
(b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2
(d) H_2^-, He_2^{2+}

37 *Ortho*-nitrophenol is less soluble in water than *p*-and *m*-nitrophenols because ➞ AIEEE 2012

(a) *o*-nitrophenol is more steam volatile than those of *m*- and *p*-isomers
(b) *o*-nitrophenol shows intramolecular H-bonding
(c) *o*-nitrophenol shows intermolecular H-bonding
(d)melting point of *o*-nitrophenol is lower than those of *m*- and *p*-isomers

38 Consider the following compounds,

I. 1, 2-hydroxybenzene
II. 1, 3-dihydroxybenzene
III. 1, 4-dihydroxybenzene
IV. hydroxybenzene

The increasing order of their boiling points is

(a I < II < III < IV
(b) IV < I < II < III
(c) IV < II < I < III
(d) I < II < IV < III

39 Given,

Reaction	**Energy change** (in kJ)
$Li(s) \longrightarrow Li(g)$	161
$Li(g) \longrightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \longrightarrow F(g)$	77
$F(g) + e^- \longrightarrow F^-(g)$	(Electron gain enthalpy)
$Li(g) + F^-(g) \longrightarrow LiF(s)$	–1047
$Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$	– 617

Based on data provided, the value of electron gain enthalpy of fluorine would be ➞ JEE Main 2013

(a) –300 kJ mol^{-1} (b) – 350 kJ mol^{-1}
(c) – 328 kJ mol^{-1} (d) –228 kJ mol^{-1}

Direction (Q. No 40-43) *In the following question, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.*

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

40 **Assertion** (A) The bond angles in molecules depend upon electronegativity of central atom, number of lone pairs, odd electrons and multiplicity of bonds.

Reason (R) NO_2 and NO_2^- have angles 134° and 115° respectively.

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

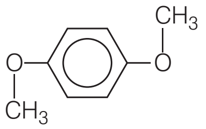
Reason (R) This is because the electronic environment around oxygen is the same even after breakage of one O—H bond.

42 **Assertion** (A) SF_4 has a lone pair of electrons at equatorial position in preference to axial position in the overall trigonal bipyramidal geometry.

Reason (R) If lone pair of electrons is at equatorial position, repulsion will be minimum.

43 **Assertion** (A) *p*-dimethoxy benzene is a polar molecule.

Reason (R) The two methoxy groups at *para* position are located as



DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Which of the following statement(s) is/are true?

(a) HF is less polar than HBr
(b) Absolutely pure water does not contain any ions
(c) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion
(d) In covalency, transference of electrons take place

2 Consider the Born-Haber cycle for the formation of ionic compound given below and identify the compound formed.

$$\left[\begin{array}{l} M(s) \xrightarrow{\Delta H_1} M(g) \xrightarrow{\Delta H_2} M^+(g) \\ \frac{1}{2}X_2(g) \xrightarrow{\Delta H_3} X(g) \xrightarrow{\Delta H_4} X^-(g) \end{array}\right] \xrightarrow{\Delta H_5} Z$$

(a) M^+X^-
(b) $M^+X^-(s)$
(c) MX
(d) $M^+X^-(g)$

3 What is the geometry of nitrogen atom in NH_3, $N(CH_3)_3$ and $N[Si(CH_3)_3]_3$ molecules?

I. Trigonal planar
II. Trigonal pyramidal
III. Square planar

Choose the correct option.

(a) II, II and I
(b) III, III and I
(c) I, II and III
(d) I, III and II

4 O_2 molecule is paramagnetic due to the presence of

(a) two unpaired electrons in anti-bonding MO
(b) one unpaired electron in anti-bonding MO
(c) two unpaired electrons in bonding MO
(d) one unpaired electron in bonding MO

5 The BCl_3 is a planar molecule whereas NCl_3 is pyramidal because

(a) B—Cl bond is more polar than N—Cl bond
(b) N—Cl bond is more covalent that B—Cl bond
(c) nitrogen atom is smaller than boron atom
(d) BCl_3 has no lone pair electrons but NCl_3 has one lone pair of electrons

6 H_2O is dipolar whereas BeF_2 is not. It is because

(a) the electronegativity of F is greater than that of O
(b) H_2O involves hydrogen bonding whereas BeF_2 is angular discrete molecule
(c) H_2O is linear and BeF_2 is angular
(d) H_2O is angular and BeF_2 is linear

7 In terms of polar character, which one of the following order is correct?

(a) $NH_3 < H_2O < HF < H_2S$
(b) $H_2S < NH_3 < H_2O < HF$
(c) $H_2O < NH_3 < H_2S < HF$
(d) $HF < H_2O < NH_3 < H_2S$

8 What will be the lattice enthalpy of $CaCl_2$, if the enthalpy of

(i) sublimation energy of Ca is 121 kJ mol^{-1}
(ii) dissociation energy of Cl_2 to Cl is 242.8 kJ mol^{-1}
(iii) ionisation energy Ca to Ca^{2+} is 2422 kJ mol^{-1}
(iv) electron gain enthalpy for Cl to Cl^- is –355 kJ mol^{-1}
(v) $\Delta_f H$ overall is –795 kJ mol^{-1}

(a) –3225.8 kJ mol^{-1}
(b) –980.8 kJ mol^{-1}
(c) –2870.8 kJ mol^{-1}
(d) –2628 kJ mol^{-1}

9 Select the correct statement(s).

(a) Both lattice energy and hydration energy decrease with the increase in ionic size
(b) Lattice energy can be calculated using Born-Haber cycle
(c) If the anion is larger than the cation, the lattice energy will remain almost constant within a particular group
(d) All of the above statements are correct

10 The bond dissociation energy of B—F in BF_3 is 646 kJ mol^{-1}, whereas that of C—F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B—F bond dissociation energy as compared to that of C—F bond is

(a) smaller size of B-atom as compared to that of C-atom
(b) stronger σ bond between B and F in BF_3 as compared to that between C and F is CF_4
(c) significant $p\pi$-$p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4
(d) lower degree of $p\pi$-$p\pi$ interaction betwen B and F in BF_3 than that between C and F in CF_4

11 If H—X bond length is $2\mathring{A}$ and H–X bond has dipole moment 5.12×10^{-30} cm, the percentage of ionic characters in the molecule will be

(a) 10%
(b) 16%
(c) 18%
(d) 20%

12 The geometrical shapes of XeF_5^+, XeF_6 and XeF_8^{2-} respectively are

(a) trigonal bipyramidal, octahedral and square planar
(b) square pyramidal, distorted octahedral and square antiprismatic
(c) planar pentagonal, octahedral and square antiprismatic
(d) square pyramidal, distorted octahedral and octahedral

13 Suppose the observed value of dipole moment of H_2O molecule is 1.83 D. What will be the H—O—H bond angle in H_2O molecule? (Given bond moment of O—H bond is 1.5 D.)

(a) 104° 20″
(b) 105°
(c) 105° 20″
(d) 104°

ANSWERS

SESSION 1

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

SESSION 2

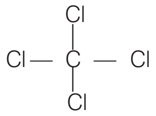
1 (c) **2** (b) **3** (a) **4** (a) **5** (d) **6** (d) **7** (b) **8** (c) **9** (d) **10** (c)
11 (b) **12** (b) **13** (a)

Hints and Explanations

SESSION 1

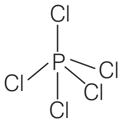
1 The compounds in which central atom has less than 8 electrons in their valence shell, are electron deficient.

(a) CCl_4,



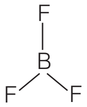
Carbon (central atom) has 8 electrons in the valence shell, 4 from carbon and 1 electron each from four chlorine atoms.

(b) PCl_5,



Phosphorus (central atom) has 10 electrons in valence shell, 5 from P and one each from five chlorine atoms.

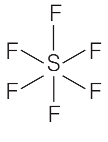
(c) BF_3,



Boron (central atom) has 6 electrons in valence shell, 3 from boron and one each from three flourine atoms.

Boron in BF_3 has less than 8 electrons. So, it is electron deficient molecule.

(d) SF_6

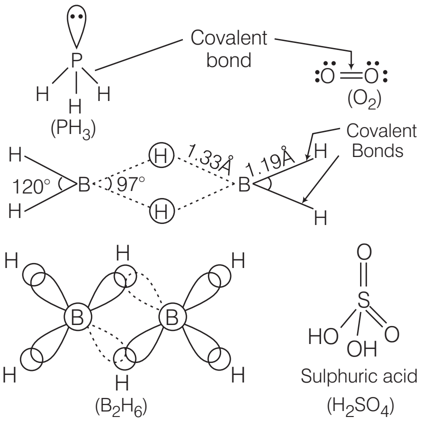


Sulphur (central atom) has 12 electrons in valence shell, 6 from sulphur and one each from six fluorine atoms.

2 For a compound to be soluble, the hydration energy must be greater than lattice energy. Since, NaCl is soluble in water but insoluble in benzence due to,

$\Delta H_{\text{Hydration}} > \Delta H_{\text{Lattice energy in water}}$ and
$\Delta H_{\text{Hydration}} < \Delta H_{\text{Lattice energy in benzene}}$

3 KCl is the only ionic compound. The covalent bonds in PH_3, O_2, B_2H_6 and H_2SO_4 are shown below:

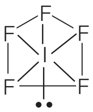


In H_2SO_4 all bond between S and O atom are covalent bonds.

4 % ionic character

$= [16\,(X_{\text{Cl}} - X_{\text{Cs}}) + 3.5\,(X_{\text{Cl}} - X_{\text{Cs}})^2]$
$= [16\,(3.0 - 0.8) + 3.5\,(3.0 - 0.8)^2]$
$= [16 \times 2.2 + 3.5 \times (2.2)^2]$
$= [35.2 + 16.94] = 52.14\%$

5 Only IF_5 is polar because of its unsymmetrical structure. Rest of the molecules have zero dipole moment as they are symmetrical in nature.



Structure of IF_5

6 SiF_4 is a symmetrical tetrahedral molecule and BF_3 is a triangular planar (symmetrical) structure and hence, have zero dipole moment.

7 % ionic character $= \dfrac{\mu_{\text{observed}}}{\mu_{\text{calculated}}} \times 100$

$\mu_{\text{calculated}} = e \times d$
$= 1.6 \times 10^{-19}\text{C} \times 9.17 \times 10^{-11}\text{m}$
$= 1.467 \times 10^{-29}$ cm

$\therefore$ % ionic character
$= \dfrac{6.104 \times 10^{-30}}{1.467 \times 10^{-29}} \times 100$
$= 41.6\%$

8 Covalent character can be determined by applying Fajan's rule.

In all the given compounds, anion is same (Cl^-), hence polarising power is decided by size and charge of cation. Al^{3+} with maximum charge and smallest size has maximum polarising power hence, $AlCl_3$ has maximum covalent character.

9 I_3^- is an ion made up of I_2 and I^- which has linear shape. While Cs^+ is an alkali metal cation.

10 The MO configuration of the given species can be written as :

$H_2\,(1 + 1 = 2) = \sigma 1s^2$
$Li_2\,(3 + 3 = 6) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$
$B_2\,(5 + 5 = 10) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi 2p_y^1$

As the number of antibonding electrons (σ^* or π^*) increases, energy increases and stability decreases.

Thus, the correct order of stability is
$H_2 > Li_2 > B_2$

11 Bond angle of H_2S is smallest because S-atom is larger in size and has low electronegativity.

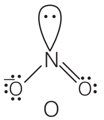
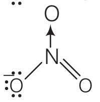
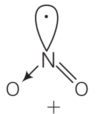
12 *lp-bp* repulsion is maximum in H_2Te due to least electronegativity of Te and minimum in H_2O due to high electronegativity of O. So, the correct order is IV < III < II < I.

13 P is most electronegative among the given options due to this there is more *bp-bp* repulsion.

14 Resonance energy;

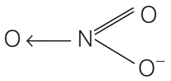
$$\Delta_{H-F} = (BE)_{H-F} - \sqrt{(BE)_{H_2} \times (BE)_{F_2}}$$
$$= 135 - \sqrt{104 \times 38}$$
$$= 135 - 62.86$$
$$= 72.14 \text{ kcal mol}^{-1}$$

15

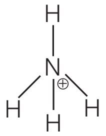
Species	Hybridisation
	sp^2
	sp^2
	sp^2
$O=\overset{+}{N}=O$	sp

16 The d_{z^2} orbital is involved in sp^3d-hybridisation. In sp^3d hybridisation, 1 *s* and 2 *p*-orbitals combine to form three planar triangular hybrid orbitals. The remaining *p*-orbital may combine with d_{z^2} orbital to form two axial orbitals.

17 Count σ-bond, lone pairs and unpaired electron or count number of atoms directly attached, lone pairs and unpaired electrons.

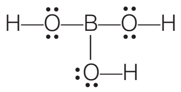
NO_3^- (I) 

NO_2^+ (II) $O=\overset{+}{N}=O$

NH_4^+ (III) 

S.No.	σ-bond	Lone pair	Unpaired electron	Total
I.	3	×	×	3 (sp^2)
II.	2	×	×	2 (sp)
III.	4	×	×	4 (sp^3)

18 H_3BO_3 has structure



Boron has three bonds, thus sp^2 hybridised. Each oxygen atom has two bonds and two lone pairs, hence sp^3 hybridised.

19 (a) $SF_4 = 4bp + 1lp = sp^3d$-hybridisation

(b) $IF_5 = 5bp + 1lp = sp^3d^2$-hybridisation

(c) $NO_2^+ = 2bp + 0lp = sp$-hybridisation

(d) $NH_4^+ = 4bp + 0lp = sp^3$-hybridisation

20 The species BF_4^- and NH_4^+ both 4*bps* and 0*lp*, thus they are sp^3-hybridised, therefore, both these species have similar shape and hybridisation. i.e. They are isostructural species.

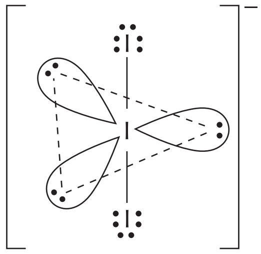
21 (a) CO_3^{2-}, NO_3^- — triangular planar

(b) PCl_4^+, $SiCl_4$ — tetrahedral

(c) PF_5, BrF_5 — trigonal bipyramidal, square pyramidal

(d) AlF_6^{3-}, SF_6 — octahedral

22 The structure of I_3^- ion is



Hence, 9 is the correct answer.

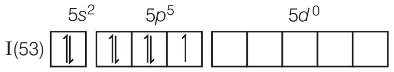
23 Xe-atom has 8 electrons in its outermost shell. In case of XeF_2 out of these 8 electrons 2 are used for bond formation while 3 pairs remain as such, i.e. it has 3 lone pairs.

In case of XeF_4, 4 electrons of Xe are used for bonding, therefore number of lone pairs (non-bonding electrons) is 2.

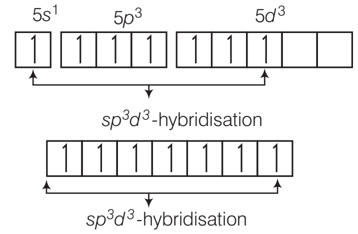
In case of XeF_6, 6 electrons are involved for bond formation, thus, number of lone pair is only 1.

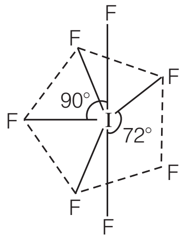
24 IF_7

In ground state



In excited state





The structure of IF_7 is pentagonal-bipyramidal.

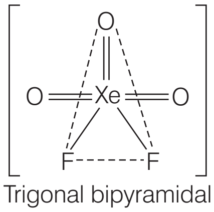
25 $XeOF_4 = 5bp + 1lp$ = square-pyramidal shape

$XeO_3 = 3bp + 1lp$ = pyramidal shape

$XeO_3F_2 = 5bp + 0lp$ = trigonal-bipyramidal shape

$XeOF_2 = 3bp + 2lp$ = T-shape

The shape is trigonal bipyramidal, if a compound have five bond pairs and zero lone pairs.



Trigonal bipyramidal

26 Number of hybrid orbital,

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

[Here V = valence e^- of central atom, C and A = positive and negative charge respectively, M = monovalent atoms]

In IF_6^-, $H = \frac{1}{2}[7 - 0 + 1 + 6] = 7$

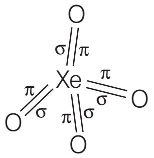
So, the hybridisation is sp^3d^3 and structure should be pentagonal bipyramidal. But it contains one lone pair and 6 bond pairs. Hence, its actual geometry is trigonally distorted octahedron.

27 SF_4 (sp^3d), CF_4 (sp^3) and XeF_4 (sp^3d^2) contain 1,0 and 2 lone pairs respectively. Therefore, their shapes are also different.

28 Although Cl^- is a weak field ligand but in case of $[PdCl_4]^{2-}$, it pair up the electrons of Pd and results in dsp^2-hybridisation because of the large size of Pd^{2+}. In all other options, pairing is not possible, so hybridisation is sp^3 with tetrahedral structure.

29 The structure of XeO_4 molecule is shown below :

It contains four $p\pi$-$d\pi$ bonds.



30 To identify the magnetic nature we need to check the molecular orbital configuration. If all orbitals are fully occupied, species is diamagnetic while when one or more molecular orbitals is/are singly occupied, species is paramagnetic.

(a) NO $(7 + 8 = 15)$

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$$
$$\pi 2p_x^2 = \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_x^1 = \pi^* 2p_y^0$$

One unpaired electron is present. Hence, it is paramagnetic.

(b) CO $(6 + 8 = 14)$ -

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$$
$$\pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$$

No unpaired electron is present.

Hence, it is diamagnetic.

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

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$
$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

Two unpaired electrons are present. Hence, it is paramagnetic.

(d) $B_2(5 + 5)$ -

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1$$
$$= \pi 2p_y^1$$

Two unpaired electrons are present.

Hence, it is paramagnetic.

31 The correct increasing order of energies of molecular orbitals of N_2 is given below

$$\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2$$
$$< (\pi 2p_x^2 \approx \pi 2p_y^2) < \sigma 2p_z^2$$

32 $C_2 = (6 + 6 = 12) =$

$$\sigma 1s^2 \ \sigma^* 1s^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi 2p_x^2 = \pi 2p_y^2$$

$N_2 = (7 + 7 = 14)$

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2,$$
$$= \pi 2p_y^2, \sigma 2p_z^2$$

As all the electrons are paired, thus both C_2 and N_2 are diamagnetic.

33 In the formation of dioxygen from oxygen atoms, ten molecular orbitals will be formed.

$$O_2 = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z{}^2, \pi 2p_x^2$$
$$= \pi 2p_y{}^2, \ \overset{*}{\pi} 2p_x^1 = \overset{*}{\pi} 2p_y^1, \overset{*}{\sigma} 2p_z^0$$

34 O_2^+ contains one unpaired electron, so it is paramagnetic and therefore it has bond order of 2.5 while O_2 contains only 2 unpaired electrons. So, it posses bond order of 2.

35 Stability of a molecule $\propto$ bond order

$$Li_2(6) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

$$Li_2^-(7) = \sigma 1s^2, \sigma^* 1s^2 \ \sigma 2s^2, \sigma^* 2s^1$$

$$\text{Bond order} = \frac{4-3}{2} = 0.5$$

$$Li_2^+(5) = \sigma 1s^2, \sigma^* 2s^2, \sigma 2s^1$$

$$\text{Bond order} = \frac{3-2}{2} = 0.5$$

As both Li_2^- and Li_2^+ has 0.5 bond order but Li_2^- is less stable because its valence electron is present in antiorbital. The stability order is $Li_2^- < Li_2^+ < Li_2$

36 Species having zero or negative bond order do not exist.

$$H_2^{2+}(1 + 1 - 2 = 0) = \sigma 1s^0$$

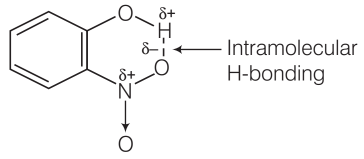
Bond order = 0

$$He_2(2 + 2 = 4) = \sigma 1s^2, \overset{*}{\sigma} 1s^2$$

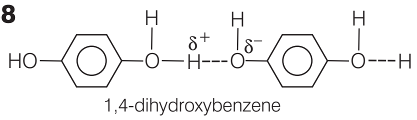
$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$$

So, both H_2^{2+} and He_2 do not exist.

37 There is intramolecular H-bonding in *o*-nitrophenol and thus, solubility in water is decreased.



38



1,4-dihydroxybenzene

1, 4-dihydroxybenzene and isomer of dihydroxybenzene shows highest boiling point due to intermolecular H-bonding followed by *meta* and *ortho* isomer which shows intramolecular H-bonding. Hence, correct option is (b).

39 From Born-Haber cycle,

$$Q = S + I + D + EA + U$$
$$-617 = 161 + 520 + 77 + EA - 1047$$

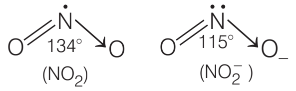
[$\because$ Here, S = sublimation energy, I = ionisation energy,

D = dissociation energy, EA = electron gain enthalpy

and U = lattice energy]

$$\therefore EA = 289 - 617 = -328 \text{ kJ mol}^{-1}$$

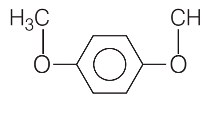
40 Reason is the correct explanation for Assertion.



41 The bond enthalpies of the two O—H bonds in H—O—H are not equal. This is because electronic environment around O is not same after breakage of one O—H bond.

42 Both Assertion and Reason are correct.

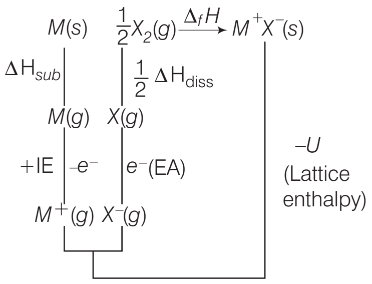
43 *p*-dimethoxy benzene is polar due to unsymmetrical orientation of CH_3 group as shown below:



SESSION 2

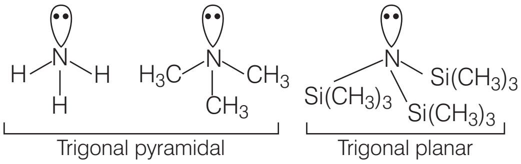
1 A chemical bond is formed when forces of attraction are greater than the forces of repulsion.

2 The Born-Haber cycle takes place as follows :



Hence, Z is $M^+X^-(s)$

3 In case of NH_3 and $N(CH_3)_3$: Trigonal pyramidal due to *lp-bp* repulsion.



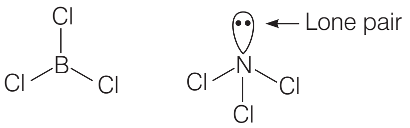
In case of $N[Si(CH_3)_3]$ it is planar. It is due to the fact that lone-pair on N-atom is transferred to the empty *d*-orbitals of silicon ($p\pi$-$d\pi$ overlapping) and its Lewis base character is lost.

4 $O_2\ (8+8=16) = \sigma 1s^2, \sigma^* 2s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

According to MO theory as there are two unpaired electron present in antibonding MO hence it is paramagnetic.

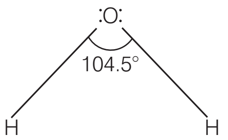
5



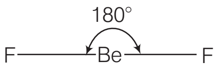
No lone pair on B

One lone pair on N

6 The structure of H_2O is angular V-shape and has sp^3 hybridisation and bond angle is 105°. Its dipole moment value is positive or more than zero.



Here, $\mu > 0$



$\mu = 0$

But in BeF_2, structure is linear due to *sp*-hybridisation ($\mu = 0$) Thus, due to $\mu > 0$, H_2O is dipolar and due to $\mu = 0$, BeF_2 is non-polar.

7 Polarity is decided by (EN) difference between two adjacent atoms. The correct order of polarity is :

$$H_2S < NH_3 < H_2O < HF$$

8 Given, $\Delta_{sub} H_{Ca} = 121\ \text{kJ mol}^{-1}$

$\Delta H_{Cl-Cl} = 242.8\ \text{kJ mol}^{-1}$

$\Delta_f H_{Ca^{2+}} = 2422\ \text{kJ mol}^{-1}$

$\Delta_{eg} H_{Cl} = -355\ \text{kJ mol}^{-1}$

$\Delta_f H_{CaCl_2} = -795\ \text{kJ mol}^{-1}$

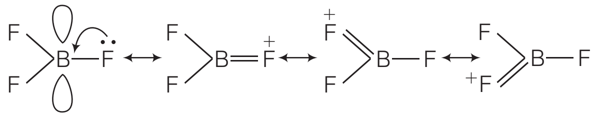
$\Delta_f H_{CaCl_2} = \Delta_{sub} H_{Ca} + \Delta H_{Cl-Cl} + \Delta_f H_{Ca^{2+}}$
$+ 2 \times \Delta_{eg} H_{Cl} + \Delta_l H_{CaCl_2}$

or $-795 = 121 + 242.8 + 2422 - (355 \times 2) + \Delta_l H_{CaCl_2}$

$\therefore$ $\Delta_l H_{CaCl_2} = -2870.80\ \text{kJ mol}^{-1}$

9 All given statements are correct.

10 In BF_3 there is significant $p\pi$-$p\pi$ interaction between unshared *p*-orbital (having no electron) of boron and the lone pair of electron of fluorine in 2*p*-orbital.



(I) (II) (III) (IV)

11 $\mu = q \times d$

$\mu_{cal} = 2.0 \times 10^{-10}\ \text{m} \times 1.6 \times 10^{-19}\ \text{C}$

$= 3.2 \times 10^{-29}$ C-m.

$$\text{Percentage of ionic character} = \frac{\mu_{exp}}{\mu_{cal}} \times 100$$

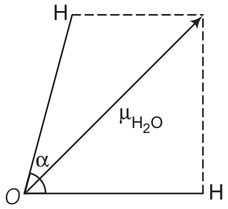
$$= \frac{5.12 \times 10^{-29}}{3.2 \times 10^{-29}} \times 100 = 16\%$$

12 $XeF_5^+ \Rightarrow 5\ bp + 1\ lp \Rightarrow$ (square pyramidal)

$XeF_6 \Rightarrow 6\ bp + 1\ lp \Rightarrow$ (distorted octahedral)

$XeF_8^{2-} \Rightarrow 8\ bp + 1\ lp \Rightarrow$ (square antiprismatic)

13 As dipole moment of H_2O is the resultant of the two vectors (O—H bonds), therefore if α is the angle between the two vectors, then



$$\mu_{H_2O} = \sqrt{\mu_{O-H}^2 + \mu_{O-H}^2 + 2\mu_{O-H}^2 \cos\alpha}$$

$$1.84 = \sqrt{(1.5)^2 + (1.5)^2 + 2(1.5)^2 \cos\alpha}$$

or $3.3856 = 2.25 + 2.25 + 4.50 \cos\alpha$

or $\cos\alpha = -0.2476$

or $\alpha = 104° 20''$

$[\cos(180 - \theta) = -\cos\theta$

i.e., $\cos(180 - \alpha) = 0.2476]$