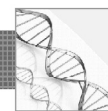


Chemical Bonding

Key Concepts



INTRODUCTION

The formation of a chemical bond between two atoms implies that the system consisting of these two atoms at stable internuclear distance is energetically more stable than the two isolated atoms. A general study on the reactivity of different elements revealed that noble gases have little tendency to combine with other elements. This leads to the fact that the noble gases have stable outer configuration $(ns)^2 (np)^6$ (octet configuration). All other atoms combine to achieve the stable octet configuration either by mutual sharing of electrons (covalent bond) or by complete transfer of electron(s) from one atom to other (ionic bond).



KÖSSEL AND LEWIS THEORY OF CHEMICAL COMBINATION

According to this theory, atoms can combine either by transfer of outer-shell electrons, known as valence electrons, from one atom to another or by sharing the valence electron(s) in order to achieve octet configuration (i.e., a total of eight electrons) in their respective valence shells.

The sharing of electron(s) leads to the formation of covalent bond while transferring of electron(s) leads to the formation of ionic bond between the two involved atoms.



REPRESENTATION OF A BOND BY LEWIS STRUCTURE

In Lewis structure, a bond between the two atoms is shown by Lewis electron-dot symbols in which valence electrons are shown by dots around the letter symbol of the atom. The dots are placed as follows.

Place a single dot on the four sides of the letter symbol followed by the second dot till all the valence-electrons have been accounted for.

Illustrations:

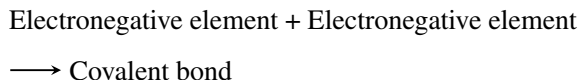
Lithium ($2s^1$)	• Li	Beryllium ($2s^2$)	• Be •
Boron ($2s^2(2p)^1$)	•• B	Carbon ($2s^2(2p)^2$)	••C••
Nitrogen ($2s^2(2p)^3$)	••• N	Oxygen ($2s^2(2p)^4$)	••O••
Fluorine ($2s^2(2p)^5$)	•••• F	Neon ($2s^2(2p)^6$)	••Ne••



FORMATION OF COVALENT BOND(S)

A covalent bond involves mutual sharing of valence electrons between two atoms. The sharing of two, four and six electron leads to the formation of a single, double and triple bond, respectively.

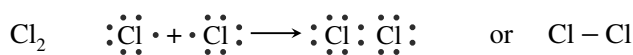
A covalent bond is formed if the atoms have lesser number of valence electrons as compared to the nearby noble gas which has octet configuration. Such elements are known as electronegative elements. Thus, the criterion of the formation of covalent bond is:



Exception to the octet rule is the hydrogen atom which can accommodate only two electrons which corresponds to the electronic configuration of nearby helium ($1s^2$) atom.

Illustrations:

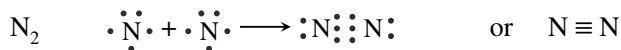
Formation of Single Bond(s)



Formation of Double Bond(s)



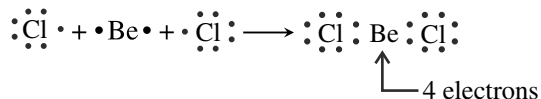
Formation of Triple Bond(s)



EXCEPTIONS TO THE OCTET RULE

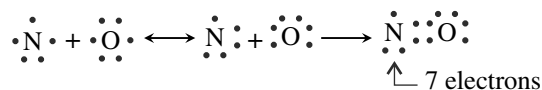
The octet rule is generally obeyed by the elements of second and third periods with the following exceptions:-

The Incomplete Octet



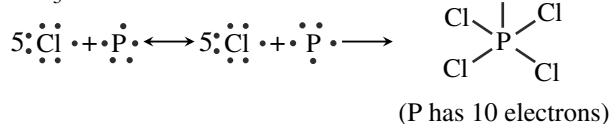
Odd-Electron Molecules

All atoms of a compound containing odd number of electrons will not satisfy octet rule as even number of electrons are required for pairing of electrons.



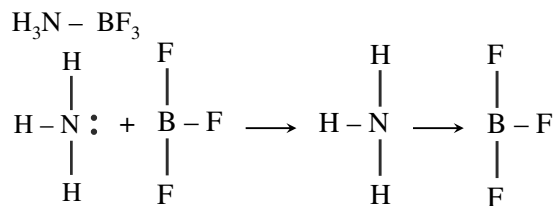
The Expanded Octet

Elements of third period and beyond can accommodate more than 8 electrons due to the availability of vacant d orbitals.



COORDINATE COVELENT (OR DATIVE) BOND

If a pair of electrons shared between two atoms comes exclusively from one of the atoms, the bond formed is said to be a coordinate covalent (or dative) bond. To keep track of electrons, a coordinate covalent bond may be represented by an arrow (\longrightarrow). Once a coordinate bond is formed, it behaves like a covalent bond.



Writing a Lewis Structure

The structure of a molecule or ion may be written by following the steps listed below:

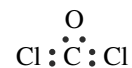
1. Calculate the total number of valence electrons of the atoms in the molecule. For an anion, add the number of negative charges and for a cation, subtract the number of positive charges.
2. Write the skeleton structure of the molecule or ion connecting every bonded pair of atoms by a single bond, i.e., a pair of electron dots.
3. Assign a total of eight electrons in each atom (except hydrogen) surrounding the central atom.
4. Distribute the remaining electrons (if any) as pairs to the central atom.

If there are fewer than eight electrons on the central atom, move one or two pairs of electron from a surrounding atom to form double or triple bond between the two atoms. Atoms that often form multiple bond are C, N, O and S.

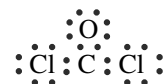
Lewis structure of COCl_2

Step 1 Valence electrons are $4 + 6 + 2 \times 7 = 24$

Step 2 Carbon being the most electropositive atoms occupies the central position to which other atoms are bonded.

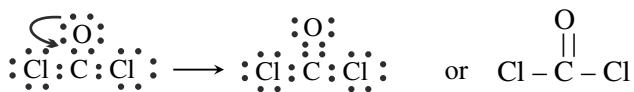


Step 3 Assign 8 electrons each to surrounding atoms



Step 4 There were 24 valence electrons and all of them have been distributed. However, the central C atom has only 6 electrons. In order that this atom also has 8 electrons, move one pair of electrons

from O to the bond connecting C atom, thus forming a double bond.



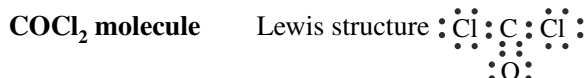
FORMAL CHARGE AND LEWIS STRUCTURE

The formal charge an atom is the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atoms in a Lewis structure. The equation for computing formal charge is,

$$\text{Formal charge} = \text{Valence electrons on free atom} - \text{Number of (Nonbonding} + \frac{1}{2} \text{ bonding) electrons in a Lewis structure}$$

The sum of the formal charges of atoms in a Lewis structure is equal to the charge on the molecular species.

Illustration



Atom	Valence electrons in a free atom	Electrons in Lewis structure		Formal Charge
		Non-bonding	Bonding	
Cl	7	6	2	$7 - (6 + \frac{1}{2} \times 2) = 0$
O	6	4	4	$6 - (4 + \frac{1}{2} \times 4) = 0$
C	4	0	8	$4 - (0 + \frac{1}{2} \times 8) = 0$



UTILITY OF FORMAL CHARGE

Computing formal charge of atoms in a molecule or ion helps deciding a possible Lewis structure of the species. The guiding principles are as follows:

- Amongst the several Lewis structures, the species having the lowest magnitude of formal charge is the preferred structure.
- Amongst Lewis structures having similar distribution of formal charges, the one having negative formal charges on the more electronegative atoms is the preferred structure.



POLAR COVALENT BOND

Each atom in a molecule has its own ability to attract the bonded pair of electrons. This ability is known as electronegativity. The bonded pair of electrons in homonuclear diatomic molecules (such as H₂, O₂, F₂, Cl₂, etc.) is shared equally by both atoms. This is not correct in the case of heteronuclear diatomic molecules (such as HCl, HF, NO, etc.) The bonded pair of electrons is closer to the atom having larger electronegativity. Consequently, this atom acquires a partial negative charge while the other atom acquires equal partial positive charge. Because of the charge separation, the covalent bond between these two atoms is said to be a polar covalent bond.



DIPOLE MOMENT

The polarization of bonded pair of electrons between two atoms is expressed in terms of physical quantity known as dipole moment (symbol : μ). It is defined as

$$\mu = (\delta q) (r)$$

where δq is the partial charge separation between two atoms and r is the distance between the two atoms.

Representation of Dipole Moment

Dipole moment is a vector quantity, i.e., it has magnitude as well as direction. In chemistry, dipole moment is indicated by the crossed arrow as shown in the following.

positive end \longleftrightarrow negative end

that is, it is directed from positive end to the negative end.

Unit of Dipole Moment

In SI system, unit of dipole moment = (unit of δq) (unit of r) = Cm

In CGS system, unit of dipole moment = (esu) (cm)

Most molecules have dipole moment of the order of 10^{-18} esu cm. This value of dipole moment is known as 1 debye (written as 1 D).

$$1\text{D} = 10^{-18} \text{ esu cm} = (10^{-18}) \left\{ (1 \text{ esu}) \left(\frac{1.6 \times 10^{-19} \text{ C}}{4.8 \times 10^{-10} \text{ esu}} \right) \right\} \\ (10^{-2} \text{ m}) = 3.33 \times 10^{-30} \text{ cm}$$



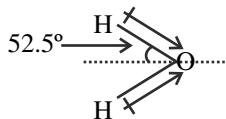
DIPOLE MOMENT OF A POLYATOMIC MOLECULE

Each bond in a molecule has a dipole moment, known as bond moment. The dipole moment of a molecule is obtained by the vector addition of these bond moments.

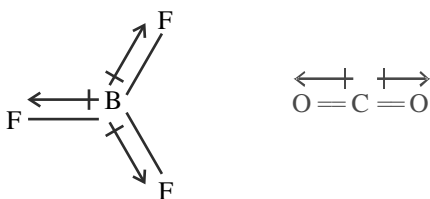
Illustration

The bond moment of O – H bond is 1.52 D. The bond angle of H₂O is 105°. The dipole moment of H₂O molecule will be

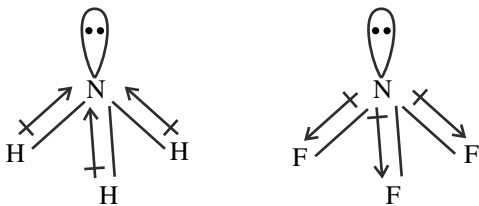
$$\mu_{\text{H}_2\text{O}} = 2\mu_{\text{OH}} \cos (105^\circ/2) = 2 (1.52 \text{ D}) (0.609) = 1.85 \text{ D}$$

**NONPOLAR POLYATOMIC MOLECULE**

The dipole moment of a nonpolar polyatomic molecule is zero inspite of the fact that the bond moments of the molecule is not zero. This is due to the fact that the individual bond moments in the molecule is symmetrically placed so that their vector additions is zero.

Illustration:**COMPARISON OF DIPOLE MOMENTS OF NH₃ AND NF₃**

Both NH₃ and NF₃ have pyramidal shapes with lone pair of electrons on nitrogen atom.



In NH₃, orbital dipole acts in the same direction as the sum of bond vectors of the three N – H bond bonds. In NF₃, orbital dipole acts in the opposite direction to the sum of bond vectors of the three N – F bond bonds. These facts make the dipole moment of NH₃ ($\mu = 1.57 \text{ D}$) larger than that of NF₃ ($\mu = 0.24 \text{ D}$).

**PERCENT IONIC CHARACTER OF A POLAR BOND**

The percent ionic character of a polar bond A – B is defined as:

$$\text{Percent ionic character} = \frac{\mu_{\text{AB}}}{\mu_{\text{ionic}}} \times 100$$

where $\mu_{\text{ionic}} = (e r_{\text{AB}})$ corresponds to 100% ionic character of the bond.

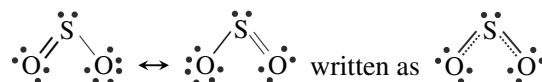
Illustration:

The bond moment of O – H bond is 1.52 D. If bond length O – H is 95 pm, its percent ionic character will be

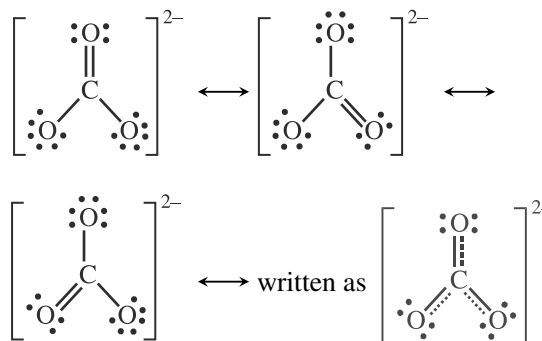
$$\begin{aligned} \text{Percent ionic character} &= \frac{\mu_{\text{OH}}}{e r_{\text{OH}}} \times 100 \\ &= \frac{(1.52 \text{ D})(3.33 \times 10^{-30} \text{ Cm / 1D})}{(1.6 \times 10^{-19} \text{ C})(95 \times 10^{-12} \text{ m})} \times 100 \\ &= 33.3 \% \end{aligned}$$

**CONCEPT OF RESONANCE**

Sometimes, one can write more than one equivalent Lewis structures differing in the distribution of electrons over a given skeleton of atoms in a molecule. None of the individual structures adequately explains the characteristics of the molecule. However, these can be explained if the actual structure of the molecule is considered as the superposition of individual structures. This phenomenon is known as resonance and the individual structures are known as resonating structures. It is represented by a double-headed arrow (\leftrightarrow) inserted between the resonating structures.

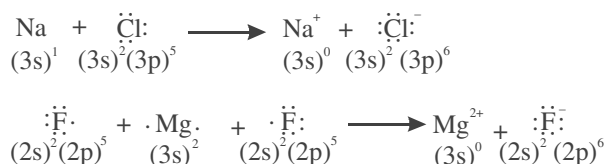
Illustrations:

The resonance hybrid of the two Lewis structures makes both the S – O bond lengths equal in size.

**FORMATION OF AN IONIC BOND**

The transfer of valence electron(s) from one atom of an element to the valence shell of the atom of some other

element leads to the formation of positive and negative ions, respectively. The electrostatic attraction between the positive and negative ions results in the formation of an ionic bond between the involved ions.



Energies Involved in the Formation of One Molecule of Sodium Chloride

The formation of $\text{Na}^+\text{Cl}^-(\text{g})$ from $\text{Na}(\text{g})$ and $\text{Cl}(\text{g})$ involves the following steps.

- (i) $\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + e^- \quad E_i = 8.24 \times 10^{-19} \text{ J}$
 (ii) $\text{Cl}(\text{g}) + e^- \rightarrow \text{Cl}^-(\text{g}) \quad E_{\text{ea}} = -5.78 \times 10^{-19} \text{ J}$
 (iii) $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{Na}^+\text{Cl}^-(\text{g}) \quad \text{PE}$

where PE is the potential energy in the formation of ionic bond. This is evaluated by the expression

$$\text{PE} = \frac{Q_1 Q_2}{(4\pi\epsilon_0)r}$$

where $Q_1 = Q_2 = 1.60 \times 10^{-19} \text{ C}$ and $r = r_{\text{Na}^+} + r_{\text{Cl}^-} = 95 \text{ pm} + 181 \text{ pm} = 276 \text{ pm}$. Considering Q_1 and Q_2 as point charges, we have

$$\begin{aligned} \text{PE} &= \frac{(1.60 \times 10^{-19} \text{ C})(-1.60 \times 10^{-19} \text{ C})}{(4)(3.14)(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(276 \times 10^{-22})} \\ &= -8.34 \times 10^{-19} \text{ J} \end{aligned}$$

Hence, for the reaction $\text{Na}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{Na}^+\text{Cl}^-(\text{g})$

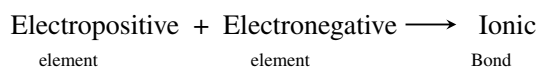
$$\begin{aligned} \text{we have } \Delta E &= E_i + \Delta E_{\text{ea}} + \text{PE} \\ &= (8.24 - 5.78 - 8.34) \times 10^{-19} \text{ J} \\ &= -5.88 \times 10^{-19} \text{ J} \end{aligned}$$

Comment: The negative value of ΔE indicates that the formation of an isolated ionic bond $\text{Na}^+\text{Cl}^-(\text{g})$ is feasible as the combination is energetically more stable than $\text{Na}(\text{g})$ and $\text{Cl}(\text{g})$ taken together.

Essential Requirement for the formation of an ionic bond: For ΔE in Equation (3) to be negative, we must have

- (i) Low value of E_i . This is shown by electropositive element(s).
 (ii) High value of E_{ea} . This is shown by electronegative element(s).

Hence



(eg, elements of Gp.1) (eg, elements of Gp. 17)

Formation of 1 mol of Solid Ionic Compound from Constituent Elements

Taking an example of sodium chloride, we have the following steps in the formation of solid compound.

- (i) $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g}) \quad \Delta H_1 = 108 \text{ kJ mol}^{-1}$
 (ii) $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g}) \quad \Delta H_2 = 120 \text{ kJ mol}^{-1}$
 (iii) $\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + e^- \quad \Delta H_3 = 496 \text{ kJ mol}^{-1}$
 (iv) $\text{Cl}(\text{g}) + e^- \rightarrow \text{Cl}^-(\text{g}) \quad \Delta H_4 = -349 \text{ kJ mol}^{-1}$
 (v) $\frac{\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{Na}^+\text{Cl}^-(\text{s}) \quad \Delta H_5 = -788 \text{ kJ mol}^{-1}}{\text{Na}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Na}^+\text{Cl}(\text{s}) \quad \Delta H = -313 \text{ kJ mol}^{-1}}$

Since ΔH is negative, the formation of solid NaCl is energetically favorable. From the values of ΔH 's listed above, it is obvious that the step (v) is the most favourable step since its highly exothermic nature counter acts the endothermic steps (i) to (iii).

The enthalpy involved in the reversal of step (v), i.e., $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$ is known as lattice energy of the ionic solid.

By definition, lattice energy of an ionic solid is the energy required to completely separate one mole of solid ionic compound into gaseous constituent ions. Larger the value of lattice energy, more stable the ionic compound.

The lattice energy is determined indirectly through the use of Born-Haber cycle. The latter involves the steps (i) to (v) listed above for the formation of solid ionic compound. In this cycle, ΔH is determined experimentally. Subtraction of ΔH_1 , ΔH_2 , ΔH_3 and ΔH_4 from the value of ΔH gives the value of ΔH_5 . The lattice energy is negative of the value of ΔH_5 .

Fajan Rules: An ionic compound has partial covalent character and vice versa. The partial covalency in an ionic compound may be explained qualitatively with the help of Fajan rules described in the following.

High charge and small size of the cation: Such an ion will exert a greater effect in polarizing anions causing cationic electronic charge to penetrate partially into the anionic electronic cloud resulting into the partial covalent bond character to the ionic bond.

High charge and large size of the anion: The electronic cloud of such an anion is most easily polarized by the cation because the anionic charge cloud is less influenced by the nuclear charge of the anion.

Electron configuration of the cation: For two cations of the same size and charge, the cations of electronic configuration $(n-1)d^x ns^0$ (i.e., transition metal ions) have

more polarizing power than the cation of electronic configuration $(n-1)s^2(n-1)p^6 ns^0$ (i.e., alkali and alkaline earth metal ions). This is due to less shielding of nucleus by the electronic cloud of transition metal ions as compared to that in the alkali and alkaline metal ions.

Hg^{2+} ion has larger polarizing effect than Ca^{2+} ion. Lithium salts have more covalent character than the alkali salts. I^- ion is more easily polarized than Cl^- ion by Ag^+ ion.



THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The covalent-bonded molecules have definite shapes which cannot be accounted for by Lewis structures.

A simple theory, known as VSEPR theory, was proposed by Sidgwick and Powell in 1940 and was developed and refined by Nyholm and Gillespie in 1957. The guiding rules of this theory are as follows.


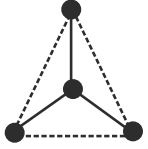
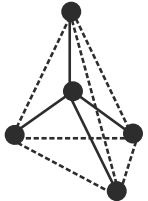
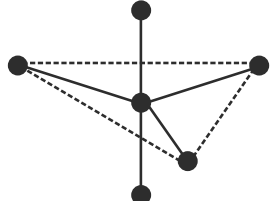
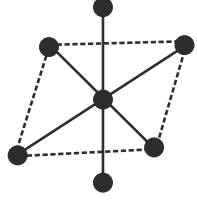
The number of electron pairs in the valence shell of the central atom of a molecule decides the shape of the molecule. These pairs of electrons occupy the specific positions so as to minimize the mutual electronic repulsion. A multiple bond is treated as if it is a single electron pair.

The repulsive interaction of electron pairs decrease in the order

Lone pair (lp) - Lone pair (lp) > Lone pair (lp) - Bond pair (bp) > Bond pair (bp) > Bond pair (bp)

The shapes of molecules as predicted by VSEPR theory are shown in Table.

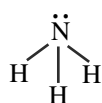
Shapes of some molecules on the basis of VSEPR model

Molecules	Number of valence				Basic shape
	Electrons around the central atom	Electron pairs	Bonding pairs	Lone pairs	
(i) $BeCl_2$	4	2	2	0	Linear 
(ii) BCl_3	6	3	3	0	Triangular planar 
(iii) CH_4	8	4	4	0	Tetrahedron 
NH_3	8	4	3	1	
H_2O	8	4	2	2	
(iv) PF_5	10	5	5	0	Trigonal bypramid 
SF_4	10	5	4	1	
ClF_3	10	5	3	2	
(iv) SF_6	12	6	6	0	Octahedron 
IF_5	12	6	5	1	

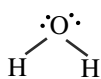
A few examples of molecules containing lone pair electrons along with their geometry are described in the following



Shape : Bent
Bond angle : 109.5°



Shape : Trigonal pyramidal
Bond angle : 107°



Shape : Bent
Bond angle : 104.5°



VALENCE BOND THEORY

The quantitative description of chemical bond is provided by the quantum mechanical theories. Two theories, namely, valence bond (VB) and molecular orbital (MO) have been developed.

The essential guidelines of VB method are as follows.

- A molecule is considered to be a collection of atoms with electrons occupying their respective atomic orbitals.
- The formation of molecule is analysed in terms of interactions amongst electrons-electrons, electrons-nuclei and nuclei-nuclei.
- For a molecule to be stable, the electrostatic attractions must predominate over the electrostatic repulsion. The difference in these two is released in the form of heat. Thus, a molecule is energetically more stable than the individual atoms.

Electron associated with atom H_A can go to the atom H_B and vice versa through the overlap region. Also in the overlap region, there will be some probability of finding both the electrons and thus according to Pauli's exclusion principle, these two electrons must have opposite spins.



STABILITY OF THE MOLECULE

The intervening electronic charge between the two nuclei has an affect of decreasing nuclear repulsion and maximises electron-nuclei attractions. This lead to the stable H_2 molecule.

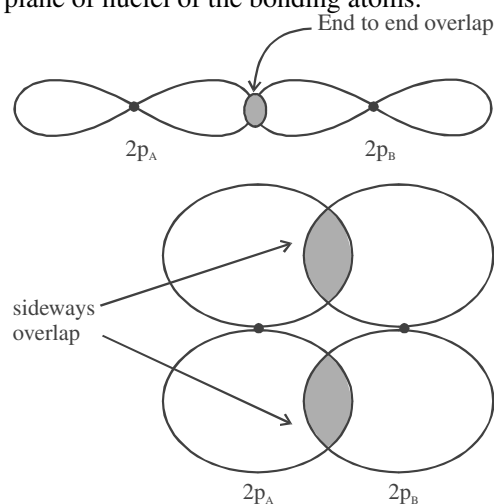


SIGMA AND PI BONDS

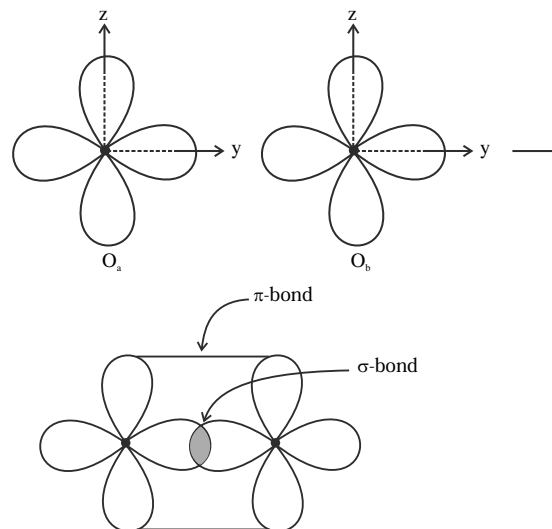
In a molecule, two of overlapping of orbitals having directional characteristics may be distinguished.

End to End Overlap - Sigma Bond (σ Bond): In this overlapping, the electronic charge is concentrated between the nuclei of bonding atoms.

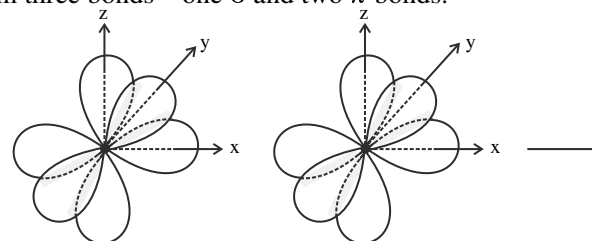
Sideways Overlap - Pi Bond (π Bond): In this overlapping, the electronic charge is concentrated above the plane of nuclei of the bonding atoms.

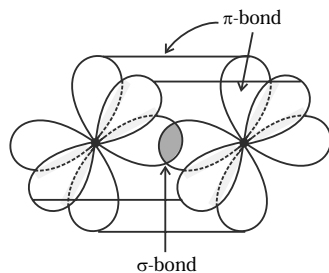


Oxygen molecule: The electronic configuration of oxygen atom is $(1s)^2 (2s)^2 (2p_x)^2 (2p_y)^1 (2p_z)^1$. There are two 2p atomic orbital, each containing one electron. Thus it can form two bonds — σ and π bonds.



Nitrogen molecule: The electronic configuration of nitrogen atom is $(1s)^2 (2s)^2 (2p_x)^1 (2p_y)^1 (2p_z)^1$. There are three 2p orbitals, each containing one electron. Thus it can form three bonds—one σ and two π -bonds.





THE CONCEPT OF HYBRIDISATION

According to the valence bond theory,

${}_4\text{Be}$ ($1s^2, 2s^2$)	Should form no chemical bond as it does not contain any unpaired electron.
${}_5\text{B}$ ($1s^2, 2s^2, 2p^1$)	Should form a single bond as it contains only one unpaired electron.
${}_6\text{C}$ ($1s^2, 2s^2, 2p_x^1, 2p_y^1$)	Should form two bond as it contains two unpaired electron.

Experimentally it is found that Be is divalent, B is trivalent and C is tetravalent.

To explain this, the concept of hybridisation is introduced. In this concept we have,

Two or more atomic orbitals of the same atom mix each other to provide a new set of identical number of degenerate orbitals. These orbitals, known as hybrid orbitals, are completely identical in size, shape and orientations.

sp^3 Hybridisation: In sp^3 (pronounced as 's-p three') hybridisation, one s orbital and three p orbitals of the same valence shell of an atom combine to give four degenerate equivalent sp^3 hybrid orbitals. These four orbitals are directed towards the four corners of a regular tetrahedron making an angle of $109^\circ 28'$ with respect to each other.



HYBRID ORBITALS INVOLVING D ORBITALS

Three main hybridisation involving d orbitals are as follows :

sp^2d or dsp^2 Hybridisation: The resultant four hybrid orbital lie in a plane with bond angle of 90° with respect to each other.

In dsp^2 , d orbital belongs to penultimate shell while in sp^2d , it belong to the valence shell.

sp^3d or dsp^3 Hybridisation: The resultant five hybrid

orbitals are directed to the corners of trigonal bipyramid three are in the same plane making an angle 120° with each other, fourth and fifth are directed perpendicular to the plane (one above and the other below).

sp^3d^2 or d^2sp^3 Hybridisation: The resultant six hybrid orbitals are directed to the corners of regular octahedron four are in the same plane making an angle 90° with each other, fifth and sixth are directed perpendicular to the plane (one above and the other below).

sp^3d^3 or d^3sp^3 Hybridisation: The resultant seven orbitals are directed to the corners of a regular pentagonal bipyramid five are in the same plane and sixth and seventh are directed perpendicular to the plane (one above and the other below).



MOLECULAR ORBITAL THEORY

Molecular orbital theory provides the explanation for the formation of bond in a molecule on the lines very similar to those of atomic orbitals. The essential guidelines of this theory are as follows.

Like atomic orbitals in an atom, there exists molecular orbitals in a molecule. The only difference is that an atomic orbital is a monocentric (i.e., exists around a single nucleus) while a molecular orbitals is a polycentric (i.e., exists around more than one nucleus and thus belongs to the molecule as a whole).

Each molecular orbitals in a molecule describes different electronic behaviour and has a fixed energy.

Electrons in a molecule occupy molecular orbitals in accordance with aufbau principle, Pauli's exclusion principle and Hund's rule.

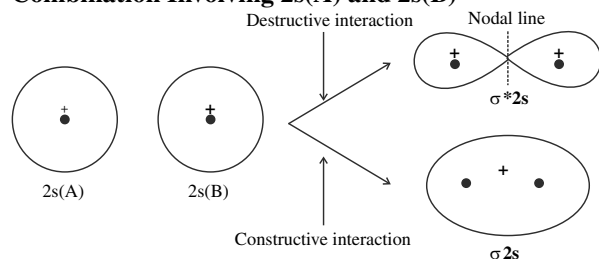
The square of molecular orbital (which a mathematical expression) evaluated at a point around the nuclei of the molecule gives the probability of finding electron at that point.

The shape of a molecular orbital is the region around the nuclei where there exists 90–95% probability of finding the electron.

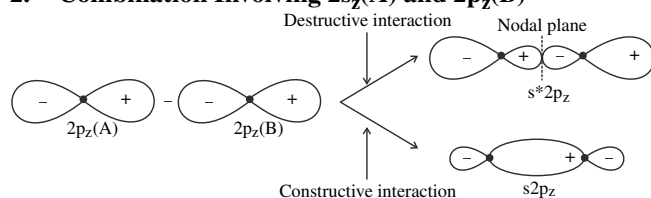
Designation of Molecular orbital: The designation of a molecular orbital starts by starting its σ or π nature followed by the atomic orbitals into which it separates at larger distance. The antibonding orbital is designated by placing an asterisk on the symbol σ or π .

The effective combinations of atomic orbitals of atoms A and B are as follows:

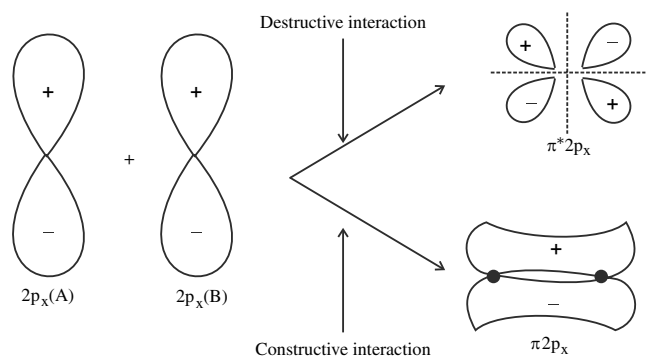
1. Combination Involving 2s(A) and 2s(B)



2. Combination Involving 2s_z(A) and 2p_z(B)



3. Combination Involving 2p_x(A) and 2p_x(B)

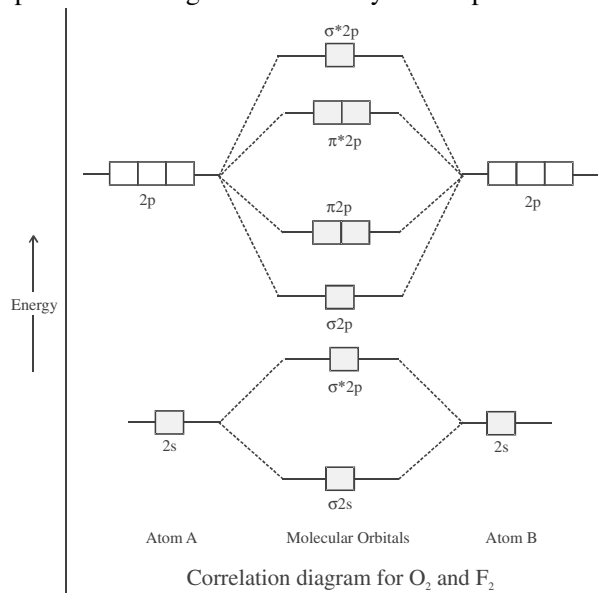


4. Combination Involving 2p_y(A) and 2p_y(B)

The molecular orbitals formed are similar to $\pi 2p_x$ and $\pi^* 2p_x$ in the direction of y-axis.

Relative Energies of Molecular Orbitals correlation

Diagram displays the correlation diagram expected for the orbitals of atoms of second period. In this diagram, $E(\sigma 2p) < E(\pi 2p)$ since the end-to-end overlap 2p orbitals is expected to be larger than side-ways overlap.



The correlation diagram shown in figure 30 is found to be applicable only for O₂ and F₂ molecules.

The relative energies of molecular orbitals is

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

For the molecules Li₂ to N₂, the energies difference in 2s(A) and 2p(A) is not large and thus these two orbitals jointly combine with the orbitals jointly combine with the orbitals 2s(B) and 2p(B). The resultant correlation is modified and is known in figure. The notable modification is that

$$E(\sigma 2p) > E(\pi 2p)$$

The relative energies of molecular orbitals is

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



ELECTRONIC STRUCTURE AND MOLECULAR CHARACTERISTICS

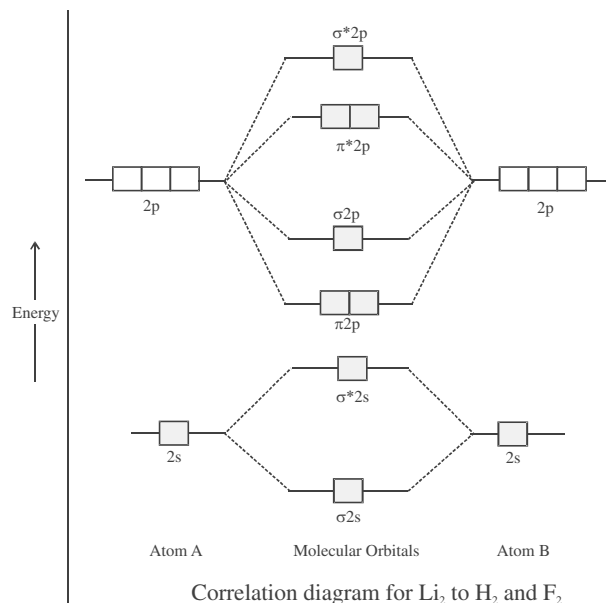
The following guidelines are helpful in describing molecular characteristics.

- The valence electrons are distributed among the molecular orbitals in accordance with aufbau principle, Pauli's exclusion principle, and Hund's rule.

Aufbau principle: Molecular orbitals are filled in the increasing order of energy.

Pauli exclusion principle: No more than two electrons can occupy a single molecular orbital. The two electrons have opposite spins.

Hund's rule: The degenerate orbitals are singly occupied by electrons with parallel spins followed by double occupancy.



2. The number of bonds in a molecule is defined by a physical quantity, known as bond order. It is defined as one half of the net excess of bonding electrons, i.e.,

$$\text{Bond order} = \frac{\text{Number of (bonding - antibonding) electrons}}{2}$$

3. The strength of a bond depends on the bond order of the molecule. The larger the bond order, the stronger the bond, the larger the dissociation energy of the molecule.

4. Addition of an electron in the bonding orbital or removal of an electron from the antibonding orbital increases bond order and hence increases stability of a molecule.
5. Removal of an electron from a bonding orbital or addition of an electron in the antibonding orbital decreases bond order and hence decreases stability of a molecule.
6. Paramagnetism in a substance is due to the presence of unpaired electrons in the molecules.

Solved Examples



1. An element (X) forms compounds of the formula XCl_3 , X_2O_5 and Ca_3X_2 but does not form XCl_5 . Which of the following is the element(X)?

- (a) B (b) Al
(c) N (d) P

Sol.(c) 'N' can form NCl_3 , N_2O_5 and Ca_3N_2 but can not form NCl_5 . Due to absence of d-orbitals, 'N' can not expand its valency to 5.

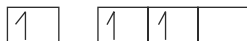
2. Which of the following anions can not be formed by boron?

- (a) BF_6^{3-} (b) BH_4^-
(c) B(OH)_4^- (d) BO_2^-

Sol.(a) Any second period element can form maximum 4 bonds (covalent and co-ordinate). After formation of 3 covalent bonds, 'B' can form only one co-ordinate bond because it has only one vacant orbital.

2s 2p

B(I excitation)



3. Which of the following would result in the formation of strongest π -bond if the molecular axis is x-axis?

- (a) $2p_x + 2p_x$ (b) $2p_y + 2p_y$
(c) $2p_y + 3d_{xy}$ (d) $2p_z + 4p_z$

Sol.(b) $2p_x + 2p_x$ will form σ -bond

$2p_y + 2p_y$ and $2p_x + 3d_{xy}$ will form π -bond but $2p\pi + 2p\pi$ bond is stronger than $2p\pi + 3d\pi$

4. Which of the following statement is wrong?

- (a) d-orbital taking part in dsp^2 is $d_{x^2-y^2}$
(b) d-orbital taking part in sp^3d is d_{xy}

(c) d-orbital taking part in sp^3d^2 are $d_{x^2-y^2}$ and d_z^2

(d) d-orbital taking part in sp^3d^3 are d_{xy} , d_z^2 and $d_{x^2-y^2}$

Sol.(b) dsp^2 (s + p_x + p_y + $d_{x^2-y^2}$)

sp^3d (s + p_x + p_y) (p_z + d_z^2)

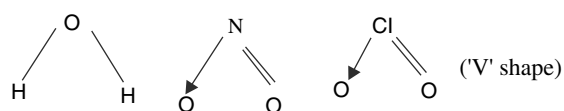
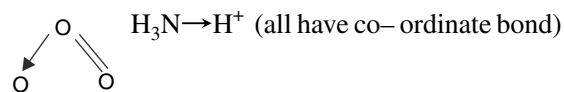
sp^3d^2 (s + p_x + p_y + $d_{x^2-y^2}$) (p_z + d_z^2)

sp^3d^3 (s + p_x + p_y + d_{xy} + $d_{x^2-y^2}$) (p_z + d_z^2)

5. Which of the following set is not correct?

- (a) N_2O , O_3 , NH_4^+ all have co-ordinate bonds.
(b) H_2O , NO_2 , ClO_2 all are 'V' shape molecules.
(c) I_3^- , ICl_2^- , NO_2^+ all are linear molecules.
(d) SF_4 , SiF_4 , XeF_4 all are tetrahedral in shape.

Sol.(d) $\text{N} \equiv \text{N} \rightarrow \text{O}$



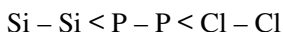
I_3^- , ICl_2^- , NO_2^+ (all are linear)

SF_4 (See-saw shape) SiF_4 XeF_4 (square planar shape)

6. The incorrect order of bond dissociation energy will be :

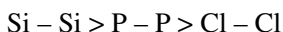
- (a) $\text{H}-\text{H} > \text{Cl}-\text{Cl} > \text{Br}-\text{Br}$
(b) $\text{Si}-\text{Si} > \text{P}-\text{P} > \text{Cl}-\text{Cl}$
(c) $\text{C}-\text{C} > \text{N}-\text{N} > \text{O}-\text{O}$
(d) $\text{H}-\text{Cl} > \text{H}-\text{Br} > \text{H}-\text{I}$

Sol.(b) Bond length depends on size of atoms order of bond length is:-



$$\text{Bond energy} \propto \frac{1}{\text{Bond length}}$$

Hence, correct order of bond energy is:



7. The incorrect order of bond dissociation energy will be :

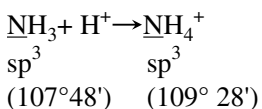
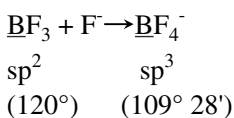
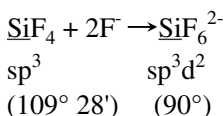
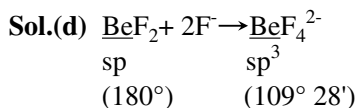
- (a) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$ (C - O bond)
 (b) $\text{CN}^- < \text{NCN}^{2-} < \text{R-CO-NH}_2$ (C - N bond)
 (c) $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$ (Cl - O bond)
 (d) $\text{SO}_2 < \text{SO}_4^{2-} < \text{SO}_3^{2-}$ (S - O bond)

Sol.(a)	CO	CO ₂	CO ₃ ²⁻	
	(3)	(2)	(1.33)	
	CN ⁻	NCN ²⁻	R-CO-NH ₂	
	(3)	(2)	(1.5)	
	ClO ⁻	ClO ₂ ⁻	ClO ₃ ⁻	ClO ₄ ⁻
	(1)	(1.5)	(1.67)	(1.75)
	SO ₂	SO ₄ ²⁻	SO ₃ ²⁻	
	(1.5)	(1.5)	(1.33)	

In bracket bond order is given.

8. In which of the following change, adjacent bond angle increases?

- (a) $\text{BeF}_2 + 2\text{F}^- \rightarrow \text{BeF}_4^{2-}$
 (b) $\text{SiF}_4 + 2\text{F}^- \rightarrow \text{SiF}_6^{2-}$
 (c) $\text{BF}_3 + \text{F}^- \rightarrow \text{BF}_4^-$
 (d) $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$



9. In which of the following processes, the value of magnetic moment does not change?

- (a) $\text{N}_2 \rightarrow \text{N}_2^{-2}$ (a) $\text{B}_2 \rightarrow \text{B}_2^{-2}$
 (c) $\text{O}_2^+ \rightarrow \text{O}_2^-$ (d) $\text{O}_2^- \rightarrow \text{O}_2^{-2}$

Sol.(c) By using molecular orbital theory, we can calculate number of unpaired e⁻ in all these species.



10. Which of the following statement(s) is not true for the given species?


N₂, CO, CN⁻ and NO⁺

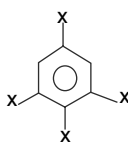
- (a) All species have linear shape
 (b) All species have some dipole moments
 (c) All species are isoelectronic
 (d) All species have identical bond order and they are diamagnetic in nature.

Sol.(b) All diatomic species are linear.

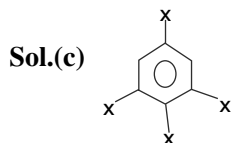
Dipole moment of N₂ is zero but remaining species have some dipole moments.

All species have 14 e⁻, bond order is 3 and diamagnetic in nature.


11. Dipole moment of  is 1.5 D. Calculate

Dipole moment of 

- (a) 1.5 D (b) 1 D
 (c) 2.35 D (d) 3 D



Three bond moments are equal in magnitude and they are 120° apart hence, their result is zero. Net dipole moment of this molecule equals to the

that of 

12. Which of the following pair of compounds are polar, planar and sp^2 hybridisation?

- (a) H_2CO_3 , SO_2 (b) $HClO_2$, H_2CO_3
(c) $BFCIBr$, ClF_3 (d) SO_3 , O_3

Sol.(a) H_2CO_3 and SO_2

(Both are polar, planar and have sp^2 hybridisation)

In $HClO_2$, hybridisation of Cl is sp^3

In ClF_3 , hybridisation of Cl is sp^3d

SO_3 is non – polar

13. Back bonding in BF_3 does not affect:

- (a) Planarity, Lewis acidic strength and bond angle
(b) Bond length, hybridization and bond strength
(c) Bond angle, planarity and geometry
(d) Lewis acidic strength, bond length and bond order (B-F)

Sol.(c) Due to back bonding in BF_3 , it's bond length, bond energy, bond strength and lewis acidic strength changes but there is no change in bond angle, hybridization, geometry and planarity.

14. Which of the following molecule has $2p\pi - 3p\pi$ back bonding?

- (a) OCl_2 (b) BF_3
(c) $:\ddot{C}Cl_2$ (d) CCl_3^-

Sol.(c)

Molecule	Type of back bonding
OCl_2	$2p\pi - 3d\pi$
BF_3	$2p\pi - 2p\pi$
CCl_3^-	$2p\pi - 3d\pi$
$:\ddot{C}Cl_2$	$2p\pi - 3p\pi$

In $:\ddot{C}Cl_2$, vacant $2p$ -orbital of 'C' and paired $3p$ -orbital of 'Cl' form back bond.

15. In which of the following molecule $2C - 2e^-$ bond is absent?

- (a) $BeCl_2$ in Vapor state (b) Al_2Cl_6
(c) BeH_2 in solid state (d) B_2H_6

Sol.(c) In BeH_2 all bonds are $3C-2e^-$.

16. In which of the following d – orbital's are not used by central atom in hybridization?

- (a) PF_5 (s) (b) PCl_5 (s)
(c) PBr_5 (s) (d) XeF_6 (s)

Sol.(c) Solid form of PF_5 is $PF_4^+ PF_6^-$
 sp^3 sp^3d^2

Solid form of PCl_5 is $PCl_4^+ PCl_6^-$
 sp^3 sp^3d^2

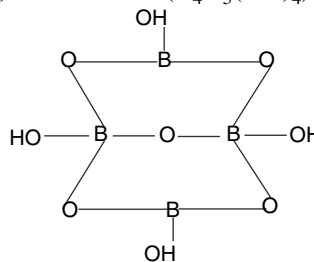
Solid form of PBr_5 is $PBr_4^+ Br^-$
 sp^3

Solid form of XeF_6 is $XeF_5^+ XeF_7^-$
 sp^3d^2 sp^3d^4

17. In $(B_4O_5(OH)_4)^{2-}$ the number of boron atoms having on octet of electron is :

- (a) 0 (b) 1
(c) 2 (d) 4

Sol.(c) Structure of $(B_4O_5(OH)_4)^{2-}$ is:-

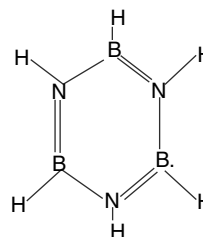


In this structure 2 Boron atoms have octet of electrons in their outermost shell.

18. Which of the following statement is not correct?

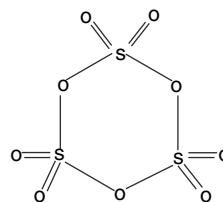
- (a) The maximum number of atoms in one plane in $B_3N_3H_6$ are 12.
(b) There is no S – S bond in S_3O_9 .
(c) Maximum number of identical bond angles in ClO_4^- are 4.
(d) Number of bridging oxygen in P_4O_{10} are 6.

Sol.(c)



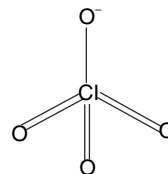
The complete structure is Planar hence, all 12 atoms are in same plane.

Structure of S_3O_9 is:-



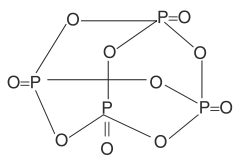
There is no S – S bond

Structure of ClO_4^- is:-



In this tetrahedral structure identical bond angles are 6.

Structure of P_4O_{10} is:-



In this structure 6, P – O – P linkage is present.

19. Which of the following compound produces only basic products on hydrolysis?

- (a) Mg_3N_2 (b) NCl_3
(c) BBr_3 (d) PCl_5

Sol.(a) $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$
(Both are basic)

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$
(One is basic and other is acidic)

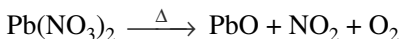
$BBr_3 + 3H_2O \rightarrow H_3BO_3 + 3HBr$
(Both are acidic)

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
(Both are acidic)

20. Which of the following reactions is incorrect?

- (a) $Pb(NO_3)_2 \xrightarrow{\Delta} PbO_2 + NO_2 + O_2$
(b) $2 NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$
(c) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$
(d) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

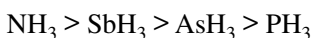
Sol.(a) The correct reaction is:



21. Which of the following is not correctly matched?

- (a) $NH_3 > SbH_3 > PH_3 > AsH_3$ (Melting point)
(b) $NH_3 > PH_3 > AsH_3 > SbH_3$ (Proton affinity)
(c) $CH_4 > SiH_4 > GeH_4 > SnH_4$ (Thermal stability)
(d) $H_2O > H_2Te > H_2Se > H_2S$ (Boiling point)

Sol.(a) The correct order of melting point is:



The order depends on strength of intermolecular bonding. In solid state, intermolecular bonding in NH_3 is much stronger than in liquid state.

22. Which of the following substance has the highest melting point?

- (a) $NaCl$ (b) KCl
(c) MgO (d) BaO

Sol.(c) For ionic compounds, melting point \propto lattice energy (U_o)

$$U_o \propto \frac{|Z^+||Z^-|}{r}$$

Here, $|Z^+|$ and $|Z^-|$ are charge of cation and anion.

$$r = r^+ + r^-$$

$$\left[\begin{array}{l} r^+ = \text{radius of cation} \\ r^- = \text{radius of anion} \end{array} \right]$$

In these four compounds, MgO has highest lattice energy.

23. The dipole moment of LiH is 1.964×10^{-29} Cm and the inter atomic distance between Li and H in this molecule is 1.596 \AA . What is the percent ionic character in LiH ?

Sol. The dipole moment of 100% ionic molecule (Li^+H)

= (1 electronic charge) (inter atomic distance)

$$= (1.602 \times 10^{-19}C) (1.596 \times 10^{-10}m)$$

$$= 2.557 \times 10^{-29} \text{ Cm}$$

Fractional ionic character = $\frac{\text{Experimental dipole moment}}{\text{Theoretical value of dipole moment}}$

$$= \frac{1.94 \times 10^{-29}}{2.557 \times 10^{-29}} = 0.768$$

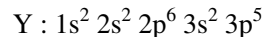
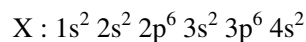
The bond in LiH is 76.8% ionic.

24. KF Combines with HF to form KHF_2 . The Compound contains the species-

- (a) K^+ , F^- and H^+ (b) K^+ , F^- and HF
(c) K^+ and $(HF_2)^-$ (d) $(KHF)^+$ and F^-

Sol.(c) $KHF_2 \rightarrow K^+ + HF_2^-$

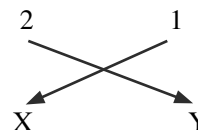
25. Two elements X and Y have following electronic configuration:



The expected compound formed by combination of X and Y Will be expressed as-

- (a) XY_2 (b) X_5Y_2
(c) X_2Y_5 (d) XY_5

Sol.(a) Valency of element X is 2 (2 electrons in the outermost shell) while that of element Y is 1 (1electron in the outermost shell). So the formula of the compound between X and Y is XY_2



26. Which of the following interaction lies in the range of 8-42 kJ/mol?

- (a) $F^- \dots HF$ (b) $Xe \dots H_2O$
 (c) $Cs^+ \dots OH^-$ (d) $O_2N-\text{C}_6\text{H}_4-OH \dots H_2O$

Sol.(d) The interaction present in $O_2N-\text{C}_6\text{H}_4-OH \dots H_2O$ is intermolecular H-bond. It's bond energy lies between 8-42 kJ/mol.

The interaction in $F^- \dots HF$ is very strong H-bond. It's strength almost equals to the covalent bond.

The interaction in $Cs^+ \dots OH^-$ is an ionic bond.

The interaction in $Xe \dots H_2O$ is dipole – induced dipole interaction which is weaker than H-bond.

27. Which of the following compound has highest lattice energy?

- (a) AlF_3 (b) Na_2S
 (c) Al_2O_3 (d) CaF_2

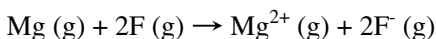
Sol.(c) Lattice energy (U_0) $\propto \frac{|Z^+||Z^-|}{r}$

Here, $|Z^+|$ and $|Z^-|$ are magnitude of charge of cation and anion respectively.

$$r \approx r^+ + r^-$$

Al_2O_3 has highest lattice energy among these four because it has highest value of $|Z^+||Z^-|$

28. What is the ΔH of the following reaction?



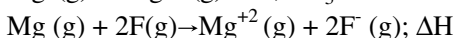
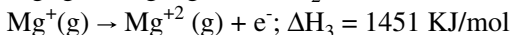
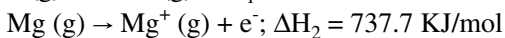
If $\Delta_{eg}H$ of F = -328 kJ/mol

First ionisation energy of Mg = 737.7 kJ/mol

Second Ionisation energy of Mg = 1451 kJ/mol

- (a) 1532.7 kJ/mol (b) 1860.7kJ/mol
 (c) 2516.7kJ/mol (d) 1451kJ/mol

Sol.(a) Given that,



$$\Delta H = \Delta H_2 + \Delta H_3 + 2\Delta H_1$$

$$\text{Or} = 737.7 + 1451 + 2(-328)$$

$$\text{Or} = 1532.7 \text{ KJ/mol}$$

29. Which of the following order is incorrect?

- (a) Ionic character : $MCl < MCl_2 < MCl_3$
 (b) Polarisibility : $F^- < Cl^- < Br^- < I^-$
 (c) Polarising power : $Na^+ < Ca^{+2} < Mg^{+2} < Al^{+3}$
 (d) Covalent character : $LiF < LiCl < LiBr < LiI$

Sol.(a) Ionic character $\propto \frac{1}{\text{Polarising power of cation}}$

As positive oxidation state increases or, size of cation decreases, polarising power of cation increases hence, the correct order of ionic character is: $MCl > MCl_2 > MCl_3$

30. Select wrong statement:

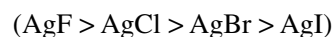
- (a) A transition metal ion has more polarising power than S-block ions of comparable size and charge.
 (b) Order of solubility in water is $AgF > AgCl > AgBr > AgI$
 (c) LiCl is soluble in organic solvents
 (d) The hydration of ions involves absorption of heat.

Sol.(d) Out of cations having comparable size and charge the one having

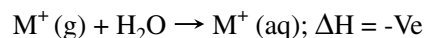
Noble gas configuration has less polarizing power.

LiCl is a covalent compound hence, it is soluble in organic solvents.

Order of solubility of heavy metal halides depends order on hydration energy.



The hydration of ions involves evolution of heat.





Exercise



LEVEL I

- The phosphate of a metal has the formula M_3PO_4 . The formula of its chloride would be:
 - MCl
 - MCl_2
 - MCl_3
 - M_2Cl_3
- Solid NaCl is a bad conductor of electricity because:
 - In solid NaCl there are no ions
 - Solid NaCl is covalent
 - In solid NaCl there is no mobility of ions
 - In solid NaCl there are no electrons
- Knowing that $Na^+ > Mg^{2+}$ and $S^{2-} > Cl^-$ (Order of size), predict which compound will be more covalent?
 - MgS
 - Na_2S
 - $MgCl_2$
 - NaCl
- Which of the following compound possesses the largest lattice energy?
 - LiF
 - NaCl
 - KH
 - CsI
- Select the incorrect statement:
 - Lithium is least reactive but the strongest reducing agent among all the metals.
 - Lithium hydrogen carbonate is not obtained in the solid form while all other alkali metals forms solid hydrogen carbonates.
 - Lithium nitrate when heated gives lithium oxide whereas other alkali metal nitrates decompose to give the corresponding nitrite.
 - Solubility of alkali metal hydroxides decreases down the group. It is due to decrement in hydration energy from Li^+ to Cs^+ .
- Which pair of element can form multiple bond with itself and oxygen?
 - F, N
 - N, Cl
 - N, P
 - N, C
- Bonds present in N_2O_5 (nitrogen pentaoxide) are:
 - Only ionic
 - Only covalent
 - Covalent and co-ordinate
 - Covalent and ionic
- The fluorine molecules is formed by:
 - p-p orbital's (sideways overlap)
 - p-p orbital's (end-to-end overlap)
 - sp-sp orbital's
 - s-s orbital's
- Among given species identify the isostructural pairs:
 - $[NF_3]$ and $[BF_3]$
 - $[BF_4^-]$ and $[NH_4^+]$
 - $[BCl_3]$ and $[BrCl_3]$
 - $[NH_3]$ and $[NO_3^-]$
- The molecule exhibiting maximum number of non-bonding electron pairs (lp) around the central atom is:
 - $XeOF_4$
 - XeO_2F_2
 - XeF_3^-
 - XeO_3
- The shapes of XeF_4 , XeF_5^- and $SnCl_2$ are:
 - Octahedral, trigonalbipyramidal and bent
 - Square pyramidal, pentagonal planar and linear
 - Square planar, pentagonal planar and angular
 - See-saw, T-shaped and linear
- Which is not correctly matched?
 - XeO_3 – Trigonalbipyramidal
 - ClF_3 – bent T-shape
 - $XeOF_4$ – Square pyramidal
 - XeF_2 – Linear shape
- The geometry of ammonia molecule can be best described as:
 - Nitrogen at one vertex of a regular tetrahedron, the other three vertices being occupied by three hydrogens
 - Nitrogen at the centre of the tetrahedron, three of the vertices being occupied by three hydrogens
 - Nitrogen at the centre of an equilateral triangle, three corners being occupied by three hydrogens
 - Nitrogen at the junction of a T, three open ends being occupied by three hydrogens

14. Which one of the following compounds has the smallest bond angle?

- (a) OH_2 (b) SH_2
(c) NH_3 (d) SO_2

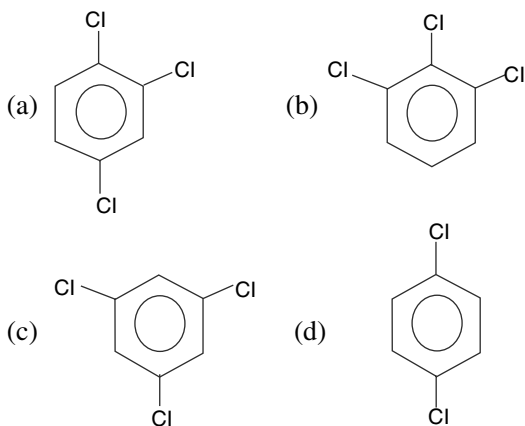
15. The bond angles of NH_3 , NH_4^+ and NH_2^- are in the order:

- (a) $\text{NH}_2^- > \text{NH}_3 > \text{NH}_4^+$
(b) $\text{NH}_4^+ > \text{NH}_3 > \text{NH}_2^-$
(c) $\text{NH}_3 > \text{NH}_2^- > \text{NH}_4^+$
(d) $\text{NH}_3 > \text{NH}_4^+ > \text{NH}_2^-$

16. Which of the following molecules will have polar bonds but zero dipole moment?

- (a) O_2 (b) CHCl_3
(c) CF_4 (d) None of these

17. Which has maximum dipole moment?



18. The hybridisation of central iodine atom in IF_5 , I_3^- and I_3^+ are respectively:

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

19. Which of the following species used axial set of d-orbital's in hybridisation of central atom?

- (a) PBr_4^+ (b) PCl_4^-
(c) ICl_4^- (d) None of these

20. Low melting point is expected for a solid:

- (a) Ionic solid (b) Metallic solid
(c) Molecular solid (d) Covalent solid

21. Which molecule does not exist?

- (a) OF_2 (b) OF_4
(c) SF_2 (d) SF_4

22. How many resonance forms can be written for the nitrate ion, (NO_3^-)?

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

23. When the substances Si, KCl, CH_3OH and C_2H_6 are arranged in order of increasing melting point, what is the correct order?

- (a) Si, KCl, CH_3OH , C_2H_6
(b) CH_3OH , C_2H_6 , Si, KCl
(c) KCl, Si, C_2H_6 , CH_3OH
(d) C_2H_6 , CH_3OH , KCl, Si

24. The H-O-H bond angles in H_3O^+ are approximately 107° . The orbitals used by oxygen in these bonds are best described as:

- (a) p-orbitals
(b) sp-hybrid orbitals
(c) sp^2 -hybrid orbitals
(d) sp^3 -hybrid orbitals

25. Which of the following fact is directly explained by the statement oxygen is a smaller atom than sulphur?

- (a) H_2O boils at a much higher temperature than H_2S
(b) H_2O undergoes intermolecular hydrogen bonding
(c) H_2O is liquid and H_2S is gas at room temperature
(d) S-H bond longer than O-H bond

26. Which of the following statement is correct about I_3^+ and I_3^- molecular ions?

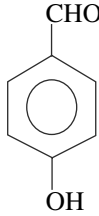
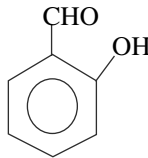
- (a) Number of lone pairs at central atoms are same in both molecular ions
(b) Hybridisation of central atoms in both ions are same
(c) Both are polar species
(d) Both are planar species

27. Iodine molecule are held in the solid lattice by.....

- (a) London forces
(b) Dipole-dipole interactions
(c) Covalent bonds
(d) Both are planar species

28. Species having maximum Cl-O bond order is:

- (a) ClO_3^- (b) ClO_3
(c) ClO_2 (d) ClO_2^-

29. Which of the following species contains minimum number of atoms in XY Plane ?
 (a) XeF_5^- (b) SF_6
 (c) IF_7 (d) All
30. In which of the following molecular shape d_{z^2} -orbital must not be involved in bonding?
 (a) Pentagonal Planar
 (b) Trigonal Planar
 (c) Linear
 (d) Square Planar
31. The correct statement regarding SO_2 molecule is:
 (a) Two $p\pi - d\pi$ bonds
 (b) Molecule has 2 lone pair, 2 σ bonds and 2 π bonds
 (c) Two $p\pi - p\pi$ bonds
 (d) One $p\pi - p\pi$ and one $p\pi - d\pi$ bonds
32. The molecule ML_X is Planar with 7 pairs of electrons around M in the valence shell. The value of X is:
 (a) 6 (b) 5
 (c) 4 (d) 3
33. In which of the following pairs, both the species have the same hybridisation?
 (I) SF_4 , XeF_4 (II) I_3^- , XeF_2
 (III) ClO_3^+ , PO_4^{3-} (IV) ClO_3^- , PO_4^{3-}
 (a) I, II (b) II, III
 (c) II, IV (d) I, II, III
34. Which of the following possess two lone pair of electrons on the central atom and square planar shape:
 (I) SF_4 (II) XeO_4
 (III) XeF_4 (IV) ICl_4^-
 (a) I, III (b) II, IV
 (c) III, IV (d) All
35. Which of the following does not follow the octet rule?
 (a) NaCl (b) CaCl_2
 (c) ClF_3 (d) CCl_4
36. Which of the following does not have coordinate bonds?
 (a) HNO_2 (b) O_3
 (c) NaBF_4 (d) NH_4Cl
37. The bonds present in KHF_2 are:
 (a) Only ionic
 (b) Covalent and coordinate
 (c) Only covalent
 (d) Covalent, ionic and H-bond
38. The correct order of dipole moment is:
 (a) $\text{CH}_4 < \text{NF}_3 < \text{NH}_3 < \text{H}_2\text{O}$
 (b) $\text{NF}_3 < \text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O}$
 (c) $\text{NH}_3 < \text{NF}_3 < \text{CH}_4 < \text{H}_2\text{O}$
 (d) $\text{H}_2\text{O} < \text{NH}_3 < \text{NF}_3 < \text{CH}_4$
39. Among the following which is polar?
 (a) CO_2 (b) SO_2
 (c) BeCl_2 (d) $\text{Cl}-\text{C}_6\text{H}_4-\text{Cl}$
40. In the reaction, $2\text{PCl}_5 \rightleftharpoons \text{PCl}_4^+ + \text{PCl}_6^-$, the change in hybridisation is from:
 (a) sp^3d to sp^3 and sp^3d^2
 (b) sp^3d to sp^2 and sp^3
 (c) sp^3d to sp^3d^2 and sp^3d^2
 (d) sp^3d^2 to sp^3 and sp^3d
41. Out of the compounds shown below, the vapour pressure of II at a particular temperature is expected to be
 I. p-hydroxybenzaldehyde \Rightarrow 
 II. o-hydroxybenzaldehyde \Rightarrow 
- (a) Higher than that of I
 (b) Lower than that of I
 (c) Same as that of I
 (d) Can be higher or lower depending upon the size of vessel
42. Which of the following have been arranged in increasing bond order as well as bond dissociation energy?
 (a) $\text{O}_2^{-2} < \text{O}_2^- < \text{O}_2^+ < \text{O}_2$
 (b) $\text{O}_2^{-2} < \text{O}_2^- < \text{O}_2 < \text{O}_2^+$
 (c) $\text{O}_2 < \text{O}_2^+ < \text{O}_2^{2-} < \text{O}_2^-$
 (d) $\text{O}_2^+ > \text{O}_2^{2-} > \text{O}_2^- < \text{O}_2$

43. The statement true for azide ion (N_3^-) is:
 (a) It has a non-linear structure
 (b) It is called pseudo halogens
 (c) The oxidation state of N in this anion is -1
 (d) It is isoelectronic with NO_2
44. The pair of strongest hydrogen bond is:
 (a) SiH_4 and SiCl_4
 (b) CH_3COOH and CH_3OCH_3
 (c) CH_3COOH and CH_3COCH_3
 (d) H_2O and H_2O_2
45. The strongest force among the following is:
 (a) London force
 (b) Ion-dipole interaction
 (c) Dipole-induced dipole interaction
 (d) Dipole-dipole interaction

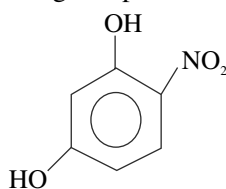


LEVEL II

1. In which of the following species maximum atoms can lie in same plane?
 (a) XeF_2O_2 (b) PCl_5
 (c) AsH_4^+ (d) XeF_4
2. The correct order of Cl - O bond order is:
 (a) $\text{ClO}_3^- < \text{ClO}_4^- < \text{ClO}_2^- < \text{ClO}^-$
 (b) $\text{ClO}^- < \text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^-$
 (c) $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$
 (d) $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- < \text{ClO}^-$
3. Resonance structures can be written for:
 (a) O_3 (b) NH_3
 (c) CH_4 (d) H_2O
4. The number of $\text{sp}^2 - \text{s}$ sigma bonds in benzene are:
 (a) 3 (b) 6
 (c) 12 (d) None of these
5. Which of the following pair of species have identical shapes?
 (a) NO_2^+ and NO_2^- (b) PCl_5 and BrF_5
 (c) XeF_4 and ICl_4^- (d) TeCl_4 and XeO_4
6. The hybridisation of the central atom will change when:
 (a) NH_3 combines with H^+
 (b) H_3BO_3 combines with OH^-
 (c) NH_3 forms NH_2^-
 (d) H_2O combines with H^+
7. Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false:
 (I) The order of repulsion between different pair of electrons is:
 $\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$
 (II) In general, as the number of lone pair of electrons on central atom increases, value of bond angle from normal bond angle also increases
 (III) The number of lone pair on O in H_2O is 2 while on N in NH_3 is 1
 (IV) The structures of xenon fluorides and xenon oxofluorides could not be explained on the basis of VSEPR theory
 (a) T T T F (b) T F T F
 (c) T F T T (d) T F F F
8. Among the following species, the least angle around the central atom is in:
 (a) O_3 (b) I_3^-
 (c) NO_2^- (d) PH_3
9. BF_3 and NF_3 both are covalent compounds but NF_3 is polar whereas BF_3 is non-polar. This is because:
 (a) Nitrogen atom is smaller than boron atom
 (b) N - F bond is more polar than B - F bond
 (c) NF_3 is pyramidal whereas BF_3 is planar triangular
 (d) BF_3 is electron deficient whereas NF_3 is not
10. Which statement is incorrect?
 (a) MP of H_2O , NH_3 , HF are maximum in their respective group due to intermolecular H-bonding
 (b) BP of CH_4 out of CH_4 , SiH_4 , GeH_4 , and SnH_4 is least due to weak intermolecular force of attraction
 (c) Acetic acid forms dimer by H-bonding
 (d) NH_3 has lower BP than SbH_3
11. The molecular size of ICl and Br_2 is approximately same, but BP of ICl is about 40°C higher than of Br_2 . It is because:
 (a) ICl bond is stronger than $\text{Br}-\text{Br}$ bond
 (b) IE of iodine $<$ IE of bromine
 (c) ICl is polar while Br_2 is nonpolar
 (d) I has larger size than Br

12. Number of S-S bond is $H_2S_nO_6$:
- (a) n (b) (n-1)
(c) (n-2) (d) (n+1)
13. The nodal plane in the π -bond of ethane is located in:
- (a) The molecular plane
(b) A plane parallel to the molecular plane
(c) A plane perpendicular to the molecular plane which bisects the carbon-carbon σ bond at right angle
(d) A plane perpendicular to the molecular plane which contain the carbon-carbon bond
14. Which set of compound in the following pair of ionic compound has the higher lattice energy?
- (i) KCl or MgO
(ii) LiF or LiBr
(iii) Mg_3N_2 or NaCl
- (a) KCl, LiBr, Mg_3N_2
(b) MgO, LiBr, Mg_3N_2
(c) MgO, LiF, NaCl
(d) MgO, LiF, Mg_3N_2
15. The bond having the highest bond energy is:
- (a) C = C (b) C = S
(c) C = O (d) P = N
16. Which of the following overlaps is incorrect (assuming Z-axis is internuclear axis)?
- (I) $2p_Y + 2p_Y \rightarrow \pi$ - Bond formation
(II) $2p_X + 2p_X \rightarrow \sigma$ - Bond formation
(III) $3d_{XY} + 3d_{XY} \rightarrow \pi$ - Bond formation
(IV) $2s + 2p_Y \rightarrow \pi$ - Bond formation
(V) $3d_{XY} + 3d_{XY} \rightarrow \delta$ - Bond formation
(VI) $2p_Z + 2p_Z \rightarrow \sigma$ - Bond formation
- (a) I, II, III (b) III, VI
(c) II, V (d) II, III, IV
17. In which of the following combination-hybridisation of central atom does not change?
- (a) $H_2O + \underline{CO}_2$
(b) $H_3\underline{BO}_3 + \underline{OH}^-$
(c) $BF_3 + \underline{NH}_3$
(d) None of these
18. Which species has the same shape as NH_3 ?
- (a) SO_3^{2-} (b) CO_3^{2-}
(c) NO_3^- (d) SO_3
19. Which of the following is the correct order for increasing bond angle?
- (a) $NH_3 < PH_3 < AsH_3 < SbH_3$
(b) $H_2O < OF_2 < Cl_2O$
(c) $H_3Te^+ < H_3Se^+ < H_3S^+ < H_3O^+$
(d) $BF_3 < BCl_3 < BBr_3 < BI_3$
20. SbF_5 reacts with XeF_4 and XeF_6 to form ionic compound $[XeF_3]^+[SbF_6]^-$ and $[XeF_5]^+[SbF_6]^-$ then molecular shape of $[XeF_3]^+$ ion and $[XeF_5]^+$ ion respectively:
- (a) Square pyramidal, T- shaped
(b) Bent – T – shape, square pyramidal
(c) See – Saw, square pyramidal
(d) square pyramidal, See–Saw
21. Melting point of calcium halides decreases in the order:
- (a) $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$
(b) $CaI_2 > CaBr_2 > CaCl_2 > CaF_2$
(c) $CaBr_2 > CaI_2 > CaF_2 > CaCl_2$
(d) $CaCl_2 > CaBr_2 > CaI_2 > CaF_2$
22. Which of the following order is incorrect?
- (a) $NaCl > KCl > RbCl > LiCl$ (Order of melting point)
(b) $LiCl > CsCl > RbCl > NaCl > KCl$ (Order of solubility in water)
(c) $LiCl > NaCl > KCl > RbCl > CsCl$ (Order of lattice energy)
(d) $NaF > MgF_2 > AlF_3$ (Order of melting point)
23. Which of the following process is correct?
- (a) $Ca(NO_3)_2 \xrightarrow{\Delta} CaO + 2NO_2 \uparrow + \frac{1}{2} O_2 \uparrow$
 $\downarrow \Delta$
 $Ca + \frac{1}{2} O_2 \uparrow$
- (b) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 \uparrow + SO_3 \uparrow$
(c) $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 \uparrow + H_2O$
(d) Both (b) and (c)
24. Choose the correct code of characteristics for the given order of hybrid orbitals of same atom, $sp < sp^2 < sp^3$
- (I) Electronegativity
(II) Bond angle between same hybrid orbitals
(III) Size
(IV) Energy level

39. Which of these is not true for metallic bond ?
- Metallic bond is non-directional in nature
 - Metallic bonds are weaker than covalent bond.
 - Energy required to vapourise a mole of Cu metal is high to the energy required to vapourise a mole of a covalent substance like diamond.
 - The valency electrons in a metallic bond are mobile.
40. Which substance has the strongest London dispersion forces?
- SiH₄
 - CH₄
 - SnH₄
 - GeH₄
41. The type of molecular forces of attraction present in the following compound is:



- Intermolecular H-bonding
 - Intramolecular H-bonding
 - van der Waals' force
 - All of these
42. Which among the following attraction is strongest?
- HF H₂O
 - Na⁺ HCl
 - H₂O Cl₂
 - Cl - Cl Cl - Cl
43. In which of the following species back- π bonding exists?
- NF₃
 - NH₃
 - BF₃
 - BF₄⁻
44. Which statement about hybridisation is correct?
- It involves the mixing of atomic orbitals of the atom at the time of their participation in bonding.
 - sp³d³ hybridisation orbital point out towards the corners of regular hexagon.
 - Hybrid orbitals form weaker bonds than pure atomic orbitals.
 - For hybridisation to occur, the atom must have vacant orbitals in the valence shell.

45. Which of the following has highest melting point?
- SF₆
 - NaCl
 - SiC
 - Xe



LEVEL III

ONE OR MORE THAN ONE CORRECT

- Which species have same bond order?
 - CO₃⁻²
 - NO₃⁻
 - NO₂⁻
 - NO
- In Which of the following molecule bonding is taking place in excited state?
 - CH₄
 - BF₃
 - ICl₃
 - PCl₃
- Which is/are in linear shape?
 - NO₂⁺
 - XeF₂
 - I₃⁻
 - I₃⁺
- The species which are paramagnetic is/are:
 - NO
 - NO₂
 - ClO₂
 - N₂O₄
- Which of the following statements are correct?
 - O-hydroxybenzaldehyde is a liquid at room temperature due to intramolecular H-bonding.
 - Order of boiling point is H₂O > H₂Te > H₂Se > H₂S
 - Order of boiling point is HF > HI > HBr > HCl
 - Order of boiling point is SbH₃ > NH₃ > AsH₃ > PH₃
- The molecule that is/are having N - N bond:
 - N₂O
 - N₂O₃
 - N₂O₅
 - N₂O₄
- There is change in the type of hybridisation when:
 - NH₃ combines with H⁺
 - AlH₃ combines with H⁻
 - NH₃ forms NH₂⁻
 - SiF₄ forms SiF₆²⁻
- Select correct statement(s) regarding σ and π -bonds:
 - σ -bond lies on the line joining the nuclei of bonded atoms
 - π -electron cloud lies on either side to the line joining the nuclei of bonded atoms

- (c) $(2p\pi-3d\pi)$ pi-bond is stronger than $(2p\pi-3p\pi)$ pi-bond.
- (d) σ -bond has primary effect to decide direction of covalent bond, while π -bond has no primary effect in direction of bond
9. In which of the following there is intermolecular hydrogen bonding?
- (a) Water (b) Ethanol
(c) Acetic acid (d) H-F
10. Which of the following statements are correct about sulphur hexafluoride?
- (a) All S-F bonds are equivalent
(b) SF_6 is a planar molecule
(c) Oxidation number of sulphur is the same as number of electrons of sulphur involved in bonding
(d) Sulphur has acquired the electronic structure of the gas argon
11. Correct order of decreasing boiling points is:
- (a) $HF > HI > HBr > HCl$
(b) $H_2O > H_2Te > H_2Se > H_2S$
(c) $Br_2 > Cl_2 > F_2$
(d) $CH_4 > GeH_4 > SiH_4$
12. Which of the following species does/do not exist?
- (a) OF_4 (b) NH_2^-
(c) NCl_5 (d) ICl_3^{2-}
13. Ionic compounds in general do not possess:
- (a) high melting points and non-directional bonds
(b) high melting points and low-boiling points
(c) directional bond and low-boiling points
(d) high solubilities in polar and non-polar solvents
- (b) **Bond order:** Bond order = $\frac{1}{2} (N_b - N_a)$
A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule.
- (c) **Nature of the bond:** Bond order 1, 2, or 3 corresponds to single, double or triple bonds respectively.
- (d) **Bond length:** Bond length decreases as bond order increases.
- (e) **Magnetic nature:** Molecular orbital's in a molecule are double occupied, the substance is diamagnetic and if one or more molecular orbital's are singly occupied, it is paramagnetic.
14. Select correct statement(s):
- (a) Among O_2^+ , O_2 and O_2^- the stability decreases as $O_2^+ > O_2 > O_2^-$
(b) He_2 molecule does not exist as the effect of bonding and anti-bonding molecular orbital's cancel each other
(c) C_2 , O_2^{2-} and Li_2 are diamagnetic
(d) In F_2 molecule, the energy of $\sigma 2p_z$ is more than π_{2px} and π_{2py}
15. N_2 has greater bond dissociation energy than N_2^+ , where as O_2 has a lower bond dissociation energy than O_2^+ because :
- (a) Bond order is reduced when O_2 is ionised to O_2^+ and bond order increased when N_2 is ionised to N_2^+
(b) Bond order is increased when O_2 is ionised to O_2^+ and bond order is decreased when N_2 is ionised to N_2^+
(c) Bond order is decreased when O_2 is ionised to O_2^+ and bond order is decreased when N_2 is ionised to N_2^+
(d) None of these.

PASSAGE BASED QUESTIONS

Passage # 1 (Q. 14 and 15)

The distribution of electrons among various molecular orbital's is called the electronic configuration of the molecule which provides us the following very important information's about the molecule.

- (a) **Stability of molecule:** The molecule is stable if number of bonding molecular orbital electrons (N_b) is greater than the number of anti bonding molecular orbital electrons (N_a) and vice – versa.

Passage # 2 (Q. 16 and 17)

Molecular geometry is the general shape of a molecule as determined by the relative positions of the atomic nuclei. VSEPR model predicts the shape of the molecules and ions in which valence shell electron pairs are arranged about the atom as far away from one another as possible. Thus minimising electron pair repulsion gives information about the geometry of a molecule. Information about the geometry of a molecule can sometimes be obtained from an experimental quantity called dipole moment.

16. The dipole moment of a tri-atomic molecule AX_2 was found to be equal to the bond moment of $A - X$ bond.

Which of the following information regarding geometry of the molecule can be drawn from the above observation?

- (a) Molecule is linear
 (b) Molecule is V shaped with $\angle X - A - X = 90^\circ$
 (c) Molecule is V shaped with $\angle X - A - X = 120^\circ$
 (d) Molecule geometry cannot be predicted with the given information.
17. Which of the following inter-halogen compounds is non-polar in nature?
 (a) ClF_3 (b) BrF_5
 (c) IF_7 (d) $BrCl$

Passage # 3 (Q. 18 and 19)

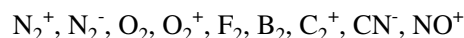
When hybridisation involving d-orbitals are considered then all five d-orbitals are not degenerate, rather $d_{x^2-y^2}$, d_{z^2} and d_{xy} , d_{yz} , d_{zx} form two different sets of orbitals and orbitals of appropriate set is involved in the hybridisation.

18. In sp^3d^2 hybridisation, which sets of d-orbitals is involved?
 (a) $d_{x^2-y^2}$, d_{z^2} (b) d_{z^2} , d_{xy}
 (c) d_{xy} , d_{yz} (d) $d_{x^2-y^2}$, d_{xy}
19. Molecule having trigonalbipyramidal geometry and sp^3d hybridisation, d-orbitals involved is:
 (a) d_{xy} (b) d_{yz}
 (c) $d_{x^2-y^2}$ (d) d_{z^2}

INTEGER TYPE QUESTIONS

20. Consider y-axis as inter-nuclear axis, how many of following will lead to π bond formation?
 (a) $p_y - p_y$ (b) $p_x - p_x$
 (c) $p_z - p_z$ (d) $d_{xy} - d_{xy}$
 (e) $d_{yz} - d_{yz}$ (f) $p_x - d_{xy}$
 (g) $d_{xy} - p_z$ (h) $d_{xz} - d_{xz}$
21. How many of the following have $p\pi - d\pi$ bonding?
 (a) CO_3^{-2} (b) NO_3^-
 (c) SO_3^{-2} (d) SO_4^{-2}
 (e) PO_4^{-3} (f) NO_2^-
 (g) $S_2O_8^{-2}$ (h) R_3PO
 (i) $S_2O_3^{-2}$ (j) ClO_4^-
 (k) ClO_3^- (l) SO_2

22. Find the number of species having fractional bond order?



23. P_4O_{10} has two different types of P - O bonds. Find the number of P - O bonds with shorter bond length.
24. In a P_4O_6 molecule, the total number of P-O-P bonds is :
25. Find the total number of polar molecules.
 PF_3Cl_2 , SF_4 , PCl_5 , PCl_3F_2 , SF_6 , XeF_2 , NO_2^+ , BF_2Cl , BF_3
26. How many of the following have hydrogen bonding?
 NH_3 , CH_4 , H_2O , HI , HF , $HCOOH$, $B(OH)_3$, CH_3COOH , HCO_2^- ion
27. In which of the following all bond length are not equal?
 PCl_5 , SF_4 , ClF_3 , XeF_2 , $[SF_5]^+$, $[ClF_4]^+$, $[XeF_3]^+$, O_3 , P_4 (white)

COLUMN MATCHING TYPE QUESTIONS

28. Match the following :

Column I	Column II
(A) BF_3	(a) sp^3 hybridisation
(B) $(SiH_3)_3N$	(b) $p\pi - p\pi$ back bond
(C) B_2H_6	(c) $p\pi - d\pi$ back bond
(D) SiO_2	(d) $3c - 2e$ bond

29. Match the following:

Column I	Column II
(A) O_2 and NO^-	(a) Same magnetic property and bond order as that in N_2^+
(B) O_2^+ and NO	(b) Same bond order but not same magnetic property as that in O_2
(C) CO and CN^-	(c) Same magnetic property and bond order as that N_2^{2-}
(D) C_2 and CN^+	(d) Same magnetic property and bond order as that in NO^+

30. Match the following:

Column - I	Column - II
(A) $H_3P_3O_9$	(a) S-O-S bond is present
(B) $H_2S_2O_7$	(b) Dibasic acid
(C) $H_2S_4O_6$	(c) P-O-P bond is present
(D) $H_4P_2O_5$	(d) Central atom (S or P) in maximum oxidation state