04

Chemical Bonding and Molecular Structure

Quick Revision

1. **Chemical Bond**

It is defined as the force of attraction which holds various constituents (atoms, ions, etc.) together in different chemical species. The combining tendency of an element or ion is called its ‘valency’.

Factors due to which atoms interact with each other are

- Forces of attraction overpowers the forces of repulsion due to decrease in energy.
- Tendency to achieve nearest noble gas configuration.

2. **Kossel-Lewis Approach to Chemical Bonding** (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.**

The group valency of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Limitations of octet rule are as follows

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

Exceptions to Octet Rule

The octet rule is violated in a significant number of cases. These are :

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

3. **Types of Chemical Bonds**

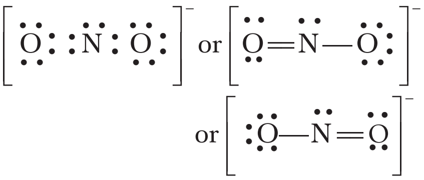
The three types of bonds or linkages which hold the atoms together in a molecule are as follows

- **Covalent bond** It is formed by mutual sharing of electrons between two atoms so as to attain nearest noble gas configuration.
- **Electrovalent bond** It is formed as a result of the electrostatic attraction between the positive and negative ions.

- **Coordinate bond** It is a type of covalent bond in which shared pair of electrons come from one atom only.

4. **Lewis Representation of Simple Molecules** (Lewis Structures)

It is representation of valence electrons, done by dots around the symbol of the element. e.g. Nitrite ion (NO_2^-)



5. **Formal Charge on Atom or Ion**

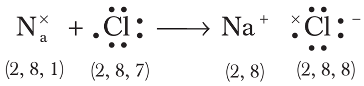
It is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structures.

Formal charge on an atom in a molecule/ion

$$= \left[\begin{array}{l}\text{total number of valence}\\ \text{electron in the free atom}\end{array}\right] - \left[\begin{array}{l}\text{total number of}\\ \text{non-bonding (lone pair)}\\ \text{electrons}\end{array}\right] - \frac{1}{2}\left[\begin{array}{l}\text{total number of bonding}\\ \text{(shared) electrons}\end{array}\right]$$

6. **Ionic or Electrovalent Bond**

It is formed by complete transfer of electrons from one atom to another. e.g. Formation of sodium chloride



Factors governing the formation of ionic bond are

- Low ionisation enthalpy of metal atom.
- High electron gain enthalpy of non-metal atom.
- High lattice enthalpy of the ionic compound.

Lattice enthalpy

It is defined as the amount of energy required to complete seperate one mole of a solid ionic compound into a gaseous constituent ions. It depends on

- charge on ions (greater is the charge, greater is the lattice enthalpy).
- size of the ion (smaller is the size, greater is the lattice enthalpy).

7. **Bond Parameters**

(i) **Bond length** The equilibrium distance between the nuclei of two bonded atoms in a molecule is called the bond length.

The various factors that affect bond length are as follows

(a) **Size of the atoms** The bond length increases with increase in the size of the atoms. Thus, the order of bond length of H—*X* bond is

$$HF < HCl < HBr < HI.$$

Similarly, C—C < Si— Si < Ge— Ge

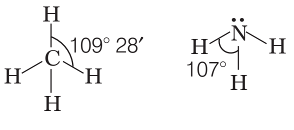
(b) **Bond multiplicity** The bond length decreases as the multiplicity of the bond increases.

Thus, the carbon-carbon bond lengths follow the order

$$C\equiv C < C=C < C—C$$

(ii) **Bond angle** The angle between the orbitals containing bonded electron pairs around central atom in a molecule/complex ion is called the bond angle.

e.g. C— H bond angle in CH_4, H—N—H bond angle in NH_3 are shown below :



(iii) **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. Its unit is kJ mol^{-1}.

$$\text{Bond enthalpy} \propto \frac{1}{\text{Size of atoms}}$$

$$\propto \frac{1}{\text{Number of lone pair(s) of electrons}}$$

$$\propto \text{Multiplicity of bond}$$

Greater the multiplicity of the bond, greater is the bond enthalpy.

e.g. $\text{H—H} < \text{O}=\text{O} < \text{N}\equiv\text{N}$

(iv) **Bond order** The number of bonds formed between the two atoms in a molecule is called the bond order.

e.g. The bond order of a few molecules are given below:

Molecule	H—H	$\text{O}=\text{O}$	$\text{N}\equiv\text{N}$	$\text{C}\overset{\leftarrow}{\equiv}\text{O}$
Bond order	1	2	3	3

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

(v) **Resonance structures** According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule.

Accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

(vi) **Dipole moment** It is a measurement of polarity in any molecule/compound/ion. It is defined as the product of charge (q) and distance between the charges (r).

Dipole moment $(\mu) = q \times r$. Its unit is Debye (D). The dipole moment of symmetrical molecule is always zero.

8. Partial Ionic Character of Covalent Bond

- Electronegative difference between combining atoms = 1.7, then bond is 50% ionic and 50% covalent.
- Electronegativity difference > 1.7, ionic character in bond is more than 50%.
- Electronegativity difference < 1.7, ionic character in bond is less than 50%.

9. Partial Covalent Character in Ionic Bonds : Fajans' Rule

According to Fajans' rule, the covalent character will be favoured by

(i) small size of cation.

(ii) large size of anion.

(iii) high charge of cation and anion.

(iv) the cation having 18-electrons shell.

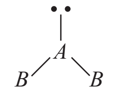
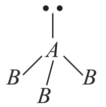
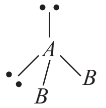
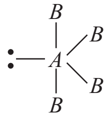
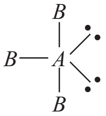
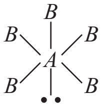
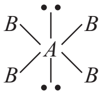
10. Valence Shell Electron Pair Repulsion (VSEPR) Theory

- According to this theory, all valence shell electron pairs surrounding the central atom arrange themselves in such a manner that they are as far away from each other as possible.
- There are two types of electron pairs around the central atom; bonding electron pairs, i.e. bond pair (bp) and non-bonding electron pairs, i.e. lone pair (lp).
- The strength of repulsion between the electron pairs varies as

$$lp\text{-}lp > lp\text{-}bp > bp\text{-}bp$$

- If central atom is linked to similar atoms and there are no lone pairs, the shape is symmetrical otherwise irregular.
- If A represents central atom, B bond pair, L lone pair, then $AB_2 \rightarrow$ linear

Shape of Some Molecules or Ions with Central Ions having One or More Lone Pairs of e^- on the Basis of VSEPR Theory

Molecule type	No. of bonding pair	No. of lone pair	Arrangement of electron pairs and geometry of molecule	Shape	Examples
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3, $SnCl_2$, $PbCl_2$, NO_2^+
AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	PH_3, $BiCl_3$, NH_3, PCl_3, $AsCl_3$, XeO_3, ClO_3^-, SO_3^{2-}, $P(CH_3)_3$
AB_2E_2	2	2	 Tetrahedral	Bent	H_2S, $\overset{-}{N}H_2$ H_2O, OF_2, Cl_2O $Cl_2\dot{O}$, ClO_2^-, $Cl\dot{O}F$, SCl_2
AB_4E	4	1	 Trigonal bipyramidal	*See-saw*	SF_4, SCl_4, $TeCl_4$, XeO_2F_2
AB_3E_2	3	2	 Trigonal bipyramidal	T-shape	ClF_3, IF_3, BrF_3, $XeOF_2$
AB_5E	5	1	 Octahedral	Square pyramidal	IF_5, BrF_5, SbF_5^{2-}
AB_4E_2	4	2	 Octahedral	Square planar	XeF_4, ICl_4^-

11. **Valence Bond Theory** (VBT)

It explains bond formation in terms of overlapping of orbitals, e.g. the formation of H_2 molecule from two hydrogen atoms involves the overlapping of 1*s*-orbital of two H-atoms which are singly occupied. Because of orbital overlapping, the electron density between the nuclei increases which helps in bringing them closer. The overlapping of orbitals may result in two types of bonds, sigma (σ) and pi (π) bond.

12. Concept of Hybridisation

(involving *s*, *p*, *d* and *f*-orbitals)

- Intermixing of orbitals of almost similar energy belonging to the same atom to form same number of orbitals of exactly equal energy is known as hybridisation.
- The new orbital thus formed are known as hybrid orbitals. The number of hybrid orbitals of the molecule can be determined by

$$H = \frac{1}{2}\ (V + Y - C + A)$$

where, V = valence shell electrons of the central metal atom

Y = number of monovalent atom

C = total positive charge

A = total negative charge on the molecule

2	3	4	5	6	7
sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Geometry and Hybridisation of Molecules

Hybridisation	Number of electron pairs	Bond angle	Molecular geometry	Examples
sp	2	180°	Linear	$BeCl_2$, $HgCl_2$, $ZnCl_2$
sp^2	3	120°	Trigonal planar	BF_3, AlF_3
sp^3	4	109.5°	Tetrahedral	CH_4, NH_4^+, CCl_4
sp^3d	5	90°, 120°	Trigonal bipyramidal	PCl_5
sp^3d^2	6	90°	Octahedral	SF_6

13. Molecular Orbital Theory (MOT)

(i) **Bonding molecular orbitals** The molecular orbitals obtained by the addition of atomic orbitals are called bonding molecular orbitals (BMOs) and are represented by σ and π.

(ii) **Anti-bonding molecular orbitals** The molecular orbitals obtained by the subtraction of atomic orbitals are called anti-bonding molecular orbitals (AMOs) and are represented by $\overset{*}{\sigma}$ and $\overset{*}{\pi}$.

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

- In the case of O_2 and F_2,

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

However, the above sequence of energy levels is not true in case of remaining molecules, like Li_2, Be_2, B_2, C_2, N_2.

For these molecules, the increasing order of energies of various molecular orbitals is

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

Stability and Magnetic Character of Molecules/Molecular Ions

- If bond order is positive, molecule or ion is stable otherwise not. Greater the bond order, greater is the stability and shorter is the bond length.
- Further, if all electrons are paired, the species is diamagnetic and if some unpaired electrons are present, the species is paramagnetic.
- Bond order

$$= \frac{1}{2}\,(\text{Number of electrons in BMOs}) - (\text{Number of electrons in AMOs})$$

$$\text{BO} = \frac{1}{2}(N_b - N_a)$$

14. Hydrogen Bonding

- The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule, is called hydrogen bonding.
- It is represented by dotted lines, e.g.

$$\ldots H^{\delta+} — F^{\delta-} \ldots\ldots H^{\delta+} — F^{\delta-} \ldots\ldots H^{\delta+} — F^{\delta-}$$

Types of H-Bonds

There are two types of H-bonds :

(i) **Intermolecular hydrogen bond** Such bond exists between two different molecules of the same or different compounds.

(ii) **Intramolecular hydrogen bond** Such bond exists when hydrogen atom is internally bonded though H-bond with highly electronegative (F, O, N) atoms present within the same molecule.

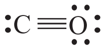
Objective Questions

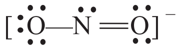
Multiple Choice Questions

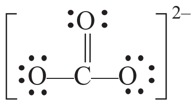
1. According to Lewis and Kossel approach, which of the following molecule has complete octet of the central atom?

(a) LiCl (b) BeH_2 (c) BCl_3 (d) CO_2

2. Lewis dot structure of CO, NO_2^- and CO_3^{2-} are I, II and III respectively


I


II


III

Which of the above structure(s) is/are wrong?

(a) Only I (b) Only II
(c) Only III (d) All of the above

3. Which of the following has octet around central atom?

(a) PF_5 (b) SF_6 (c) CCl_4 (d) BF_3

4. Number of electrons surrounding Kr in KrF_2 is

(a) 10 (b) 6 (c) 4 (d) 8

5. Which of the following species contains equal number of σ and π-bonds?

(a) HCO_3^- (b) X_eO_4
(c) (CN_2) (d) $CH_2(CN)_2$

6. In PO_4^{3-} ion the formal charge on the oxygen atom of P—O bond is

(a) +1 (b) −1 (c) −0.75 (d) +0.75

7. Which of the following is not the characteristic of a covalent compound?

(a) No definite geometry
(b) Insoluble in polar solvent
(c) Small difference in electronegativity between the combining atoms
(d) Low melting point

8. Ionic compounds are formed most easily with

(a) low electron affinity, high ionisation energy
(b) high electron affinity, low ionisation energy
(c) low electron affinity, low ionisation energy
(d) high electron affinity, high ionisation energy

9. Which of the following has electrovalent linkage?

(a) $CaCl_2$ (b) $AlCl_3$
(c) $SiCl_2$ (d) PCl_3

10. The correct order of the lattice energies of the following ionic compounds is ……

(a) $NaCl > MgBr_2 > CaO > Al_2O_3$
(b) $NaCl > CaO > MgBr_2 > Al_2O_3$
(c) $Al_2O_3 > MgBr_2 > CaO > NaCl$
(d) $MgBr_2 > Al_2O_3 > CaO > NaCl$

11. The higher lattice energy corresponds to

(a) MgO (b) CaO
(c) SrO (d) BaO

12. The correct order of increasing bond length of C—H, C—O, C—C and C$=$C is

(a) $C-H < C-O < C-C < C=C$
(b) $C-H < C=C < C-O < C-C$
(c) $C-C < C=C < C-O < C-H$
(d) $C-O < C-H < C-C < C=C$

13. Which of the following has lowest bond angle?

(a) H_2S (2*lp*) (b) NH_3 (1*lp*)
(c) SO_2 (1*lp*) (d) H_2O (2*lp*)

14. The bond angle in NF_3 (102.3°) is smaller than NH_3 (107.2°). This is because of

(a) large size of F compared to H
(b) large size of N compared to F
(c) opposite polarity of N in the two molecules
(d) small size of H compared to N

15. In case of H_2O molecule, the enthalpy needed to break the two O — H bonds is not the same, i.e.

$$H_2O(g) \longrightarrow H(g) + OH(g); \quad \Delta_a H_1^{\ominus} = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g); \quad \Delta_a H_2^{\ominus} = 427 \text{ kJ mol}^{-1}$$

What should be the mean bond enthalpy of O—H bonds in case of H_2O molecule?

(a) 75 kJ mol^{-1} (b) –75 kJ mol^{-1}
(c) 464.5 kJ mol^{-1} (d) 929 kJ mol^{-1}

16. Which of the following molecules have same bond order?

$$\underset{\text{I}}{H_2}, \underset{\text{II}}{Cl_2}, \underset{\text{III}}{CO}, \underset{\text{IV}}{Br_2}, \underset{\text{V}}{N_2}$$

Choose the correct option.

(a) I, II and IV have same bond order
(b) III and V have same bond order
(c) Both (a) and (b)
(d) None of the above

17. Dipole moment is usually expressed in Debye units (D). From the formula, the unit of dipole moment is Coulomb metre (Cm). The relation between both units of dipole moment is

(a) 1 D = 1 Cm
(b) 1D = 3.33564×10^{-30} Cm
(c) 1D = 2.22564×10^{-30} Cm
(d) 1D = 1.11564×10^{-30} Cm

18. In case of polyatomic molecules, dipole moment

(a) only depends upon the individual dipole moments of bonds
(b) is vector sum of the dipole moments of various bonds
(c) is substraction of dipole moments of various bonds
(d) All of the above are correct

19. Which of the following molecules has the maximum dipole moment ?

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

20. Which of the following is correct?

(a) Bond order $\propto \dfrac{1}{\text{bond length}} \propto \dfrac{1}{\text{bond enthalpy}} \propto$ stability

(b) Stability $\propto \dfrac{1}{\text{bond order}} \propto \dfrac{1}{\text{bond length}} \propto \dfrac{1}{\text{bond enthalpy}}$

(c) Stability $\propto$ bond order $\propto$ bond length $\propto$ bond enthalpy

(d) Stability $\propto$ bond order $\propto$ bond enthalpy $\propto \dfrac{1}{\text{bond length}}$

21. The most ionic one is ....

(a) P_2O_5 (b) MnO_2 (c) Mn_2O_7 (d) P_2O_3

22. The correct sequence of increasing covalent character is represented by

(a) $LiCl < NaCl < BeCl_2$ (b) $BeCl_2 < NaCl < LiCl$
(c) $NaCl < LiCl < BeCl_2$ (d) $BeCl_2 < LiCl < NaCl$

23. Which of the following has covalent bond?

(a) Na_2S (b) $AlCl_3$ (c) NaH (d) $MgCl_2$

24. Which of the following molecules can be represented in terms of resonance?

(a) O_3 (b) CO_3^{2-}
(c) CO_2 (d) All of these

25. The bond order of the N—O bonds in NO_3^- ion is

(a) 0.33 (b) 1.00 (c) 1.33 (d) 1.50

26. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be

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

27. The two *sp*-hybrid points in the opposite direction along the *z*-axis with projecting lobes are of size. (taking positive sign as overlapping end)

(a) more negative and less positive
(b) same positive and negative
(c) more positive and less negative
(d) Both (a) and (b)

28. Which of the following pair of ions are isoelectronic and isostructural?

(a) CO_3^{2-}, SO_3^{2-} (b) ClO_3^-, CO_3^{2-}

(c) SO_3^{2-}, NO_3^- (d) ClO_3^-, SO_3^{2-}

29. Match the compounds given in Column I with the shape given in Column II and mark the correct option.

	Column I		Column II
A.	XeF_6	1.	Distorted octahedral
B.	XeO_3	2.	Square planar
C.	$XeOF_4$	3.	Pyramidal
D.	XeF_4	4.	Square pyramidal

Codes

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

30. The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O etc. in terms of

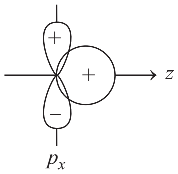
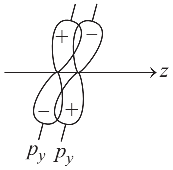
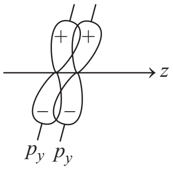
(a) overlapping of atomic orbitals

(b) hybridisation of atomic orbitals

(c) Both (a) and (b)

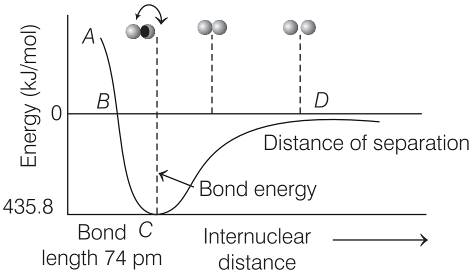
(d) None of the above

31. Match the following columns and choose the correct option from the codes given below.

	Column I (Representation)	Column II (Type)
A.		1. Positive overlap
B.		2. Zero overlap
C.		3. Negative overlap

Codes

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

32. 

The above potential energy curve is given for the formation of H_2 molecule as a function of internuclear distance of H-atoms. At what point in the curve H_2 is found in the most stable state?

(a) *A* (b) *B* (c) *C* (d) *D*

33. The pair of electron in the given carbanion, $CH_3C \equiv C^-$, is present in which orbitals?

(a) sp^3 (b) sp^2 (c) sp (d) $2p$

34. Match the shape of molecules in Column I with the type of hybridisation in Column II.

	Column I		Column II
A.	Tetrahedral	1.	sp^2
B.	Trigonal	2.	sp
C.	Linear	3.	sp^3

Codes

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

35. Which of the following statements are correct about CO_3^{2-}?

(a) The hybridisation of central atom is sp^3

(b) Its resonance structure has one C—O single bond and two C ═ O double bonds

(c) The average formal charge on each oxygen atom is 0.67 units

(d) All C—O bond lengths are not same

36. Match the species in Column I with the type of hybrid orbitals in Column II.

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

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	5	4	(b)	1	2	3	4
(c)	2	3	5	1	(d)	4	2	3	1

37. The electron probability distribution around a group of nuclei in a molecule is given by

(a) atomic orbital

(b) molecular orbital

(c) only antibonding molecular orbital

(d) only bonding molecular orbital

38. The paramagnetic behaviour of B_2 is due to the presence of ......

(a) 2 unpaired electrons in π_b MO

(b) 2 unpaired electrons in $\overset{*}{\pi}$ MO

(c) 2 unpaired electrons in $\overset{*}{\sigma}$ MO

(d) 2 unpaired electrons in σ_b MO

39. Bond order of which among the following molecules is zero?

(a) F_2 (b) O_2

(c) Be_2 (d) Li_2

40. Which of the following diatomic molecular species has only π-bonds according to molecular orbital theory?

(a) N_2 (b) C_2

(c) Be_2 (d) O_2

41. The correct statement with regards to H_2^+ and H_2^- is

(a) both H_2^+ and H_2^- do not exist

(b) H_2^- is more stable than H_2^+

(c) H_2^+ is more stable than H_2^-

(d) both H_2^+ and H_2^- are equally stable

42. Match the following Columns and choose the correct option from the codes given below.

Column I		Column II	
A.	He_2	1.	Paramagnetic
B.	O_2	2.	Diamagnetic
C.	Li_2	3.	Does not exist
D.	C_2		

Codes

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

43. Which of the following molecule does not show hydrogen bonding?

(a) HF (b) H_2O

(c) NH_3 (d) H_2S

44. The higher boiling point of water is due to which reason?

(a) Coordinate bonding

(b) Covalent bonding

(c) Electrostatic force of attraction

(d) Hydrogen bonding

45. The boiling point of a substance increases with increase in

(a) intermolecular hydrogen bonding

(b) intramolecular hydrogen bonding

(c) molecular mass

(d) Both (a) and (c)

Assertion-Reasoning MCQs

Directions In the following questions (Q.No. 46-60) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(a) Both Assertion and Reason are correct statements and Reason is the correct explanation of the Assertion.

(b) Both Assertion and Reason are correct statements, but Reason is not the correct explanation of the Assertion.

(c) Assertion is correct, but Reason is incorrect statement.

(d) Assertion is incorrect but Reason is correct statement.

46. Assertion SF_6 and PF_5 are examples of expanded octed molecules.

Reason P in PF_5 and S in SF_6 are in sp^3d and sp^3d^2-hybridisation respectively.

47. Assertion Octet theory cannot account for the shape of the molecule.

Reason Octet theory can predict relative stability and energy of a molecule.

48. Assertion Sodium chloride formed by the action of chorine gas on sodium metal is a stable compound.

Reason This is because sodium and chloride ions acquire octet in sodium chloride formation. ***(NCERT Exemplar)***

49. Assertion Ionic bond is non-directional.

Reason Each ion is surrounded by a uniformly distributed electric field

50. Assertion Order of lattice energy for same halides are as $LiF > NaF > KF$.

Reason Size of alkali metals increases from Li to K.

51. Assertion In NH_3, N is sp^3-hybridised, but angle is found to be 107°

Reason The decrease in bond angle is due to repulsion between the lone pair on nitrogen and bond pair between N and H.

52. Assertion Bond energy and bond dissociation energy has identical value for diatomic molecules.

Reason Greater the bond dissociation energy, less reactive is the bond.

53. Assertion BF_3 molecule has zero dipole moment.

Reason F is electronegative and B—F bonds are polar in nature

54. Assertion According to Fajan's rule, covalent charcacter is favoured by small cation and large anion.

Reason The magnitude of covalent character in the ionic bond depends upon the extent of polarisation.

55. Assertion Shape of NH_3 molecule is tetrahedral.

Reason In NH_3, nitrogen is sp^3-hybridised.

56. Assertion Through the central atom of both NH_3 and H_2O molecules are sp^3-hybridised, yet H — N — H bond angle is greater than that of H—O—H.

Reason This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

57. Assertion The hybridisation possed by boron atom in BCl_3 molecule is sp^3.

Reason sp^2-hybrid structure have trigonal planar geometry.

58. Assertion Fluorine molecule has bond ordcer one.

Reason The number of electrons in the anti-bonding molecular orbitals is two less than that in bonding molecular orbitals.

59. **Assertion** 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 bond is the not same.

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

60. **Assertion** Water is one of the best solvents.

Reason H-bonding is present in water molecules.

Case Based MCQs

61. Read the given passage and answer the 1 to 5 that follows :

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

The ideas that helped to establish the nature of chemical bonding came to fruition during the early 20th century, after the electron had been discovered and quantum mechanics had provided a language for the description of the behaviour of electrons in atoms.

However, even though chemists need quantum mechanics to attain a detailed quantitative understanding of bond formation, much of their pragmatic understanding of bonds is expressed in simple intuitive models. These models treat bonds as primarily of two kinds–namely, ionic and covalent.

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

A key concept in a discussion of chemical bonding is that of the molecule. Molecules are the smallest unit of compounds that can exist. One feature of molecules that can be predicted with reasonable success is their shape.

Molecular shapes are of considerable importance for understanding the reactions that compounds can undergo, and so the link between chemical bonding and chemical reactivity is discussed briefly in this article.

The following questions are multiple choice questions. Choose the most appropriate answer:

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

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

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

(a) NaCl (b) $NaClO_4$
(c) PCl_3 (d) $POCl_3$

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

(a) – 0.75, 1.25 (b) – 0.75, 1.0
(c) – 0.75, 0.6 (d) – 3, 1.25

(iv) On the basis of valence bond theory, the formation of H_2 molecules from two H-atoms involves.

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

(c) The maximum energy of the system at the equilibrium internuclear distance
(d) Stabilisation of the molecule; when the nuclei are brought still closer to each other from the equilibrium inter-nuclear distance

Or

The dipole moment is highest for

(a) *trans*-2-butene (b) 1, 3-dimethyl benzene
(c) acetophenone (d) ethanol

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

In order to explain the shapes of molecules adequately, Sidgwick and Powell in 1940 proposed a theory based on the repulsive interaction of the electron pairs in the valence shell of the atoms. Nyholm and Gillespie (1950) further developed and redefined the concept.

The main postulates of this theory are as follows :

The number of valence shell electron pairs (bonded or non-bonded) present around the central atom decides the shape of the molecules. The shared electron pairs are called bond pairs and unshared or non-bonding electrons are called lone pairs.

Electron pairs of valence shell repel one another because their electron clouds are negatively charged.

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

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

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

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

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

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

(a) HF (b) H_2O
(c) BF_3 (d) $CHCl_3$

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

(a) H_2O (b) BF_3
(c) NH_2^- (d) PCl_3

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

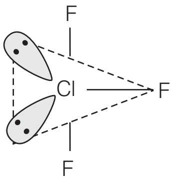
(a) Same hybridisation
(b) Different hybridisation
(c) Repulsive effect
(d) None of the above

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

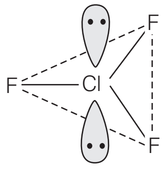
(a) PH_3 (b) ClF_3
(c) NCl_3 (d) BCl_3

Or

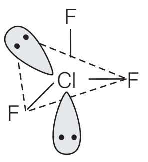
Which of the following structures is most stable?



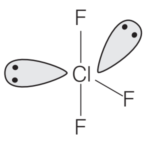
(a)



(b)



(c)



(d)

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

Lewis postulated that atoms achieve the stable octet(or duplet in case of H and He) when they are joined through chemical bonds or in other words atoms join together either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to complete their octet (i.e. eight electrons in the valence shell). This is known as octet rule. Octet rule has not been followed in all molecules.

Elements of the third and higher periods of the periodic table, because of the availability of d-orbitals can expand their covalency and can accommodate more than eight valence electrons around the central atom. This is referred as **expanded octet**.

Here, also the octet rule is not applicable. e.g. PF_5 (10 electrons around P-atom), SF_6 (12 electrons around S-atom), H_2SO_4 (12 electron around S atom). Compound having expanded octet are also termed as hypervalent compounds. Formal charge is a factor which is based on pure covalent view of bonding in which electron pairs are shared equally by neighbouring atom. It may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is represented as :

$$\text{FC} = V - L - \frac{1}{2}S$$

where,

FC = formal charge on an atom in a Lewis structure,

V = total number of valence electrons in the free atom,

L = total number of non-bonding (lone pair) electrons and

S = total number of bonding (shared) electrons.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

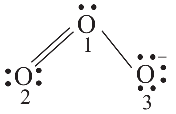
(c) Assertion is correct statement but Reason is incorrect statement.

(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom.

Reason The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure.

(ii) **Assertion** The correct Lewis structure of O_3 may be drawn as :



Reason The formal charges on atom 1, 2 and 3 are +1, 0 and −1, respectively.

(iii) **Assertion** Formal charges do not indicate real charge separation within the molecule.

Reason Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.

(iv) **Assertion** H_2SO_4 does not follow the octet rule.

Reason In sulphur atom 3*d*-orbitals also available for bonding and hence, it have 12 electrons around itself in H_2SO_4.

Or **Assertion** Sulphur forms many compounds in which the octet rule is obeyed.

Reason Due to the absence of *d*-orbitals in sulphur, it follows the octet rule.

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

Dipole moment is the measure of degree of polarity and is defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually represented by a Greek letter μ (mu).

It is a result of polarisation.

Mathematically, it is expressed as :

Dipole moment (μ) = charge $(Q) \times$ distance of separation (r)

It is usually expressed in Debye units (D).

$1\,\text{D} = 3.33564 \times 10^{-30}$ C m

where, C is coulomb and m is metre.

or $1\,\text{D} = 1 \times 10^{-18}$ esu (or, stat C m)

Here, esu = electrostatic unit

stat C cm = static coulomb centimeter

It is a vector quantity and is represented by the crossed arrow ($+\!\!\longrightarrow$) pointing towards the more electronegative atom.

$\overset{+\!\!\rightarrow}{\text{H} —} \ddot{\underset{\cdot\cdot}{\text{F}}}\!: \rightarrow$ More electronegative atom

This arrow symbolises the direction of the shift of electron density in the molecule.

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

(i) The relation between resultant dipole moment of NH_3 and NF_3 is
(a) $\mu_{NH_3} = \mu_{NF_3}$ (b) $\mu_{NH_3} > \mu_{NF_3}$
(c) $\mu_{NH_3} < NF_3$ (d) None of these

(ii) In a diatomic molecule, the bond distance is 1×10^{-8} cm and its dipole moment is 1.2 D. What is the fractional electronic charge on each atom?
(a) 0.25 (b) 2.5 (c) 1 (d) 0.5

(iii) In water molecule, the two O—H bonds are oriented at an angle of 104.5°. In BF_3, the three B—F bonds are oriented at an angle of 120°. In BeF_2, the two Be—F bonds are oriented at an angle of 180°. Which will have highest dipole moment?
(a) BeF_2
(b) BF_3
(c) H_2O
(d) All have equal dipole moment

(iv) CO_2 molecule is
(a) polar (b) non-polar
(c) linear (d) Both (b) and (c)

Or

Dipole moment is given by
(a) $\mu = q \times d$ (b) $\mu = 2qd$
(c) $\mu = \frac{qd}{2}$ (d) None of these

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

The formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave function. The molecular orbital formed by the addition of atomic orbital is called bonding melecular orbital.

The molecular orbitals obtained by the subtraction of atomic orbitals are called antibonding molecular orbitals (AMOs) and are represented by σ^* and π^*. In the formation of AMOs, the electron waves cancel each other due to destructive interference.

In these orbitals, most of the electron density is located away from the space in between the nuclei.

Infact, they have a nodal plane (on which the electron density is zero) in between the nuclei and hence, the repulsion between the nuclei is high.

In contrast to the bonding molecular orbitals, the electrons placed in these orbital destabilise the molecule because of more mutual repulsion of the electrons in this orbital as compared to the attraction between the electrons and the nuclei which cause a net increase in energy.

In these questions (i)-(iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

Reason The energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals.

(ii) **Assertion** The combining atomic orbitals must have the same or nearly the same energy.

Reason $1s$-orbital can combine with another $2s$-orbital but not with $1s$-orbital because the energy of $2s$-orbital is appreciably higher than that of $1s$-orbital. This is not true if the atoms are very different.

(iii) **Assertion** Bond energy and bond dissociation energy have identical value for diatomic molecules.

Reason Greater the bond dissociation energy, less reactive is the bond.

(iv) **Assertion** Bond energy has order like

$$C-C < C=C < C\equiv C$$

Reason Bond energy increases with increase in bond order.

Or **Assertion** The bond order of helium is zero.

Reason The number of electrons in bonding molecular orbital and antibonding molecular orbital is equal.

ANSWERS

Multiple Choice Questions

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

Assertion-Reasoning MCQs

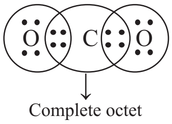
46. (b) 47. (c) 48. (a) 49. (a) 50. (b) 51. (a) 52. (b) 53. (b) 54. (a) 55. (d)
56. (a) 57. (b) 58. (a) 59. (d) 60. (b)

Case Based MCQs

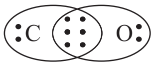
60. (i)-(d), (ii)-(b), (iii)-(a), (iv)-(b, c)
61. (i)-(c), (ii)-(d), (iii)-(c), (iv)-(d, a)
63. (i)-(a), (ii)-(a), (iii)-(b), (iv)-(a, c)
64. (i)-(b), (ii)-(a), (iii)-(c), (iv)-(d, a)
65. (i)-(b), (ii)-(c), (iii)-(b), (iv)-(a, a)

EXPLANATIONS

1. According to Lewis and Kossel approach, CO_2 molecule has complete octet of central atom LiCl, BeH_2 and BCl_3 are the molecules with incomplete octet of central atom. Lewis structure of CO_2 can be represented as :



2. Lewis dot structure (I) of CO, is wrong.
It may be correctly represented as :

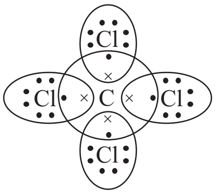


or $:C \equiv O:$
(Correct)

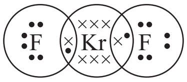
3. Carbon tetrachloride (CCl_4) has octet around central atom. The number of bonded electrons in other given compounds are as follows :

$PF_5 (10e^-)$, $SF_6 (12e^-)$, $BF_3 (6e^-)$

Structural representation of CCl_4 is as follows :



4. Krypton (Kr) forms two covalent bonds with two fluorine atoms (one with each fluorine).



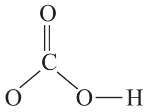
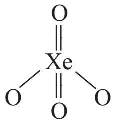
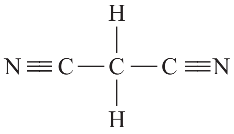
or F — Kr — F

Number of electrons in valence shell of Kr = 8

Number of electrons its shares with two F-atoms = 2

∴ Total number of electrons found around Kr in $KrF = 8 + 2 = 10$

5. XeO_4 contain equal number of σ and π-bonds. number of σ and π-bonds present in species are as follows:

	Column I	Column II
(a)		σ-bond-4 π-bond-1
(b)		σ-bond-4 π-bond-4
(c)	$N \equiv C — C \equiv N$	σ-bond-3 π-bond-4
(d)	 $N \equiv C — CH_2 — C \equiv N$	σ-bond-6 π-bond-4

6. In PO_4^{3-} ion, formal charge on each O-atom of P— O bond

$$= \frac{\text{total charge}}{\text{Noumber of O - atom}} = -\frac{3}{4} = -0.75$$

7. Covalent bonds are directional. Therefore, covalent compounds have definite shape (geometry), e. g. acetylene is linear, methane is tetrahedral in shape.

8. Formation of ionic bond is favoured by

(i) low ionisation potential of metal.
(ii) greater value of electronaffinity of non-metal.
(iii) higher value of lattice energy of resulting ionic compound.

9. In $CaCl_2$, Ca—Cl bonds are electrovalent or ionic bonds because of the higher electronegativity difference between Ca and Cl-atom.

10. Lattice energy depends upon

(i) the product of ionic charges.
(ii) the interionic distance.
(iii) nature of the crystal structure.

Hence, more is the ionic charge, more will be the lattice energy.

So, the correct order of lattice energy is $Al_2O_3 > MgBr_2 > CaO > NaCl$.

11. Lattice energy $\propto$ charge of ion $\propto \frac{1}{\text{size of ion}}$

On moving downward, the size of alkaline earth metals increases due to increase in number of shells. Thus, Mg has the smallest size.

Hence, lattice energy is higher for MgO.

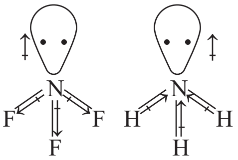
12. The C—H is the shortest due to small size of both atoms and large electronegativity difference. The double bonds are shorter than single bonds. Hence, C=C bond is shorter than C—O and C—C. Due to electronegativity difference between C and O, the C—O bond length is shorter than C—C bond. Hence, the correct order is

$$C-H < C{=}C < C-O < C-C$$

13. H_2S has the lowest bond angle because two lone pairs are present in it and S has low electro negativity.

$$\underset{92^\circ}{H_2S} < \underset{104^\circ}{H_2O} < \underset{107^\circ}{NH_3} < \underset{119^\circ 30'}{SO_2}$$

14. In NF_3, N is less electronegative as compared to F but in NH_3, it (N) is more electronegative than H. In case of same central atom, as the electronegativity of other atoms increases, bond angle decreases. Thus, bond angle in NF_3 is smaller than that in NH_3 because of the opposite polarity of N in these molecules.



15. In case of H_2O molecule, the enthalpy needed to break the two O — H bonds is not the same, i.e.

$$H_2O(g) \longrightarrow H(g) + OH(g); \Delta_a H_1^\ominus = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g); \Delta_a H_2^\ominus = 427 \text{ kJ mol}^{-1}$$

The **mean or average bond enthalpy** of O—H bonds in case of H_2O molecule is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule.

$$\text{Average bond enthalpy} = \frac{502 + 427}{2}$$

$$= 464.5 \text{ kJ mol}^{-1}$$

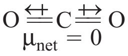
16. In CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3. H_2, Cl_2 and Br_2 have bond order 1.

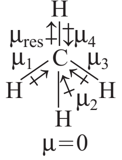
Hence, both (a) and (b) options are correct.

17. $1D = 3.33564 \times 10^{-30}$ cm

18. In case of polyatomic molecule dipole moment is the vector sum of the dipole moments of various bonds.

19. CO_2 and CH_4 have zero dipole moment as these are symmetrical in nature. Between NH_3 and NF_3, NH_3 has greater dipole moment though in NH_3 and NF_3 both, N possesses one lone pair of electrons. This is because in case of NH_3, the net N—H bond dipole is in the same direction as the direction of dipole of lone pair but in case of NF_3, the direction of net bond dipole moment of three N—F bonds is opposite to that of the dipole moment of the lone pair.

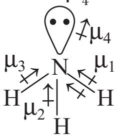




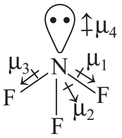
$\because \quad \mu_{res} = \mu_1 + \mu_2 + \mu_3 = -\mu_4$

$\therefore \quad \mu_{net} = \mu_1 + \mu_2 + \mu_3 + \mu_4$

$= -\mu_4 + \mu_4 = 0$



Resultant of 3 N—H bond lie in the same direction as μ_4.



Resultant of 3 N—F bond lie opposite to $\mu_4 \mu_{net} = 0.2$ D.

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

Therefore, stability $\propto$ bond order $\propto$ bond enthalpy and stability increases with decrease in bond length.

Therefore, $\quad \text{stability} \propto \frac{1}{\text{bond length}}$

21 According to Fajan's rule, compounds having large charge on cation are more covalent or least electrovalent.

So, compounds having low charge on cation will be more electrovalent or ionic.

$\overset{+4}{MnO_2}$ $\overset{+7}{Mn_2O_7}$ $\overset{+5}{P_2O_5}$ $\overset{+3}{P_2O_3}$

So, P_2O_3 will be most ionic.

22 On the basis of Fajan's rule, lower the size of cation, higher will be its polarising power and higher will be covalent character.

$$\therefore \text{ Polarising power} \propto \frac{1}{\text{size of cation}}$$

Covalent character ∝ polarising power

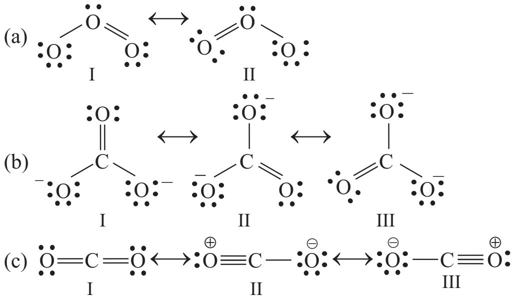
(The order of size of cation is $Na^+ > Li^+ > Be^{2+}$)

So, the correct order is $NaCl < LiCl < BeCl_2$.

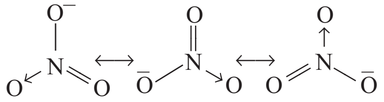
23 Al^{3+} cation is smaller than Na^+ (because of greater nuclear charge). According to Fajans' rule, small cation polarises anion upto greater extent.

Hence, Al^{3+} polarises Cl^- ions up to greater extent, therefore $AlCl_3$ has covalent bond between Al and Cl-atoms.

24. All the given molecules can be represented in terms of resonance. These are shown below :



25 The resonance structures of NO_3^- ions are as :



The N—O bond order

$$= \frac{\text{number of bonds between two atoms}}{\text{total number of resonating structure}}$$

$$= \frac{4}{3} = 1.33$$

26. The type of hybrid orbitals of nitrogen can be decided by using VSEPR theory counting *bp* and as *lp* in

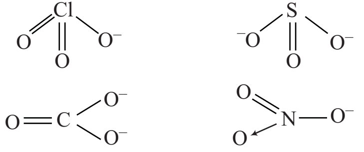
$NO_2^+ = 2\ bp + 0\ lp =$ linear $=$ *sp*-hybridised

$NO_3^- = 3\ bp + 0\ lp \Rightarrow sp^2$-hybridised

$NH_4^+ = 4\ bp + 0\ lp \Rightarrow sp^3$-hybridised

27. The two *sp*-hybrid points in the opposite direction along the *z*-axis with projecting more positive lobes a less negative lobes, which provides more effective overlapping resulting in the formation of stronger bond.

28. $ClO_3^-, = SO_3^{2-}$



Number of electrons

$CO_3^{2-} = 6 + 2 + 24 = 32$

$SO_3^{2-} = 16 + 2 + 24 = 42$

$ClO_3^- = 17 + 24 + 1 = 42$

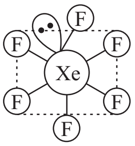
$NO_3^- = 7 + 1 + 24 = 32$

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

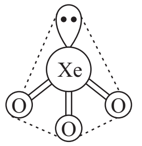
29. The correct match is

$A \rightarrow 1, B \rightarrow 3, C \rightarrow 4, D \rightarrow 2$

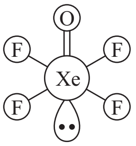
The structure of the xenon compounds are represented below:



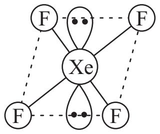
Distorted octahedral XeF_6



Pyramidal XeO_3



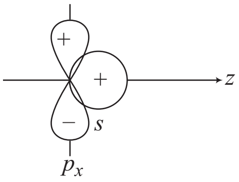
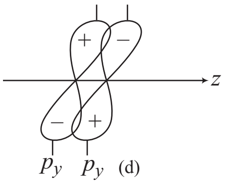
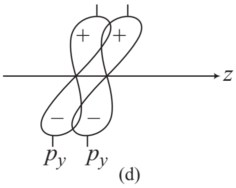
Square pyramidal $XeOF_4$



Square planar XeF_4

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

31. The correct match is (A) → (2), (B) → (3), (C) →(1).

A.		Zero overlap (Out of phase due to different orientation or direction of approach)
B.		Negative overlap (Orbitals forming bond have different sign and orientation)
C.		Positive overlap (Orbitals forming bond have same sign and orientation in space)

32. At C point in the curve, H_2 is found in the most stable state due to minimum energy, as the energy gets released when bond is formed between two hydrogen atoms.

33 Hybridisation $= \dfrac{\text{Number of } \sigma\text{-electrons}}{2}$

$$= \frac{2 + 2 \text{ (negative ion)}}{2}$$

$$= 2 = sp$$

Hence, in the carbanion, $CH_3C \equiv C^{\ominus}$, pair of electron as negative charge is present in sp-hybridised orbital.

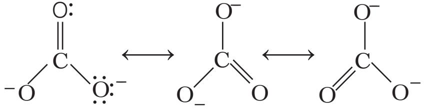
34. A → (3); B → (1); C → (2)

A. Tetrahedral shape – sp^3-hybridisation

B. Trigonal shape – sp^2-hybridisation

C. Linear shape – sp-hybridisation

35. The hybridisation of central atom in CO_3^{2-} is sp^2. Hence, (a) is wrong.



Due to resonance all C—O bond lengths are equal.

Formal charge on each O-atom

$$= \frac{\text{Total charge}}{\text{Number of O-atoms}}$$

$$= \frac{-2}{3} = -0.67 \text{ units.}$$

All C— O bond lengths are equal as mentioned above.

36. The correct match is

(A) → (3); (B) → (1); (C) → (5); (D) → (4).

(A) SF_4 = number of bp (4) + number of lp (1)
= sp^3d-hybridisation

(B) IF_5 number of bp (5) + number of lp (1)
= sp^3d^2-hybridisation

(C) NO_2^+ = number of bp (2) + number of lp (0)
= sp-hybridisation

(D) NH_4^+ = number of bp (4) + number of lp (0)
= sp^3-hybridisation.

37. The electron probability distribution on around a group of nuclei in a molecule is given by molecular orbital.

38. $B_2 = 5 + 5 = 10e^-$

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

Due to the presence of 2 unpaired bonding electrons in π_b MO, B_2 shows paramagnetic behaviour.

39. (a) F_2 molecule

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

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

(b) O_2 molecule

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

$$\text{Bond order} = \frac{1}{2}(10 - 6) = 2$$

(c) Be_2 molecule $= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2$

$$\text{Bond order} = \frac{1}{2}(4 - 4) = 0$$

(d) Li_2 molecule $= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2$

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

Therefore, Be_2 molecule has zero bond order.

40. According to MO theory, C_2 is the diatomic molecular species that has only π-bonds.

The molecular orbital configuration of C_2 is
$C_2(Z = 12) \Rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$
$\pi 2p_x^2 = \pi 2p_y^2.$

Double bond in C_2 consists of both π-bonds because of the presence of last (valence) four electrons in two π-molecular orbitals.

The configuration of N_2, Be_2 and O_2 are as follows:

$N_2(Z = 14)$ - $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$
$\pi 2p_x^2 = \pi 2p_y^2,\ \sigma 2p_z^2$ (1 σ and 2π-bonds)

$Be_2(Z = 8)$ - $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$ (σ bonds only)

$O_2(Z = 16)$ - $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_z^2,$
$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_z^1$ (σ, π and 1π*-bond)

41. $H_2^+ : (\sigma 1s^1)$

$\therefore\ BO = \frac{1}{2}(1 - 0) = \frac{1}{2}$

$H_2^- : (\sigma 1s)^2(\overset{*}{\sigma} 1s^1)$

$\therefore\ BO = \frac{1}{2}(2 - 1) = \frac{1}{2}$

Even though, the bond order of H_2^+ and H_2^- are equal but H_2^+ is more stable than H_2^- as in the latter, an electron is present in the higher energy antibonding $(\overset{*}{\sigma} 1s)$ orbital.

42. C_2, Li_2 are diamagnetic.

O_2 is paramagnetic, He_2 does not exist.
Hence, correct match is
(A) → (3), (B) → (1), (C) → (2), (D) → (2).

43. H_2S does not show hydrogen bonding, that's why it exists as a gas, other given molecules such as HF, H_2O and NH_3 show hydrogen bonding.

44. The higher boiling point of water is due to hydrogen bonding. O-atom of each H_2O molecule is covalently linked with two H-atoms of its own molecule and with another H-atom of adjacent H_2O molecule by H-boiling.

45. The boiling point of a substance increases with increase in intermolecular hydrogen bonding and molecular mass. Association of molecules takes place due to intermolecular hydrogen bonding which increases the boiling point of a substance.

46. In such type of compounds, participation of *d*-orbitals in bonding increase the number of vlence electrons more than eight. Thus, it is termed as expanded octet.

Both Assertion and Reason are correct but Reason is not the correct explanation of the Assertion.

47. Octet theory is totally silent about the energy of a molecule and about its relative stability

∴ Assertion is correct but Reason is incorrect.

48. Both Assertion and Reason are correct and Reason is correct explanation of Assertion.

49. Each ion, because of uniformly distributed electric field, is non directional.

Both Assertion and Reason are correct and Reason is correct explanation of Assertion.

50. Both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.

51. Lone pair lone pair repulsion > lone pair - bond pair repulsion > bond pair - bond pair repulsion. In NH_3 there are three bond pairs and one lone pair. The three N—H bond pairs are pushed closer because of the lone pair - bond pair repulsion and N—H—H bond angle gets reduced from 109° 28 (the tetrahedral angle) to 107°.

Both Assertion and Reason are correct and Reason is correct explanation of Assertion.

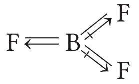
52. Bond dissociation energy is the energy required to break one mole of bond of a particular type. So as to separate them into gaseous atoms.

Bond energy of the same type of bond present in the molecule. Bond energy of C—H bond in methane is 99.2. kcal/mol.

Thus, for polyatomic molecules, average bond energy is taken as the dissociation bond energy.

Both Assertion and Reason are correct but Reason is not the correct explanation of the Assertion.

53. BF_3 is sp^2-hybridised. Dipole moment is a vector quantity. The three bond moments give a net sum of zero, as the resultant of any two is equal and opposite to the third.



Resultant dipole moment = 0

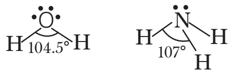
Both Assertion and Reason are correct but Reason is not the correct explanation of the Assertion.

54. Assertion and Reason both are correct and Reason is the correct explanation of Assertion.

55. NH_3 molecule is pyramidal in shape and sp^3-hybridised because out of four electron pairs, three are bonding pairs and one is lone pair.

Thus, Assertion is incorrect but Reason is correct.

56. Assertion and Reason both are correct and Reason is the correct explanation of Assertion.



sp^3-hybridised sp^3-hybridised

57. Hybridisation $= \frac{1}{2}(VE + MA - c + a)$

$$= \frac{1}{2}(3 + 3 - 0) = 3 \Rightarrow sp^2$$

Both Assertion and Reason are correct but Reason is not the correct explanation of the Assertion.

58. Electronic configuration of F_2 molecule is

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

No. of electron in bonding MOs

$$= -\frac{\text{No. of electrons in anti-bonding MOs}}{2}$$

$$= \frac{10 - 8}{2} = 1$$

Both Assertion and Reason are correct but Reason is the correct explanation of Assertion.

59. **Correct Assertion** The bond enthalpies of the two O—H bonds in H—O—H are not equal.

Correct Reason This is because electronic environment around O is not same after breakage of one O—H bond.

Thus, Assertion is incorrect but Reason is correct.

60. Water is an excellent solvent because it has high value of dielectric constant.

Due to high value of dielectric constant, the electrostatic forces of attraction between the ions decrease and these ions get separated and ultimately get solvated by the solvent molecules.

Both Assertion and Reason are correct but Reason is not the correct explanation of the Assertion.

61. (i) If bond order of any species is zero, that can not exist.

So, bond order of $H_2^{2-} = \sigma_1 s^2, \sigma_1^* s^2 = \frac{2 - 2}{2} = 0$

(ii) $NaClO_4$ contains two parts: It have ionic bonding as Na^+ and ClO_4^- ions. However, in ClO_4^- (perchlorate ion) there is sp^3-hybridisation and Cl—O bonds are covalent.

(iii) The formal charge on each O-atom in $PO_4^{3-} = -\frac{3}{4} = -0.75$.

P—O bond order in PO_4^{3-}

$$= \frac{\text{Total number of bonds between atoms}}{\text{Total number of resonating structures}}$$

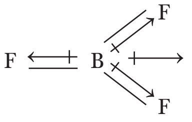
$$= \frac{5}{4} = 1.25$$

(iv) On the basis of VB theory, the formations of H_2 molecule from two H-atoms involves lowering of potential energy of the system as the two H-atoms come near to each other. This energy will be minimum at the equilibrium internuclear distance.

Or

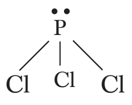
The dipole moment of acetophenones is 3 Debye which is highest amongst the given compounds, as it has strong electron withdrawing group.

62. (i) In BF_3, the dipole moment is zero although the B—F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third. Structure of BF_3 molecule is as follows :



(ii) PCl_3 contains three bond pairs and one lone pair around the central atom.

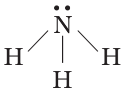
$PCl_3 \Rightarrow$



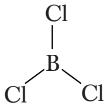
$(3bp + 1lp)$

(iii) Repulsive effects result in deviations from idealised shapes and alterations in bond angles in the molecules. Presence of lone pair of electrons causes repulsion between lone pair-bond pair.

In $H—\ddot{\underset{\cdot\cdot}{O}}—H$, two lone pairs of oxygen repel two bond pairs of —OH.

In  one lone pair of nitrogen repel three bond pairs of N—H.

(iv) The species having bond angles of 120° is BCl_3. It is sp^2-hybridised and central atom does not have any lone pair of electrons.



(BCl_3)

Or

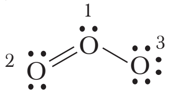
Structure (a) is the most stable geometry because both the lone pairs are present at equatorial position.

Due to which repulsion is minimum in molecule as compared to the repulsion in other molecules where lone pair is at axial position.

63. (i) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

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

(ii) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

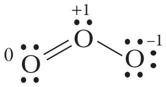


$$\text{Formal charge on } O_1 = 6-2-\frac{1}{2}(6) = +1$$

$$\text{Formal charge on } O_2 = 6-4-\frac{1}{2}(4) = 0$$

$$\text{Formal charge on } O_3 = 6-6-\frac{1}{2}\times 2 = -1$$

Hence, correct representation of O_3 is



(iii) Real formal charge helps in the selection of lowest energy structure from a number of possible structures for a given species. Formal charge do not indicate real charge separation within the molecule.

Hence, both Assertion and Reason are correct but Reason is not the correct explanations of Assertion.

(iv) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

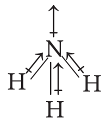
Due to presence of vacant *d*-orbital on S-atom it can expand its octet as in the case of H_2SO_4.

Or

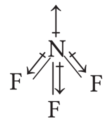
Sulphur has vacant *d*-orbital so it can expand its octet. In general, it forms many compounds which obey octet rule. Hence, Assertion is correct but Reason is incorrect.

64. (i) The lone pair of nitrogen opposed the dipole moment of NF_3 while it is added to the dipole moment of NH_3.

So, $\mu_{NH_3} > \mu_{NF_3}$



Dipole moment
⇒ 4.90 × 10^{-30} cm



Dipole moment
⇒ 0.80 × 10^{-30} cm

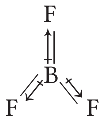
(ii) $$\text{Partial charge} = \frac{\text{Dipole moment}}{\text{Bond distance}} = \frac{1.2\times10^{-18}\text{ esu cm}}{1\times10^{-8}\text{ cm}} = 1.2\times10^{-10}\text{ esu}$$

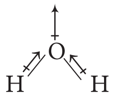
$$\text{Fractional charge} = \frac{1.2\times10^{-10}}{4.8\times10^{-10}} = 0.25$$

(4.8×10^{-10} is a theoretical value of μ)

(iii)

$BeF_2 : \mu = 0$ 

$BF_3 : \mu = 0$ 

$H_2O : \mu = 1.84$ D 

(iv) $\mathrm{O}\overset{\longleftarrow\!\!\!+}{=\!=}\mathrm{C}\overset{+\!\!\!\longrightarrow}{=\!=}\mathrm{O}$ is a linear molecule. It's dipole moment is zero and hence non-polar.

Or

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

65. (i) According to assumptions of MOT, the atomic orbitals which undergo LCAO must have the comparable energy because each specific orbital have its own specific energy depending upon various quantum number and their sum.

Thus, both Assertion and Reason are correct, Reason is not the correct explanation of Assertion.

(ii) The linear combination of atomic orbitals to form molecular orbitals takes place, if the combining atomic orbitals must have the same or nearly the same energy.

1*s*-orbital can not combine with another 2*s*-orbital but with 1*s*-orbitals because the energy of 2*s*-orbitals is appreciably higher than that of 1*s*-orbital. This is not true, if the atoms are very different.

Thus, Assertion is correct but Reason is incorrect.

(iii) Bond dissociation energy is the energy required to break one mole of bonds of a particular type. So as to separate them into gaseous atoms. Bond energy is the average value of dissocation energies of the same type of bond present in the molecule.

Bond energy of $\mathrm{C}\text{—}\mathrm{H}$ bond in methane is 99.2 kcal/mol.

Thus, for polyatomic molecules, average bond energy is taken as the dissociation bond energy.

Hence, both Assertion and Reason are correct and Reason is not he correct explanation of Assertion.

(iv) With increase in bond order, bond length decreases and hence bond energy increases.

So, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

Or

Both Assertion and Reason are correct but Reason is the correct explanation of Assertion.