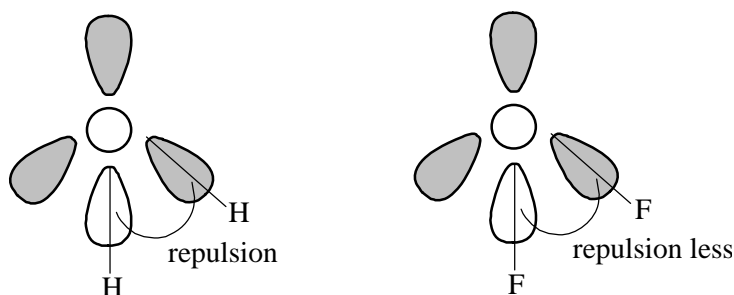


Solved Problems

SUBJECTIVE

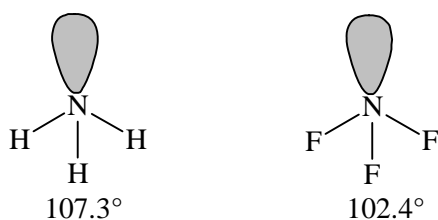
Problem 1: *The bond angle of H_2O is 104° while that of F_2O is 102° .*

Solution: Both H_2O and F_2O have a lone pair of electrons. But fluorine being highly electronegative, the bond pair electrons are drawn more towards F in F_2O . The bond pairs being displaced away from the central atom has very little tendency to open up the angle. But in H_2O , this opening up is more as bond pair electrons are closer to each other. So bond angle of F_2O is less than H_2O .

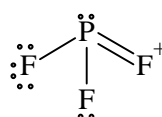


Problem 2: *Explain why bond angle of NH_3 is greater than NF_3 while bond angle of PH_3 is less than that of PF_3 .*

Solution: Both NH_3 and NF_3 are pyramidal in shape with one lone pair on N. However F has higher electronegativity than H, the electron pair is attracted more towards F in NF_3 i.e. the bond pairs of electrons are away from N or in other words distance between bond pairs ion is more. Hence repulsion between bond pairs in NF_3 is less than NH_3 . Hence the lone pair repels the bond pairs of NF_3 more than it does in NH_3 . As a result, the bond angle decreases to 102.4° . Whereas in NH_3 it decreases to 107.3° only.



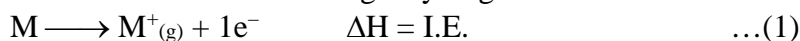
PH_3 and PF_3 are also pyramidal in shape with one lone pair on P. But PF_3 has greater bond angle than PH_3 (opposite to NH_3 and NF_3). This is due to resonance in PF_3 , leading to partial double bond character as shown below



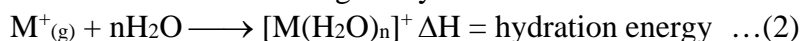
As result repulsions between P – F bonds are large and hence the bond angle is large. There is no possibility of formation of double bonds in PH_3 .

Problem 3: *Though Cs is most electropositive element in periodic table, Li has highest oxidation potential why?*

Solution: A metal ionizes in following way in gaseous state



But in water cation undergoes hydration



I.E. has positive value but hydration energy has –ve value. For Cs, I.E. is less than Li but for Li, hydration energy is more than Cs as Li^+ has higher charge density. The resultant of these two values is more –ve for Li rather than Cs. Therefore in aqueous solution Li ionizes more than Cs.

Problem 4: *A diatomic molecule has a dipole moment of 1.2D. If its bond distance is 1.0Å. What fraction of an electronic charge exist on each atom?*

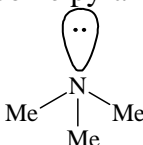
Solution: Dipole moment for a diatomic molecule (μ) = $e \times d$

$$\therefore \text{electronic charge} = \frac{\mu}{d} = \frac{1.2 \times 10^{-18} \text{ esu.cm}}{1.0 \times 10^{-8} \text{ cm}} = 1.2 \times 10^{-10} \text{ esu}$$

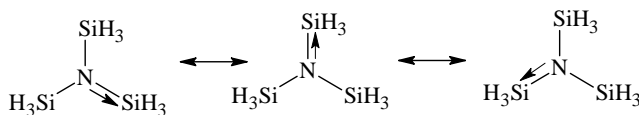
$$\therefore \text{fraction of electronic charge} = \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25$$

Problem 5: *In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $\text{N}(\text{SiH}_3)_3$, it has a planar geometry. What is the reason behind this ?*

Solution: In $\text{N}(\text{CH}_3)_3$, there is sp^3 hybridization at nitrogen but due to lone pair-bond pair repulsion, shape become pyramidal.

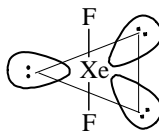


In trisilyl amine, there is vacant d-orbital at silicon, hence formation of $p\pi - p\pi$ back bonding takes place and geometry becomes planar.

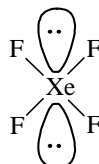


Problem 6: *Draw the molecular structures of XeF_2 and XeF_4 , indicating the location of lone pair(s) of electrons.*

Solution: Structure of XeF_2
Hybridization – sp^3d
Shape – linear



Structure of XeF_4
 Hybridization sp^3d^2
 Shape – square planar



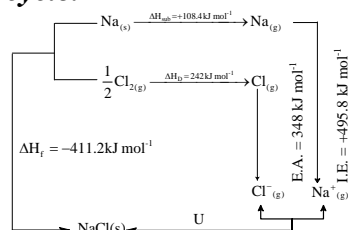
Problem 7: *Anhydrous AlCl_3 is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution [Ionisation energy for Al = $-5137 \text{ kJ mol}^{-1}$, $\Delta H_{\text{Hydration}}$ for $\text{Al}^{3+} = -4665 \text{ kJ mol}^{-1}$, $\Delta H_{\text{Hydration}}$ for $\text{Cl}^- = -381 \text{ kJ mol}^{-1}$]*

Solution: Total energy released during hydration of ions (Al^{3+} and 3 Cl^-) of $\text{AlCl}_3 = -4665 + (-3 \times 381) = -5808 \text{ kJ mole}^{-1}$. Since the energy released during hydration is more ($5808 \text{ kJ mole}^{-1}$) than the ionization energy for Al ($5137 \text{ kJ mole}^{-1}$), AlCl_3 would be ionic in aqueous solution.

Problem 8: *Dipole moment of HX is 2.59×10^{-30} coulomb-metre. Bond length of HX is 1.39 \AA . Calculate percentage ionic character of molecule.*

Solution: dipole moment = $q \times d$
 $\mu_{\text{cal}} = q \times 1.39 \times 10^{-10} \text{ coulomb - metre}$
 $\mu_{\text{cal}} = 1.6 \times 10^{-19} \times 1.39 \times 10^{-10}$
 % age ionic character = $\frac{\mu_{\text{exp}}}{\mu_{\text{cal}}} \times 100 = \frac{2.59 \times 10^{-30}}{1.6 \times 10^{-19} \times 1.36 \times 10^{-10}} \times 100 = 11.65\%$

Problem 9: *Calculate lattice energy of NaCl, from following data using Born-Haber's cycle.*



Solution: $\Delta H_f = \Delta H_{\text{sub}} + \frac{1}{2} \Delta H_D + \text{IE} + \text{EA} + U$ (using Hess' Law)
 $-411.2 = 108.5 + \frac{1}{2} \times 242 + 495.8 - 348 + U$
 $U = -788.4 \text{ kJ mol}^{-1}$

Problem 10: *Why is that Lithium salts have a greater degree of covalent character than other halides of the alkali metal.*

Solution: The small size of Li^+ gives it a large polarizing power, hence covalent nature of its compound increases. It can be viewed in terms of Fajan's rule, smaller the cation, larger the anion, greater the charge density at the surface causes greater polarizing power of Li^+ . Hence, greater the covalent nature.

SECTION – I

- Which of the following is required for the formation of an ionic bond?
 - An electron from the more electronegative element should be transferred to the less electronegative element.
 - The total energy of the resulting molecule should be less than the total energy of the reactants.
 - The lattice energy of the resultant molecule should be as low as possible.
 - The ionic potentials of the reactants should be identical.
 - Which of the following statements is incorrect ?
 - NH_3 is more basic than PH_3
 - NH_3 has a higher boiling point than that of HF
 - N_2 is less reactive than P_4
 - The dipole moment of NH_3 is less than that of SO_2 .
 - AlCl_3 is covalent while AlF_3 is ionic. This can be justified on the basis of
 - the valence-bond theory
 - Fajans' rules
 - the molecular-orbital theory
 - hydration energy
 - Which of the following pairs have nearly identical values of bond energy ?
 - O_2 and H_2
 - N_2 and CO
 - F_2 and I_2
 - O_2 and Cl_2
 - Which of the following is the most ionic ?
 - P_4O_{10}
 - MnO
 - CrO_3
 - Mn_2O_7
 - Among LiCl , BeCl_2 , BCl_3 and CCl_4 , the covalent bond character varies as
 - $\text{LiCl} < \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$
 - $\text{LiCl} > \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$
 - $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$
 - $\text{LiCl} > \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$
 - In a metallic crystal the
 - valence electrons remain within the fields of influence of their own kernels
 - valence electrons constitute a sea of mobile electrons
 - valence electrons are localized between the two kernels
 - kernels as well as the electrons move rapidly
-

-
8. Polarization involves the distortion of the shape of an anion by an adjacently placed cation. In this context, which of the following statements is correct ?
(a) Maximum polarization is brought about by a cation of high charge.
(b) Minimum polarization is brought about by a cation of low radius
(c) A large cation is likely to bring about a high degree of polarization
(d) The polarizing power of a cation is less than that of an anion.
9. Which of the following oxyacids of phosphorus are monoprotic (monobasic) ?
(a) H_3PO_4 (b) H_3PO_3
(c) H_3PO_2 (d) $\text{H}_4\text{P}_2\text{O}_7$
10. Which of the following has greater bond length ?
(a) P—O (b) S—O
(c) Cl—O (d) O=O
11. Which of the following has been arranged in order of increasing covalent character?
(a) $\text{KCl} < \text{CaCl}_2 < \text{AlCl}_3 < \text{SnCl}_4$ (b) $\text{SnCl}_4 < \text{AlCl}_3 < \text{CaCl}_2 < \text{KCl}$
(c) $\text{AlCl}_3 < \text{CaCl}_2 < \text{KCl} < \text{SnCl}_4$ (d) $\text{CaCl}_2 < \text{SnCl}_4 < \text{KCl} < \text{AlCl}_3$
12. Orthonitrophenol is steam volatile but paranitrophenol is not because
(a) orthonitrophenol has intramolecular hydrogen bonding while paranitrophenol has intermolecular hydrogen bonding.
(b) both ortho and paranitrophenol have intramolecular hydrogen bonding.
(c) orthonitrophenol has intermolecular hydrogen bonding and paranitrophenol has intramolecular hydrogen bonding.
(d) Van der Waals forces are dominant in orthonitrophenol.
13. During the formation of a molecular orbital from atomic orbitals, the electron density is
(a) minimum in the nodal plane (b) maximum in the nodal plane
(c) zero in the nodal plane (d) zero on the surface of the lobe
14. Which of the following have been arranged in increasing order of 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) $\text{O}_2^+ < \text{O}_2^{2-} < \text{O}_2^- < \text{O}_2$
15. How many sigma and pi bonds are present in tetracyanoethylene ?
(a) Nine σ and nine π (b) Five π and nine σ
(c) Nine σ and seven π (d) Eight σ and eight π
16. Which has maximum ionic mobility
(a) Li^+ (b) Na^+
(c) K^+ (d) Cs^+
17. In PO_4^{3-} , P—O bond order is
-

- (a) 1.25 (b) 2
(c) -0.75 (d) -3
18. Which of the following has least covalent P—H bond?
(a) PH₃ (b) P₂H₆
(c) P₂H₅ (d) PH₆⁺
19. Which of the following diatomic molecules would be stabilized by the removal of an electron?
(a) O₂ (b) CN
(c) N₂ (d) C₂
20. In which of the following species the bonds are non-directional?
(a) NCl₃ (b) RbCl
(c) BeCl₂ (d) BCl₃
21. Which contains both polar and non-polar bonds?
(a) NH₄Cl (b) HCN
(c) H₂O₂ (d) CH₄
22. The bond angle between two hybrid orbitals is 105°. The percentage s-character of hybrid orbital is between
(a) 50 – 55% (b) 9 – 12%
(c) 22 – 23 % (d) 11 – 12%
23. The first I.E. of lithium is 5.41 eV and first electron affinity of Cl is 3.61 eV. Calculate ΔH in kJ mol⁻¹ for the reaction:
$$\text{Li}_{(g)} + \text{Cl}_{(g)} \longrightarrow \text{Li}_{(g)}^{+} + \text{Cl}_{(g)}^{-}$$

(a) 133.6 kJ (b) 347.4 kJ
(c) 173.7 kJ (d) None of these
24. which type of bond is not present in HNO₂ molecule?
(a) Covalent (b) Co-ordinate
(c) Ionic (d) Ionic as well as co-ordinate
25. KF combines with HF to form KHF₂. The compound contains the species
(a) K⁺, F⁻ and H⁺ (b) K⁺, F⁻ and HF
(c) K⁺ and [HF₂]⁻ (d) [KHF]⁺ and F₂

SECTION – II

1. There is no S—S bond in:
(a) S₂O₄²⁻ (b) S₂O₅²⁻
(c) S₂O₃²⁻ (d) S₂O₇²⁻

-
2. Among KO_2 , AlO_2^- , BaO_2 and NO_2^+ , unpaired electron is present in
- (a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^-
(c) KO_2 only (d) BaO_2 only
3. Angle between two hybridized orbital is 105° and hence the percentage of s-character in the hybridized orbital would be in the range
- (a) 23–24% (b) 20–21%
(c) 19–20% (d) 21–22%
4. There are four species CO_2 , N_3^- , NO_2^+ and I_3^- . Which of the following statement is correct about these species?
- (a) All are linear and having sp hybridization of central atoms
(b) All are linear but only CO_2 and N_3^- and I_3^- have sp hybridization on their central atom.
(c) All are linear but only CO_2 , N_3^- and NO_2^+ have sp hybridization on their central atom.
(d) CO_2 , N_3^- , NO_2^+ are linear but I_3^- is not
5. If one assumes linear structure instead of bent structure for water, then which one of the following properties cannot be explained
- (a) The formation of intermolecular hydrogen bond in water.
(b) The high boiling point of water.
(c) Solubility of polar compounds in water.
(d) Ability of water to form co-ordinate covalent bond.
6. The shapes of PCl_4^+ , PCl_4^- and AsCl_5 are respectively
- (a) square planar, tetrahedral and see-saw.
(b) tetrahedral, see-saw and trigonal bipyramidal.
(c) tetrahedral, square planar and pentagonal bipyramidal.
(d) trigonal bipyramidal, tetrahedral and square pyramidal.
7. The I_3^- ion has
- (a) five equatorial lone pair on the central I atom and two axial bonding pairs in a trigonal bipyramidal arrangement.
(b) five equatorial lone pair on the central I atom and two axial bonding pairs in a pentagonal bipyramidal arrangement.
(c) three equatorial lone pair on the central I atom and two axial bonding pairs in a trigonal bipyramidal arrangement.
(d) two equatorial lone pairs on the central I atom and three axial bonding pairs in a trigonal bipyramidal arrangement.
8. Dipole moment of H_2O is 1.84 D. If the bond angle is 105° and O—H bond length is 0.94Å , what is magnitude of charge on the oxygen atom in water molecule.
- (a) 2×10^{-10} esu (b) 3.28×10^{-10} esu
(c) 3.22×10^{-10} esu (d) 1.602×10^{-19} coulomb
-

9. In the reaction $2\text{PCl}_5 \rightleftharpoons \text{PCl}_4^+ + \text{PCl}_6^-$, the change in hybridization 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^3 (d) sp^3d^2 to sp^3 and sp^3d
10. A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is 1.0\AA , what fraction of an electronic charge, e , exists on each atom?
 (a) 11% (b) 20%
 (c) 25% (d) none of these
11. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
 (a) A : tetrahedral, sp^3 ; B : tetrahedral, sp^3
 (b) N : pyramidal, sp^3 ; B : pyramidal, sp^3
 (c) N : pyramidal, sp^3 ; B : planar, sp^2
 (d) N : pyramidal, sp^3 ; B : tetrahedral, sp^3
12. Select correct orders for corresponding property as indicated in bracket for the following.
 (a) $\text{NH}_3 > \text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$ (Boiling point)
 (b) $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$ (Boiling point)
 (c) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$ (Basic character)
 (d) $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ (Acidic character)
13. Which one or more among the following involve(s) $\text{p}\pi - \text{d}\pi$ bonding?
 (a) $(\text{SiH}_3)_3\text{N:}$ (b) $(\text{CH}_3)_3\text{N:}$
 (c) $:\overset{\ominus}{\text{C}}\text{Cl}_3$ (d) $:\overset{\ominus}{\text{C}}\text{F}_3$
14. Choose the correct choice(s):
 (a) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is paramagnetic with a moment of about 6.0 B.M.
 (b) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is paramagnetic with a moment of about 4.0 B.M.
 (c) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is paramagnetic with a moment of about 1.7 B.M.
 (d) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is an octahedral complex formed by sp^3d^2 hybridisation.
15. Paramagnetic pair(s) among the following is (are):
 (a) $[\text{BaO}_2, \text{NO}_2]$ (b) $[\text{KO}_2, \text{NO}]$
 (c) $[\text{H}_2\text{O}_2, \text{NO}]$ (d) $[\text{K}_3(\text{CN})_6, \text{CuCl}_2]$
16. Which of the following have tetrahedral structure?
 (a) CrO_4^{2-} (b) $[\text{Ni}(\text{CN})_4]^{2-}$
 (c) $[\text{Ni}(\text{CO})_6]$ (d) $[\text{NiCl}_4]^{2-}$
17. Which of the following orders are correct for property indicated in brackets
 (a) $\text{NH}_3 > \text{NF}_3 > \text{BF}_3$ (dipole moment)
 (b) $\text{Cl} > \text{S} > \text{O} > \text{N}$ (electron affinity)
 (c) $\text{Si} > \text{Mg} > \text{Al} > \text{Na}$ (first ionization enthalpy)
 (d) $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$ (pK_a values)

18. Which among the following are diamagnetic?
 (a) $[\text{Fe}(\text{CN})_6]^{3-}$ (b) $[\text{Fe}(\text{CN})_6]^{4-}$
 (c) $[\text{Ni}(\text{CN})_4]^{2-}$ (d) $[\text{Ni}(\text{CO})_4]$
19. Which among the following are having sp^3d hybridization of the central atom.
 (a) XeF_4 (b) XeO_2F_2
 (c) ClO_3^- (d) BrF_3
20. Which of the following statements are correct:
 (a) The bond angle of NCl_3 is greater than that of NH_3 .
 (b) The bond angle in PH_3 is greater than that of PF_3 .
 (c) ClO_3^- and SO_3^{2-} are isostructural
 (d) It is not necessary that in TBP structure the lone pairs always would occupy the equatorial positions.
21. Bond angle in PH_3 is
 (a) much less than NH_3 (b) Much less than PF_3
 (c) slightly more than NH_3 (d) much more than PF_3
22. Which among the following are isostructural
 (a) CO_2 , I_3^- (b) XeO_2F_2 , SF_4
 (c) SO_3^{2-} , CO_3^{2-} (d) ClF_3 , XeF_2
23. Stability of ions of Ge, Sn and Pb will be in the order
 (a) $\text{Ge}^{2+} < \text{Sn}^{2+} < \text{Pb}^{2+}$ (b) $\text{Ge}^{4+} > \text{Sn}^{4+} > \text{Pb}^{4+}$
 (c) $\text{Sn}^{4+} > \text{Sn}^{2+}$ (d) $\text{Pb}^{2+} > \text{Pb}^{4+}$
24. Select the correct statements:
 (a) the heat of hydration of the dipositive alkaline earth metals ions decrease with an increase in their ionic size.
 (b) hydration of alkali metal ions is less than that of IIA
 (c) alkaline earth metal ions, because of their much larger charge to size ratio exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.
 (d) melting point of sodium halides follow order
 $\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}$
25. The first element of groups 13-16 differ from rest of the elements. This is due to
 (a) small size and high electronegativity
 (b) inability to expand to the octet
 (c) ability to form strong $p\pi - p\pi$ multiple bonds
 (d) Due to greater abundance

SECTION – III

Write-up I

The shape of a molecule is determined by electron-pair repulsions in the valence shell. A lone pair occupies larger space than a bond pair because it is not shared by two nuclei.

Thus the lone pair-lone pair repulsion is greater than the lone pair-bond pair repulsion, which in turn is greater than the bond pair-bond pair repulsion. The presence of lone pairs causes distortion of bond angles and hence a deviation from an ideal shape. The extent of distortion depends upon the orientation of the lone pairs around the central atom. In a trigonal bipyramid, the lone pairs occupy equatorial positions than the apical ones.

In AB_n type molecules, as the electronegativity of A increases, the bond pairs come closer and the repulsion between them increases. On the other hand, as electronegativity of B increases, the bond pairs get farther and repulsion decreases.

- Which of the following statements is true?
 - F-N-F angle in NF_3 is greater than H-N-H angle in NH_3
 - F-N-F angle in NF_3 is smaller than H-N-H angle in NH_3
 - H-O-H angle in H_2O is greater than H-N-H angle in NH_3
 - F-O-F angle in F_2O is greater than H-O-H angle in H_2O
- Bond angle in which of the following molecules is the largest?

(a) PF_3	(b) PCl_3
(c) PBr_3	(d) PI_3
- The shape of which of the following molecules will not be distorted?

(a) BrF_3	(b) CIF_3
(c) XeF_4	(d) XeF_6
- Which of the following species will have the lone pair effects cancelled?

(a) ICl_2^-	(b) ClF_3
(c) PCl_3	(d) BrF_5

Write-up II

The molecular orbital energy diagrams for homonuclear diatomic molecules are given below. For systems containing up to 14 electrons:

For systems containing more than 14 electrons:

Electrons taken from both the atoms are filled from lower to higher energy molecular orbitals (MO's) following Hund's rules.

The energy diagram of a heteronuclear diatomic molecule is similar. However, the energies of the atomic orbitals (AO's) of the atom having higher atomic number being lower, the diagram will be unsymmetrical, but that will not make a difference in the electron count.

Bond order is given by half the difference in the number of electrons of the bonding (σ and π) and anti-bonding (σ^* and π^*) molecular orbitals. For a bond to have been formed, the bond order should be greater than zero. The greater the bond order, the shorter is the bond distance and the greater is the bond dissociation energy. But if the bond order is the same in two cases, the bond distance will be greater and the bond dissociation energy smaller in the case which has more populated anti-bonding orbitals. The presence of unpaired electron(s) in a molecular orbital will make the system paramagnetic.

- Which of the following species is not expected to exist?

(a) He_2^+	(b) H_2^+
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-
- (c) Be_2 (d) Be_2^+
6. Which among the following will have a triple bond order?
(a) CO (b) CN^-
(c) NO^+ (d) All of these
7. Which of the following orders is correct in respect of bond dissociation energy?
(a) $\text{N}_2^+ > \text{N}_2^-$ (b) $\text{O}_2^+ > \text{O}_2^-$
(c) $\text{NO}^+ > \text{NO}$ (d) All of these
8. Which of the following species is expected to be paramagnetic?
(a) NO^- (b) O_2^-
(c) O_2^+ (d) All of these

✎ **Write-up III**

Hydrogen bond is a feeble bond formed between hydrogen atoms and highly electronegative elements. It is of two types – intermolecular, intramolecular. It is weaker than ionic, covalent and metallic bonds.

9. Number of hydrogen bonds in H_9O_4^+ species
(a) 2 (b) 3
(c) 4 (d) 1
10. Which is correct statement
(a) Para nitrophenol is steam volatile but not orthnitrophenol
(b) Ethyl alcohol is more viscous than glycerol
(c) if a dry paper is torn sound is heard is due to breaking of hydrogen bonds one after another in a rhythmic manner.
(d) In Fermic salt bonds present are covalent, metallic and hydrogen bond
11. Which is correct statement?
(a) Keto form of acetoacetic ester involves in hydrogen bonding
(b) In water vapour hydrogen bonding exists
(c) For first ionization maleic acid is stronger acid than fumaric acid. This can be explained on basis of concept of hydrogen bonding
(d) Boiling point of HCl is higher than that of HF
12. In a suitable solvent like benzene, benzoic acid associates and exists as
(a) dimer (b) trimer
(c) tetramer (d) hexamer

✎ **Write-up IV**

In the ionic bond, a cation tend to polarize the electron cloud of the anion by pulling electron density towards itself. This causes development of covalent character in ionic bond because the electron density gets localized in between the nuclei. The tendency of cation to bring about the polarization of anion is expressed as its polarizing power. The

ability of ion to undergo polarization is called its polarisability. The polarizing power of cation and polarisability of anion are decided on the basis of Fajan rules as given below:

- i) The smaller the cation, the higher is its polarizing power.
- ii) Cations with pseudo noble gas configuration ($ns^2np^6nd^{10}$) having relatively high polarizing power than those with noble gas configuration (ns^2np^6).
- iii) The larger the size of the anion, the higher is its polarisability.

13. Arrange the following species in increasing order of polarizing power?

Ag^+ , Tl^+ , Na^+

- | | |
|--------------------------|--------------------------|
| (a) $Tl^+ > Ag^+ > Na^+$ | (b) $Tl^+ > Na^+ > Ag^+$ |
| (c) $Ag^+ > Tl^+ > Na^+$ | (d) $Na^+ > Tl^+ > Ag^+$ |

14. Among the following $LiCl$, $BeCl_2$, BCl_3 , CCl_4 which will have the lowest melting point and the highest solubility

- | | |
|------------------------|------------------------|
| (a) CCl_4 , $LiCl$ | (b) $LiCl$, CCl_4 |
| (c) $BeCl_3$, BCl_3 | (d) BCl_3 , $BeCl_2$ |

15. The correct order of polarisability is

I^- , Br^- , Cl^- , F^-

- | | |
|-------------------------------|-------------------------------|
| (a) $I^- > Br^- > Cl^- > F^-$ | (b) $I^- > Br^- = Cl^- > F^-$ |
| (c) $I^- = Br^- = Cl^- > F^-$ | (d) $I^- = Br^- < Cl^- = F^-$ |

16. The ionic conductance of which of the following is the highest?

- | | |
|-----------------|-----------------|
| (a) Li^+ (aq) | (b) Na^+ (aq) |
| (c) K^+ (aq) | (d) Cs^+ (aq) |

Write-up V

To explain the nature of bonding beautifully in transition metal complexes, out of lot of theories, valence bond theory (VBT) has great importance which is based on the theory of covalent bonding. It deals with electronic structures of central metal ion in its ground state, kinds of geometry and magnetic properties of the complex.

According to VBT

- i) The central metal ion or atom makes available a number of s , p & d atomic orbitals equal to its co-ordination number. First of all, these atomic orbital hybridise together to form hybrid orbital which are same in number as the atomic orbital hybridizing together. These are vacant, equivalent in energy and have definite geometry.
- ii) The complexes having unpaired electron is known as para-magnetic complex & having no unpaired electron is known as diamagnetic complex.

$$\text{Magnetic moment due to spin only} = \mu_{\text{spin only}} = \sqrt{n(n+2)} \text{ B.M.}$$

Where, n = no. of unpaired electron.

- iii) Nature of ligands, also influences the nature of the complex compounds. Stronger ligands make pairing of electron against Hund's rule, and generally produces inner orbital complex are complexes in which ligands use the inner d -orbital of central metal ion.

Weaker ligands does not make pairing of electron and obey's Hund's rule and generally produces outer d-orbital complexes.

Keep in mind that the chelated complex is more stable than that of the non-chelated complex.

17. Which of the following is not the square planar complex?
 (a) $[\text{Ni}(\text{CN})_4]^{-2}$ (b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (c) $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (d) $[\text{Ni}(\text{CO})_4]$
18. In square planar complex, which of the following d-orbitals are used up?
 (a) $d_{x^2-y^2}$ (b) d_{z^2}
 (c) d_{xy} (d) d_{xy}
19. What is the magnetic moment (spin only) and hybridisation of the brown ring complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$?
 (a) $\sqrt{3}$ B.M., sp^3d^2 (b) $\sqrt{3}$ B.M., d^2sp^3
 (c) $\sqrt{15}$ B.M., sp^3d^2 (d) $\sqrt{15}$ B.M., d^2sp^3
20. Which of the following complex is more stable?
 (a) $[\text{Cr}(\text{en})_3]^{2+}$ (b) $[\text{Cr}(\text{CN})_6]^{3-}$
 (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (d) $[\text{Cr}(\text{EDTA})]^-$

SECTION – IV

1. Predict the shapes of the following molecules using the VSEPR model: BeCl_2 , SiCl_4 , AsF_5 , H_2S .
2. Explain why NH_3 is pyramidal whereas CH_4 is tetrahedral although both nitrogen and carbon in NH_3 and CH_4 are sp^3 hybridised?
3. Explain why BeH_2 molecule has a zero dipole moment although the Be – H bonds are polar.
4. The dipole moment of hydrogen halides decreases from HF to HI. Explain this trend.
5. O_2 molecule is paramagnetic. Why?
6. Sodium chloride solution gives a precipitate of AgCl with AgNO_3 whereas CCl_4 , does not, why ?
7. Why He_2 does not exist?
8. CO_2 and SO_2 both are triatomic molecules but there is big difference in their dipole moment, why ?
9. The molecule SO_2 has dipole moment. Is the molecule linear or bent? Give reason.
10. H_2S has more vapour pressure than H_2O under similar conditions. Why?

- The dipole moment of LiH is 1.965×10^{-29} Cm and the interatomic distance between Li and H in this molecule is 1.596Å. Calculate the percent ionic character in LiH.
- At room temperature NO₂ is paramagnetic in nature. When it is cooled below 0°C it acquires diamagnetic behaviour. Explain the reason for this observation.
- Write the electronic configuration and calculate the bond order of H₂⁺, H₂ and He₂. Bond length in H₂⁺ is longer than in H₂. Explain why ?
- o-nitrophenol is more volatile than p-nitrophenol, explain why?
 - Valency of oxygen is generally two whereas sulphur shows valency of two, four and six. Explain.
- Which of the following halides have different bond lengths between central atom and halogen and why?
BF₃, PCl₅, SF₆, CCl₄
- Arrange the following in order of increasing (a) dipole moment: H₂O, H₂S, BF₃; (b) covalent character: LiCl, LiBr, LiI; (c) melting point: NaCl, MgCl₂, AlCl₃.
- NH₄⁺ has bond angle identical to CH₄ but NH₃ has different bond angle; explain with proper reasoning.
- Explain the hybridization of carbon atoms in allene (C₃H₄) and show that the π-orbital overlaps.
- Boiling point of ethyl alcohol is much higher than that of diethyl ether. Why?
- Is there any change in the hybrid state of B and N atoms as a result of the following reaction?
$$\text{BF}_3 + \text{NH}_3 \longrightarrow \text{H}_3\text{N}^+ - \text{B}^-\text{F}_3$$

- Fill in the blanks:
 - The shape of CH₃⁺ is
 - The valence atomic orbitals on C in silver acetylide is hybridized.
- What type of hybrid orbital is used by the chlorine in ClO₂⁻ ?
 - The cyanide ion, CN⁻ and N₂ are isoelectronic. But in contrast to CN⁻, N₂ is chemically less reactive because of
 - The maximum possible number of hydrogen bonds a water molecule can form is
- Pick out the isoelectronic structure from the following:
CH₃⁺, H₃O⁺, NH₃, CH₃⁻
- Using the VSEPR theory, identify the type of hybridization and draw the structure of OF₂. What are the oxidation states of O and F?
- What are two types of bonds present in B₂H₆ ?

6. The experimentally determined N—F bond length in NF_3 is greater than the sum of the single covalent bond radii of N and F. Explain.
7. a) Among the following species identify the isostructural pairs:
 NF_3 , NO_3^- , BF_3 , H_3O^+ , NH_3
- b) What is the type and number of bonds between two carbon atoms in CaC_2 ?
- c) Arrange (A) toluene, (B) m-dichlorobenzene, (C) o-dichlorobenzene and (D) p-dichlorobenzene in order of increasing dipole moment.
- d) When N_2 goes to N_2^+ , the N—N bond distance and when O_2 goes to O_2^+ the O—O bond distance
8. What is the geometry and the type of hybrid orbital present about the central atom in BF_3 .
9. The central C—C bond in 1, 3-butadiene is shorter than that of n-butane. Explain.
10. Interpret the non-linear shape of H_2S molecule and non-linear shape of PCl_3 using VSEPR theory.

SECTION – V	
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1. Match List I (species) with List II (Hybridisation) and select the correct answer using the codes given below

List – I

- A. BCl_3
 B. NH_3
 C. PCl_5
 D. XeF_4

Codes

- | A | B | C | D |
|-------|---|---|---|
| (a) c | a | d | b |
| (c) a | c | d | b |
| (c) a | b | d | c |
| (d) c | a | b | d |

List – II

- a. sp^3
 b. $\text{sp}^3 \text{d}^2$
 c. sp^2
 d. $\text{sp}^3 \text{d}$

2.

List I

- i) Boiling water
 ii) Molten Iron
 iii) Sub-lime dry ice

Code

- | (i) | (ii) | (iii) |
|-------|------|-------|
| (a) z | x | y |
| (b) y | z | x |
| (c) x | y | z |
| (d) x | z | y |

List – II

- x) van der Waal's force of attraction
 y) Molecular bonding
 z) Binding energy

3.

	List - I		List - II
i)	C—H bond in Ethyne	(x)	sp-s overlap
ii)	P—Cl bond in POCl_3	(y)	$\text{sp}^3 \text{d}$ -p overlap
iii)	Br—Br bond in Br_3^-	(z)	sp^3 -p overlap

Code

- | (i) | (ii) | (iii) |
|-------|------|-------|
| (a) z | x | y |

- (b) y z x
 (c) x y z
 (d) x z y

4. $\text{Na}_2\text{C}_2\text{O}_4$ in basic solution, $\text{H}_2\text{C}_2\text{O}_4$ in acidic solution and K_2SO_4 solution is completely titrated separately with same stock solution of KMnO_4 . Then match the following:

List I (type of reductant)

- i) $\text{Na}_2\text{C}_2\text{O}_4$
 ii) $\text{H}_2\text{C}_2\text{O}_4$
 iii) KCl

List – II (Eq. wt. of KMnO_4)

- x) $M/5$
 y) M
 z) $M/3$
 w) cannot be calculated

Code

- | | (i) | (ii) | (iii) |
|-----|-----|------|-------|
| (a) | y | x | w |
| (b) | z | x | w |
| (c) | x | y | z |
| (d) | x | z | y |

5. **List – I (Type of solid)**

- (A) Covalent
 (B) Molecular
 (C) Ionic
 (D) Metallic

List – II (Examples)

- SiO_2
- CaO
- CCl_4
- Bronze

Codes

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

6. **List – I (Compound)**

- (A) $\text{H}_2\text{S}_2\text{O}_3$
 (B) H_2SO_5
 (C) $\text{H}_2\text{S}_2\text{O}_8$
 (D) $\text{H}_2\text{S}_2\text{O}_6$

List – II (No. of σ and π bonds)

- 6σ and 2π
- 11σ and 4π
- 9σ and 4π
- 7σ and 2π

Codes

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

7. **List – I (Molecule/ion)**

- (A) P_4
 (B) ICl_2^-
 (C) XeF_6
 (D) BF_4^-

List – II (Bond angle)

- 180°
- $109^\circ 28'$
- 60°
- 90°

Codes

- | (A) | (B) | (C) | (D) |
|-----|-----|-----|-----|
|-----|-----|-----|-----|

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

8 **List – I**

- A sp^2
 B sp^3
 C sp^3d
 D sp^3d^2

Code

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

List – II

- XeF₄
- BF₃
- Br₃⁻
- SO₄²⁻

9 **List – I (Compound)**

- (A) [Ni(NH₃)₆]²⁺
 (B) [PtCl₄]²⁻
 (C) [Ni(CO)₄]
 (D) [Co(ox)₃]³⁻

Codes

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

List – II (Hybridisation of central atom)

- sp^3
- sp^3d^2
- dsp^2
- d^2sp^3

10. **List – I**

- (A) H₂O < H₂S < H₂Se < H₂Te
 (B) H₂O > H₂S > H₂Se > H₂Te
 (C) H₂O >> H₂S < H₂Se < H₂Te

Codes

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

List – II

- Bond angle
- melting and boiling point
- acidic strength

True and False

11. Acidic strength order

- I. Cl₂O₇ > SO₂ > P₄O₁₀
 II. HClO > HBrO > HIO
 III. NH₃ > PH₃ > AsH₃ > BiH₃

- (a) I – T, II – T, III – F
 (c) I – F, II – T, III – F

- (b) I – T, II – F, III – F
 (d) I – T, II – F, III – T

12. I. XeO₃ is a trigonal pyramidal moleculeII. The lanthanoid ions other than the f^0 type and f^{14} type are all paramagnetic.

- III. In aqueous solution, acidity increases as $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
 IV. Grey hexagonal form of selenium is thermodynamically stable.
- (a) I – T, II – T, III – T, IV – T (b) I – T, II – T, III – T, IV – F
 (c) I – T, II – T, III – F, IV – T (d) I – T, II – F, III – T, IV – F
13. I. The oxidizing ability follow order $\text{ClO}_4^- > \text{BrO}_4^- > \text{IO}_4^-$
 II. The order of melting points of alkali metal halides follow order
 $\text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl} > \text{LiCl}$
 III. LiHCO_3 and $\text{Ca}(\text{HCO}_3)_2$ are not found in solid state.
 (a) I – T, II – F, III – F (b) I – T, II – T, III – T
 (c) I – T, II – F, III – T (d) I – F, II – T, III – T
14. Consider the following statements about diborane. Pick the correct one/s
 (a) There are total 12 electrons take part in bonding
 (b) It is highly toxic
 (c) Each B atom is sp^2 hybridised
 (d) All the atoms lie in the same plane
15. Peroxo bond ($-\text{O}-\text{O}-$) is present in
 (a) CrO_5 (b) SrO_2
 (c) PbO_2 (d) Na_2O_2
16. Which of the following statements are false?
 (a) Dipole-dipole interactions between molecules are greatest if the molecules possess only temporary dipole moments
 (b) All compounds containing hydrogen atoms can participate in hydrogen bonding.
 (c) Dispersion forces exist between all atoms, molecules and ions.
 (d) The extent of ion induced dipole interaction depends only on the charge of the ion.

The following questions (to) consists of two statements, one labelled as **ASSERTION (A)** and **REASON (R)**. Use the following key to chose the correct appropriate answer.

- (a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
 (b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
 (c) If (A) is correct, but (R) is incorrect.
 (d) If (A) is incorrect, but (R) is correct.

	ASSERTION (A)	REASONING (R)
17.	NCl_3 reacts with water but NF_3 is inert towards hydrolysis.	Nitrogen does not possess vacant d-orbitals
18.	Boiling point of $\text{SiH}_4 > \text{CH}_4$ whereas boiling point of $\text{SiCl}_4 < \text{CCl}_4$.	Chlorine posses vacant d-orbitals but hydrogen does not.
19.	Sulfur forms SF_6 and also SCl_6	Sulfur has vacant d-orbitals.
20.	Bond angles of NH_3 , PH_3 , AsH_3 and SbH_3 decreases in order of their mention.	The central atom in each possess a lone pair.
21.	SiF_6^{2-} anion exists but CF_6^{2-} does not.	Si atom has vacant d-orbital while

	C – atom has not
22. In case of $(\text{CH}_3)_3\text{N}$ geometry is pyramidal but in case of $(\text{SiH}_3)_3\text{N}$ it is planar.	The maximum covalency of Si is six but that of C is four.
23. MgCl_2 is more soluble as compare to BeCl_2	BeCl_2 is covalent and MgCl_2 is ionic compound
24. LiF is practically insoluble in water	LiF has very high lattice energy.
25. O_2 and N_2^{2-} have same number of electrons and same molecular orbital configuration.	O_2 and N_2^{2-} have the same bond order.

1. (b) 2. (b) 3. (b) 4. (d)
 5. (b) 6. (c) 7. (b) 8. (a)
 9. (c) 10. (a) 11. (a) 12. (a)
 13. (c) 14. (b) 15. (a) 16. (d)
 17. (a) 18. (d) 19. (a) 20. (b)
 21. (c) 22. (c) 23. (c) 24. (d)
 25. (c)

1. (d) 2. (a) 3. (a) 4. (c)
 5. (c) 6. (b) 7. (c) 8. (c)
 9. (a) 10. (c) 11. (a) 12. (b), (c), (d)
 13. (a), (c) 14. (b), (d) 15. (b), (d) 16. (a), (c), (d)
 17. (a), (b), (c) 18. (b), (c), (d) 19. (b), (d) 20. (a), (c)
 21. (a), (b) 22. (a), (b) 23. (a), (c), (d) 24. (a), (b), (c), (d)
 25. (a), (b), (c)

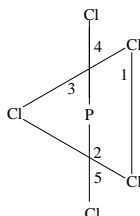
1. (b) 2. (d) 3. (c) 4. (a)
 5. (c) 6. (d) 7. (d) 8. (d)

3. The number of electrons, their configurations, etc., for the given species are :

Species	No. of electrons	Configuration	N_b	N_a	Bond order $= \frac{1}{2}[N_b - N_a]$
H_2^+	1	$(\sigma 1s)^1$	1	0	$\frac{1}{2}$
H_2	2	$(\sigma 1s)^2$	2	0	1
He_2	4	$(\sigma 1s)^2 (\sigma^* 1s)^2$	2	2	0

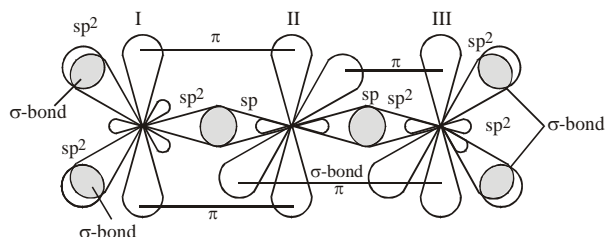
The bond length in H_2^+ is longer than in H_2 because in H_2^+ only one electron is present to shield the two nuclei from mutual repulsion. In H_2 there are two electrons to hold the two nuclei thus nuclear repulsion is less than that in H_2^+ . Hence, nuclear separation in H_2^+ is more than in H_2 .

4. a) Due to intramolecular H-bonding in o-nitrophenol it is more volatile.
 b) There are no d-orbitals in oxygen hence it cannot extend its covalency. Vacant d-orbitals are present in sulphur and paired orbitals can be made unpaired by shifting electrons to d-orbitals, i.e., either making four orbitals singly occupied or six orbitals singly occupied showing valency 4 or 6 besides 2.
5. PCl_5 has two types of bonds: axial and equatorial. These two types of bonds have different bond lengths.
 1, 2, 3-equatorial bonds
 4, 5-axial bonds.



6. a) BF_3 is a symmetrical molecule. It has zero dipole moment. Oxygen being more electronegative than S, bond moment of O – H is more than S – H. So, the dipole moments are in the order of
 $BF_3 < H_2S < H_2O$
- b) The anion size in increasing order is
 $Cl^- < Br^- < I^-$
 Hence, LiCl is least covalent and LiI most. The order is
 $LiCl < LiBr < LiI$
- c) Cation charge increases in the order
 $Na^+ < Mg^{2+} < Al^{3+}$
 Thus, Al^{3+} ion has maximum polarization effect and Na^+ ion has least. Thus, the decreasing order of melting point is
 $NaCl < MgCl_2 < AlCl_3$

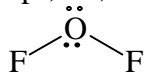
7. In NH_4^+ there are four bond pairs and no lone pair like CH_4 . However, NH_3 has only three bond pairs and one lone pair, hence, its bond angle is less due to lone pair-bond pair repulsion.
8. Allene is $\text{CH}_2 = \overset{\text{I}}{\text{C}} = \overset{\text{II}}{\text{C}} = \overset{\text{III}}{\text{C}}\text{H}_2$. Carbon atoms I and III are in sp^2 hybridized state while carbon II is in sp hybridized state. Two unhybridised orbitals of carbon II overlap sidewise with unhybridised orbital of each of carbon I and carbon III to form π -bonds besides it also forms a sigma bond with each of the carbon atoms using hybridized orbitals. Two hybridized orbitals of each of carbon I and III form sigma bonds with hydrogen atoms.



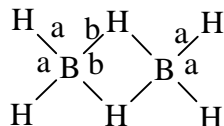
9. Due to hydrogen bonding.
10. During the combination of NH_3 and BF_3 . N atom is donor and B atom of BF_3 is acceptor. The hybrid state of N in NH_3 is sp^3 whereas that of B in BF_3 is sp^2 . In the compound $\text{H}_3\text{N}^+ - \text{B}^-\text{F}_3$, both B and N atoms are surrounded by 4 bond pairs. The hybrid state of N remains as sp^3 but that of B atom changes from sp^2 to sp^3 .

- Planar-triangular
 - sp
- sp^3
 - Absence of bond polarity
 - 4
- H_3O^+ , NH_3 , CH_3^-

4. sp^2 , +2, -1



- Which are formed by two e^-
 - Which are formed by one e^-



- N and F both have high e^- density due to smaller atomic radii thus lp-lp repulsion increases bond length.
- $(\text{NF}_3, \text{H}_3\text{O}^+)$, $(\text{NO}_3^-, \text{BF}_3)$ pair isostructural.
 - 1 sigma and 2 pi bond

-
- c) $D < A < B < C$
d) increases, decreases
8. Trigonal planar, sp^2
9. Due to resonance in conjugate diene.

-
- | | | | | | | | |
|-----|-----|-----|--------|-----|-----------|-----|-----------|
| 1. | (a) | 2. | (c) | 3. | (d) | 4. | (a) |
| 5. | (a) | 6. | (c) | 7. | (b) | 8. | (c) |
| 9. | (b) | 10. | (c) | 11. | (a) | 12. | (c) |
| 13. | (d) | 14. | (a, b) | 15. | (a, b, d) | 16. | (a, b, d) |
| 17. | (b) | 18. | (b) | 19. | (b) | 20. | (b) |
| 21. | (a) | 22. | (b) | 23. | (a) | 24. | (a) |
| 25. | (d) | | | | | | |
-