5 Periodic Properties, Chemical Bonding and Complexes

• NUMERICAL PROBLEMS •

1. Specific heats of Li(s), Na(s), K(s), Rb(s) and Cs(s) at 398 K are 3.57, 1.23, 0.756, 0.363 and 0.242 $J\,g^{-1}K^{-1}$ respectively. Compute the molar heat capacities of these elements and identify any periodic trend. If there is trend, use it to predict molar heat capacity of Fr.
2. Calculate the energy required tc convert 5 mole of sodium atom in the gaseous state to form sodium ion. Ionisation enthalpy of Na = 5.1 eV / atom.
3. Calculate the energy required to convert 7.974 g of cesium atom in the gaseous state to form Cs^+ ions. Ionisation enthalpy of Cs = 374 kJ mol^{-1} and atomic mass of Cs is 132.9 amu.
4. Calculate the effective nuclear charge at the periphery of nitrogen atom when an extra electron is added in the formation of anion. Also calculate the effective nuclear charge of N-atom and O-atom.
5. Shielding constant for Ne is 4.15. Calculate the effective nuclear charge on Na^+ and F^- using only this value.
6. The ionization energy of Li is 5.39 eV. If ionization energy of H is 13.6 eV, then calculate the effective charge acting upon outermost electron of Li.
7. How much energy is given out when 1.0 g of chlorine atoms are converted into $Cl^-(g)$? Electron affinity of Cl = – 349 kJ /mol and atomic mass of Cl is 35.5 amu.
8. For the gaseous phase reaction,
$$K + F \longrightarrow K^+ + F^-,$$
ΔH was calculated under conditions where the cations and anions by electrostatic separation from combining with each other. The ionisation energy of K is 4.3 eV. What is electron affinity of fluorine?
9. The first IP of lithium is 5.41 eV and electron affinity of Cl is –3.61 eV. Calculate ΔH in kJ mol^{-1} for the reaction:
$$Li(g) + Cl(g) \longrightarrow Li^+(g) + Cl^-(g)$$
10. You are given Avogadro's no. of 'X' atoms. If half of the atoms of X transfer one electron to the other half of 'X' atoms, 409 kJ must be added. If these X^- ions are subsequently converted to X^+, an additional 733 kJ must be added. Calculate IP and EA of X in eV. Use ($1\,eV = 1.602 \times 10^{-19}$ J and $N = 6.023 \times 10^{23}$).
11. Helium can be excited to the $1s^1 2p^1$ configuration by light of 58.44 nm. The lowest excited singlet state, with the configuration $1s^1, 2s^1$ lies 4857 cm^{-1} below the $1s^1 2p^1$ state. What would the average He—H bond energy have to be in order that HeH_2 could form non-endothermically from He and H_2? Assume that the compound would form from the lowest excited singlet state of helium. Neglect any differences between ΔE and ΔH. Take $\Delta H_f\,(H) = 218.0$ kJ / mol.
12. 1 g of Mg atoms in the vapour phase absorbs 50.0 kJ of energy. Find the composition of Mg^+ and Mg^{2+} formed as a result of absorption of energy. IE_1 and IE_2 for Mg are 740 and 1450 kJ mol^{-1} respectively.
13. 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 $AlCl_3$ = 5137 kJ mol^{-1}; $\Delta_{Hydration}$ for Al^{3+} = – 4665 kJ mol^{-1}; $\Delta_{Hydration}$ for Cl^- = – 381 kJ mol^{-1}). **(IIT July 1997)**

14. A mixture contains atoms of fluorine and chlorine. The removal of an electron from each atom of sample absorbs 284 kJ while the addition of an electron to each atom of mixture releases 68.8 kJ. Determine the percentage composition of mixture. Given IE_1 for F and Cl are 27.91×10^{-22} and 20.77×10^{-22} kJ / atom respectively and EA_1 for F and Cl are -5.53×10^{-22} and -5.78×10^{-22} kJ / atom respectively.

15. The first ionisation energy of H and He are 13.6 eV and 24.6 eV respectively. How much energy would be given out during the formation of ground state of He atom from He^{2+} nucleus if it combines with two electrons?

16. The ionisation energy of lithium is 5.40 eV. If ionisation energy of H is 13.6 eV, then calculate the effective charge acting upon outermost electron of Li.

17. Calculate the electronegativity of fluorine from the following data:

$$E_{H-H} = 104.2 \text{ kcal mol}^{-1}$$
$$E_{F-F} = 36.6 \text{ kcal mol}^{-1}$$
$$E_{H-F} = 134.6 \text{ kcal mol}^{-1}$$ **(UPSEAT 1996)**

18. Ionisation potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. Calculate electronegativity of fluorine.

19. Calculate the electronegativity X of silicon using Allred-Rochow equation : $X = \frac{0.359Z'}{r^2\ (Å)} + 0.744$ where Z' is $Z_{effective}$ calculated on the basis of Slater's rule taking all the electrons. Covalent radius of Si = 1.175 Å.

20. The boiling point of krypton (Kr) and radon (Rn) are $-152°C$ and $-62°C$ respectively. Calculate the approximate boiling point of xenon.

21. Calculate the % ionic character in HCl molecule. Given bond length of HCl is 1.275 Å and $\mu_{HCl} = 1.03$ debye.

22. The dipole moment of LiH is 1.964×10^{-29} cm and the intermolecular distance between Li and H in this molecule is 1.596 Å. What is per cent ionic character in molecule?

23. The dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus. Calculate percentage ionic character of KCl. **(IIT 1993)**

24. A diatomic molecule has a dipole moment equal to 1.2 D. If bond length is 1.0 Å, what fraction of electronic charge 'e' exists on each atom?

25. The experimental dipole moment of water molecule is 1.84 D. Calculate the bond angle H—O—H in water molecule, if dipole moment of OH bond is 1.5 D.

26. The H—O—H bond angle in the water molecule is 105°, the H—O bond distance being 0.94 Å. The dipole moment for the molecule is 1.85 D. Calculate the charge on the oxygen atom.

27. Assuming that all the four valency of carbon atom in propane pointing towards the corners of a regular tetrahedron, calculate the distance between the terminal carbon atoms in propane. Given, C—C single bond length is 1.54 Å.

28. In BI_3 molecule, distance between two I atoms is found to be 3.54 Å. Also BI_3 has sp^2-hybridised boron atom. If radius of covalently bonded I atom is 1.33, what will be covalent radius of boron?

29. Calculate the molar mass of HF if density of HF gas is 3.17 g / L at 300 K and 1.0 atm. Comment on the result.

30. Atomic radius of $F_{(g)}$ and $F^-_{(g)}$ are 72 and 136 pm respectively. Calculate the ratio and percentage increase in terms of volume during the formation of $F^-_{(g)}$ from $F_{(g)}$.

31. The multiple double bond radii of C is 0.67 Å. Calculate the multiple double bond radii of O if oxygen to oxygen bond length in CO_2 is 2.323 Å.

32. The atomic radius of Li and Li^+ are 1.23 Å and 0.76 Å respectively. Assuming that the difference in ionic radii relates to the space occupied by 2s-electron, calculate the % volume of Li-atom occupied by single valence electron.

33. In solid ammonia, each NH_3 molecule has six other NH_3 molecules as nearest neighbours. ΔH of sublimation of NH_3 at the melting point is 30.8 kJ/mol and the estimated ΔH of sublimation in the absence of hydrogen bonding is 14.4 kJ / mol. What is the strength of hydrogen bond in solid ammonia?

34. Assuming covalent radii to be additive property; calculate the iodine-iodine distances in o^-, m^-, p-di-iodobenzene. The benzene ring is regular hexagon and each C—I bond lies on a line passing through the centre of hexagon. The C—C bond length in C_6H_6 are 1.40 Å and covalent radius of iodine and carbon atom are 1.33 Å and 0.77 Å. Also neglect different overlapping effect.

35. Calculate the I—I distance in the given compound $H_2C = CI_2$ if C—I bond length is 2.10 Å.

36. What type of hybridisation are expected on central atom of each of the following molecule:

(a) BeH_2 (b) CH_2Br_2 (c) PF_6^- (d) BF_3 (e) CH_2^{2+} (f) CH_3^+ (g) CH_3^- (h) SF_6 (i) ICl_3 (j) AlH_3 (k) NH_3 (l) SbF_6^- (m) BH_4^- (n) ClO_4^- (o) I_3^- (p) ClO_3^- (q) ClO_3^+.

37. Point out the nature of hybridisation on underlined atoms:
(a) $F_2\underline{C}=\underline{C}=\underline{C}F_2$ (b) $F_2\underline{B}-\underline{C}\equiv\underline{C}-\underline{B}F_2$
(c) $\underline{C}(\underline{C}N)_4$

38. Draw the molecular structures of XeF_2, XeF_4 and XeO_2F_2 indicating the location of lone pair(s) of electrons.

39. Using VSEPR theory, identify the type of hybridisation and draw the structure of OF_2. What are oxidation states of O and F? **(IIT 1994)**

40. Write the MO configuration of O_2. Specify its bond order and magnetic properties. **(IIT 2000)**

41. Predict the type of hybridisation of each carbon atom in the following:
(a) CH_3CN,
(b) $CH_3CH=CH_2$,
(c) $H_3C-C\equiv C-CH_3$,
(d) $HC\equiv C-CH=CH_2$ **(IIT 1998)**

42. Draw the geometry of OSF_4 using VSEPR theory. **(IIT 2004)**

43. Arrange the following compounds/species in the order of O—O bond lengths. O_2, O_2 [AsF_4], [KO_2] **(IIT 2004)**

44. A solution containing 2.665 g of $CrCl_3\cdot 6H_2O$ is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 2.87 g of AgCl. Deduce the structure of compound.

45. 1 g of the complex $[Cr(H_2O)_5Cl]Cl_2\cdot H_2O$ was passed through a cation exchanger to produce HCl. The acid liberated was diluted to 1 litre. What is normality of this acid solution?

46. A solution containing 0.319 g of complex $CrCl_3\cdot 6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 mL of 0.125 M NaOH. What is the correct formula of complex?

47. Metal carbonyls having formula $M(CO)_x$, where x is the number of carbonyl units co-ordinated to metal M are formed by Fe, Cr and Ni. If effective atomic number of each metal is 36, what are the formula of metal carbonyls?

48. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (*A*) and (*B*). The form (*A*) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (*B*) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formulae of (*A*) and (*B*) and state the hybridisation of chromium in each. Calculate their magnetic moments (Spin-only value). **(IIT 2009)**

49. Predict the number of water molecules (s) directly bonded to metal centre in $CuSO_4\cdot 5H_2O$.

50. What is the co-ordination number of Al in the crystalline state of $AlCl_3$? **(IIT 2009)**

51. What type of hybridisation exists in BeF_2 in solid state?

52. Nitrogen forms oxides as N_2O, NO, NO_2, N_2O_3, N_2O_4 and N_2O_5. Which oxides contain N–N bonds? **(IIT 2009)**

SOLUTIONS (Numerical Problems)

1. Molar heat capacity = Atomic mass × specific heat
($J\,mol^{-1}\,K^{-1}$) ($J g^{-1}\,K^{-1}$)

Li(*s*) = $6.94 \times 3.57 = 24.78$
Na(*s*) = $22.99 \times 1.23 = 28.28$
K(*s*) = $39.10 \times 0.756 = 29.56$
Rb(*s*) = $85.47 \times 0.363 = 31.03$
Cs(*s*) = $132.91 \times 0.242 = 32.16$

There is a trend on plotting these values with atomic number, the extra polation of graph gives the value of $Fr(s) = 33.5\,JK^{-1}\,mol^{-1}$.

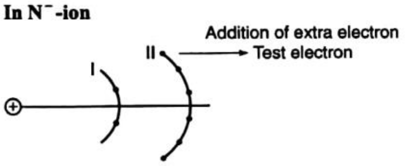
2. *IE* of Na $= 5.1\,eV/atom = 5.1 \times 6.023 \times 10^{23}\,eV/mol$
$= 5.1 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\,J/mol$
$= 492.091 \times 10^{3}\,J/mol$

∴ Energy required to convert 5 mole Na(*s*) to Na^+
$= 5 \times 492.091 \times 10^{3}\,J = \mathbf{2.46 \times 10^{6}\,J}$

3. Mole of Cs atom $= \frac{7.974}{132.9} = 0.06$

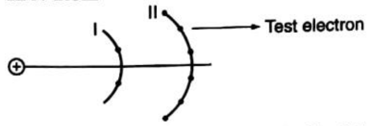
∴ Energy required for 7.974 g Cs atom to form $Cs^+(g)$
$= 374 \times 0.06 = \mathbf{22.44\,kJ}$

4. In N^--ion



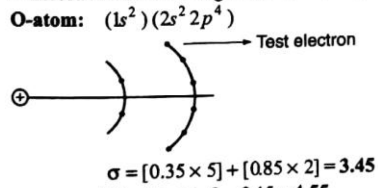
$\sigma = [(0.35 \times$ no. of electron in *n*th shell excluding valence electron) + ($0.85\times$ no. of electrons in $(n-1)$th shell) + ($1.0 \times$ no. of electrons in inner shells)]
$\sigma = [0.35 \times 5] + [0.85 \times 2] = \mathbf{3.45}$
Effective nuclear charge $Z^* = Z - \sigma = 7 - 3.45 = \mathbf{3.55}$

In N-atom



$\sigma = [0.35 \times 4] + [0.85 \times 2] = \mathbf{3.1}$
∴ Effective nuclear charge $= Z - \sigma = 7 - 3.1 = \mathbf{3.9}$

O-atom: $(1s^2)(2s^2 2p^4)$



$\sigma = [0.35 \times 5] + [0.85 \times 2] = \mathbf{3.45}$
∴ $Z^* = Z - \sigma = 8 - 3.45 = \mathbf{4.55}$

5. $_{10}Ne : (1s^2)(2s^2 2p^6)$
$_{11}Na^+ : (1s^2)(2s^2 2p^6)$
$_{9}F^- : (1s^2)(2s^2 2p^6)$

Thus, shielding constant σ is same for all these, *i.e.*, 4.15.
$Z^{*}_{Ne} = Z_{Ne} - \sigma = 10 - 4.15 = \mathbf{5.85}$
$Z^{*}_{Na^+} = Z_{Na^+} - \sigma = 11 - 4.15 = \mathbf{6.85}$
$Z^{*}_{F^-} = Z_{F^-} - \sigma = 9 - 4.15 = \mathbf{4.85}$

6. For Li, electronic configuration is $1s^2, 2s^1$, so given ionization energy value is for ($n = 2$).

We know that: $E_n \frac{Z^2_{eff}}{n^2} \times E_1$

E_n = Energy of *n*th level, Z_{eff} = Effective nuclear charge, E_1 = Energy of first orbit of H-atom.

or $Z_{eff} = n \cdot \sqrt{\frac{E_n}{E_1}}$

Given $E_1 = -13.6\,eV$; $E_n = -5.39\,eV$ and $n = 2$
$Z = 2 \times \sqrt{\frac{5.39}{13.6}} = \mathbf{1.26}$

Thus, effective nuclear charge is 1.26 because 2*s*-electron is shielded by $1s^2$-electrons.
Also from Slater's rule $\sigma_{Li} = 0.85 \times 2 = 1.70$
$Z^{*}_{Li} = 3 - 1.70 = 1.30$

7. Mole of Cl atom $= \frac{1}{35.5}$

Thus energy released during
$Cl + e \longrightarrow Cl^-(g) = \frac{1}{35.5} \times 349 = \mathbf{9.83\,kJ}$

8. $\Delta H = 19 \times 10^{3}\,cal/mol$
$= 19 \times 10^{3} \times 4.18\,J/mol = \frac{19 \times 4.18 \times 10^{3}}{1.602 \times 10^{-19}}\,eV/mol$
$= \frac{19 \times 10^{3} \times 4.18}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}\,eV/atom$
$= 0.82\,eV/atom$

Also, $\Delta H = IE_1 + EA_1$
$0.82 = 4.3 + EA_1$
∴ $EA_1 = \mathbf{3.48\,eV / atom}$

9. ΔH/molecule of Li^+ and Cl^- $= IP_{1\,Li} + EA_{Cl}$
$= 5.41 - 3.61 = 1.80\,eV$

∵ $Li \longrightarrow Li^+ + e$ $IP_1 = +ve$
and $Cl + e \longrightarrow Cl^-$ $EA = -ve$

∴ $\Delta H / mol = 1.8 \times 6.023 \times 10^{23}\,eV$
$= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\,J$
$= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \times 10^{-3}\,kJ$
$= \mathbf{173.7\,kJ}$

10. $X \longrightarrow X^+ + e; \quad \Delta H = IP_1 = a\,\text{eV}$

$X + e \longrightarrow X^-; \quad \Delta H = -EA_1 = -b\,\text{eV}$

if $N/2$ atoms of X lose electrons which are taken up by remaining $N/2$ of X to give X^-, then

$$a \times \frac{N}{2} - b \times \frac{N}{2} = \frac{409 \times 10^3}{1.602 \times 10^{-19}}\,\text{eV}$$

or $$a - b = \frac{409 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$\therefore \quad a - b = 8.477$

Now, $N/2$ of X^- lose two electrons to give X^+

$X^- \longrightarrow X + e; \quad \Delta H = +EA_1 = +b$

$X \longrightarrow X^+ + e; \quad \Delta H = +IP_1 = +a$

$$\therefore \quad a \times \frac{N}{2} + b \times \frac{N}{2} = \frac{733 \times 10^3}{1.602 \times 10^{-19}}\,\text{eV}$$

or $$a + b = \frac{733 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$a + b = 15.194$

$\therefore \quad$ **$a = 11.835$ eV**

and **$b = 3.358$ eV**

11. Formation of HeH_2 requires energy equal to sum of (i) energy for excitation from $1s^2$ to $1s^1 2s^1$ to form He singlet is equal to : [Energy needed for excitation from $1s^2$ to $1s^2 2p^1$–energy level difference in between $1s^1 2s^1$ and $1s^1 2p^1$]

Thus, E_{He} single $t = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = 3.40 \times 10^{-18} - 9.66 \times 10^{-20}$ J

$= 3.30 \times 10^{-18}$ J / molecule

where $\lambda_1 = 58.44 \times 10^{-9}$ m and $\frac{1}{\lambda_2} = 4857\,\text{cm}^{-1}$

(ii) energy to produce two mole of H, *i.e.*, $2 \times 218.0 = 436$ kJ/ mol

Thus, E for 2 mole bonds of He—H

$= [3.30 \times 10^{-18} \times 6.023 \times 10^{23} + 436 \times 10^3]$ J/ mol

$= 2423.5\,\text{kJ mol}^{-1}$

$\therefore E_{He—H}$ **$= 1211.8\,\text{kJ mol}^{-1}$**

12. Mole of Mg $= \frac{1}{24}$

These mole of Mg will be converted to Mg^+ and Mg^{2+}. Let a mole of Mg^+ are formed, then

$$a \times 740 + \left(\frac{1}{24} - a\right) \times 2190 = 50$$

$\therefore \quad a = 0.02845$

$\therefore \quad$ % of $Mg^+ = \frac{0.02845}{1/24} \times 100 =$ **68.28**

% of Mg^{2+} = **31.72**

13. $AlCl_3 + aq. \longrightarrow AlCl_3\,(aq.); \quad \Delta H = ?$

ΔH = Energy released during hydration + Energy used during ionisation

$= -4665 - 3 \times 381 + 5137 = -671$

Thus, formation of ions will take place because $\Delta H_h > \Delta H_{ionisation}$.

14. Let the mixture contains a, b atoms of F and Cl respectively. Thus, total energy absorbed is:

$$284 = a \times 27.91 \times 10^{-22} + b \times 20.77 \times 10^{-22} \quad ...(1)$$

Also total energy released is:

$$-68.8 = a \times (-5.53 \times 10^{-22}) + b \times (-5.78 \times 10^{-22})$$

or $$68.8 = 5.53 \times 10^{-22} \times a + 5.78 \times 10^{-22} \times b \quad ...(2)$$

By Eqs. (1) and (2),

$\therefore \quad a = 4.57 \times 10^{22}$

$b = 7.53 \times 10^{22}$

$\therefore \quad$ % of F $= \left[\frac{4.57 \times 10^{22}}{4.57 \times 10^{22} + 7.53 \times 10^{22}}\right] \times 100 =$ **37.76**

% of Cl = **62.24**

15. Given $H \longrightarrow H^+ + e; \quad IE_1 = 13.6$ eV

$He \longrightarrow He^+ + e; \quad IE_1 = 24.6$ eV

We have to determine the values of

$He^{2+} + e \longrightarrow He^+; \quad \Delta H = a$

$He^+ + e \longrightarrow He; \quad \Delta H = b$

$He^{2+} + 2e \longrightarrow He; \quad \Delta H = (a + b)$

The IE_1 of $He^+ = IE_{1H} \times 2^2 = 13.6 \times 4 = 54.4$ eV

$\therefore \quad a = -54.4$ eV

Also for $He^+ + e \longrightarrow He; \quad IE_1 = 24.6$ eV

$\therefore \quad b = -24.6$ eV

Thus, Total energy given out $= a + b = -54.4 + (-24.6)$

$= -79$ eV

16. Li : $1s^2, 2s^1 \therefore n = 2$

Also $E_{Li} = \frac{Z^2}{n^2} \times E_H$

where Z is effective charge

$\therefore \quad Z = n\sqrt{\frac{E_{Li}}{E_H}} = 2 \times \sqrt{\frac{5.40}{13.6}} =$ **1.26**

Thus effective charge is 1.26 because $2s$ electron is shielded by $1s^2$ electrons.

17. Let X_H and X_F be the electronegativity of H and F, then

$X_H \sim X_F = 0.208\,[E_{H—F} - (E_{H—H} \times E_{F—F})^{1/2}]^{1/2}$

$X_H \sim X_F = 0.208\,[134.6 - (104.2 \times 36.6)^{1/2}]^{1/2}$

$X_H \sim X_F = 1.78$ and $X_H < X_F$

Since, $X_H = 2.1$ (although this value is not given in problem)

$X_F = 2.1 + 1.78 =$ **3.88**

18. The various equations to calculate electronegativity (X) are as:

$$\text{Mulliken scale } X_M = \frac{IE+EA}{2} \quad ...(1)$$

where IE and EA are in eV

Pauling values are $\frac{1}{2.8}$ times lesser than Mulliken value

$$X_P = 0.336[X_M - 0.615] \quad ...(2)$$

$$\text{By eq. (1)} \therefore \quad X_P = \frac{IE+EA}{2\times 2.8} = \frac{IE+EA}{5.6} \quad ...(3)$$

Also if IE and EA are in kJ mol^{-1} then by Eq. (1)

$$X_M = \frac{IE+EA}{2\times 96.48} = \frac{IE+EA}{192.96} \quad ...(4)$$

$$\text{and} \quad X_P = \frac{IE+EA}{2\times 2.8\times 96.48} = \frac{IE+EA}{540.28} \quad ...(5)$$

Thus, electronegativity of F on Pauling scale

$$= \frac{17.42+3.45}{5.6} = \mathbf{3.73}$$

Electronegativity of F on Mulliken scale

$$= \frac{17.42+3.45}{2} = \mathbf{10.435}$$

19. Electronic configuration of Si : $1s^2, 2s^2 2p^6, 3s^2 3p^2$

$Z_{effective} = Z - \sigma$ (where σ is screening constant) and

$\sigma = [ns$ and np electrons excluding test electron $\times 0.35]$
$+ [(n-1)\text{ electrons} \times 0.85] + [(n-2)\text{ electrons} \times 1.0]$

$Z = 14 - [3\times 0.35 + 8\times 0.85 + 2\times 1.0] = 4.15$

$$\therefore \quad X = \frac{0.359\times 4.15}{(1.175)^2} + 0.744 = \mathbf{1.82}$$

(**Note :** if $n = 1$ then for $1s$ electron the value = $1s$ electrons $\times 3.0$)

20. The zero gp. members are He, Ne, Ar, Kr, Xe, Rn. Law of triad suggests that property of a middle element in a group of three is average of its two adjacent elements.

$$\therefore \text{ b. pt. of Xe} = \frac{\text{b. pt. of Kr + b. pt. of Rn}}{2}$$

$$= \frac{-152+(-62)}{2} = -\frac{214}{2} = \mathbf{-107°C}$$

21. $\underset{\text{(Dipole moment)}}{\mu_{HCl}} = \delta \times d$

$\because \quad \mu = 1.03\text{ D} = 1.03\times 10^{-18}$ esu cm

and $\quad d = 1.275\text{ Å} = 1.275\times 10^{-8}$ cm

$\therefore \quad 1.03\times 10^{-18} = \delta \times 1.275\times 10^{-8}$

$\therefore \quad \delta = 0.808\times 10^{-10}$ esu

$\because \quad 4.803\times 10^{-10}$ esu charge, % ionic nature of HCl = 100

$\therefore \quad 0.808\times 10^{-10}$ esu charge, % ionic nature of HCl

$$= \frac{100\times 0.808\times 10^{-10}}{4.803\times 10^{-10}} = \mathbf{16.82\%}$$

22. $\mu_{molecule} = \delta \times d$

$\therefore \quad 1.964\times 10^{-29} = \delta \times 1.596\times 10^{-10}$

$\therefore \quad \delta = 1.2306\times 10^{-19}$ coulomb

$\therefore \quad$ % of ionic nature

$$= \frac{1.2306\times 10^{-19}}{1.602\times 10^{-19}} \times 100 = \mathbf{76.82\%}$$

23. Dipole moment $\mu = \delta \times d$

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

$$\therefore \quad \delta = \frac{3.336\times 10^{-29}}{2.6\times 10^{-10}} = 1.283\times 10^{-19} \text{ coulomb}$$

$\because \quad 1.602\times 10^{-19}$ charge on each, % character = 100

$\therefore \quad 1.283\times 10^{-19}$ charge on each, % character

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

If one unit charge, then $\delta = 1.602\times 10^{-19}$ C

$\therefore \quad \mu = 1.602\times 10^{-19} \times 2.6\times 10^{-10}$

$= \mathbf{4.1652\times 10^{-29}}$ **coulomb metre.**

24. $$\delta = \frac{\text{Dipole moment}}{d} = \frac{1.2\times 10^{-18}\text{ esu cm}}{1.0\times 10^{-8}\text{ cm}} = 1.2\times 10^{-10} \text{ esu}$$

Thus, fraction of electronic charge on each end

$$= \frac{1.2\times 10^{-10}}{4.8\times 10^{-10}} = 0.25 = \mathbf{25\%\ of\ 'e'}$$

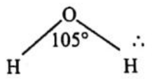
25. $$\mu = \sqrt{\mu_1^2 + \mu_1^2 + 2\mu_1\mu_1 \cos\alpha}$$

In H_2O only two dipoles equal to μ_1 are operating due to two O—H bonds.

Thus, $\quad 1.84 = \sqrt{(1.5)^2 + (1.5)^2 + 2\times(1.5)\times(1.5)\cos\alpha}$

$\therefore \quad \cos\alpha = -0.2476$

$\therefore \quad \alpha = \mathbf{104°20'}$

26. 

$$\therefore \mu_{H_2O} = \sqrt{\mu_{OH}^2 + \mu_{OH}^2 + 2\mu^2 \cos(105°)}$$

Since, H_2O has two vectors of O—H bond acting at 105°. Let dipole moment of O—H bond be 'a'

$\therefore \quad 1.85 = \sqrt{2a^2(1+\cos 105°)}$

or $\quad a$, *i.e.*, $\mu_{O-H} = 1.52$ debye $= 1.52\times 10^{-18}$ esu cm

Now $\quad M_{O-H} = \delta \times d \quad$ where, δ is charge on either end

$\therefore \quad 1.52\times 10^{-18} = \delta \times 0.94\times 10^{-8}$

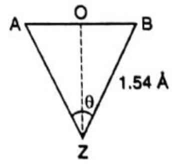
$\therefore \quad \delta = 1.617\times 10^{-10}$ esu

Since, O acquires 2δ charge, one δ charge from each bond and thus,

Charge on O atom = $2\delta = 2\times 1.617\times 10^{-10}$

$= \mathbf{3.23\times 10^{-10}}$ **esu cm**

27. The angle $\theta = 109°28'$ and $ZB = AZ = 1.54$ Å



Now, $\frac{AO}{AZ} = \sin\left(\frac{\theta}{2}\right) = \sin\left(\frac{109°28'}{2}\right)$

$= \sin 54°44' = \sin 54.73°$

or $AO = 0.816 \times AZ = 0.816 \times 1.54 = 1.257$ Å

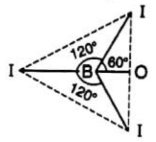
$\therefore$ $AB = 2 \times AO = 1.257\text{Å} \times 2 = \mathbf{2.514}$ **Å**

28. The BI_3 molecule is coplaner in nature as shown in figure.

$\frac{IO}{BI} = \sin 60°$

or $IO = BI \sin 60°$

$\frac{3.54}{2} = BI \times 0.867$



$\therefore$ $BI = 2.04$ Å

$\therefore$ Covalent radius of boron = BI − covalent radius of I

$= 2.04 - 1.33 = \mathbf{0.71}$ **Å**

29. $\because$ $PV = \frac{w}{M}RT$

or $P = \frac{w}{V \cdot M}RT$

or $M = \frac{dRT}{P} = \frac{3.17 \times 0.0821 \times 300}{1} = \mathbf{78.08\ g\ mol^{-1}}$

molar mass of HF in gaseous state is 78.08, whereas its normal molar mass is $1 + 18 = 19\,g\,mol^{-1}$.

Thus, HF in gaseous state forms a tetramer due to strong H-bonding.

30. Volume of $F_{(g)} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \pi \times (72)^3 = 1.56 \times 10^6$

Volume of $F^-_{(g)} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \pi \times (136)^3 = 10.53 \times 10^6$

$\therefore$ $\frac{V_{F^-}}{V_F} = \frac{(136)^3}{(72)^3} = 6.74$

Also increase in volume $= (10.53 - 1.56) \times 10^6 = 8.97 \times 10^6$

$\therefore$ % increase $= \frac{8.97 \times 10^6}{1.56 \times 10^6} \times 100 = \mathbf{5.75 \times 10^2}$

31. CO_2 is O=C=O

Thus, O to O bond length in CO_2 can be given as

$2.323 = 2 \times$ radius of (O=) + $2 \times$ radii of (C=)

$2.323 = 2 \times$ radius of (O=) + 2×0.67

$\therefore$ radius of (O=) = **0.49 Å**

32. Volume of $Li^+ = \frac{4}{3}\pi \times (0.76 \times 10^{-8})^3$

Volume of $Li = \frac{4}{3}\pi \times (1.23 \times 10^{-8})^3$

$\therefore$ Volume occupied by 2*s* '*e*'

$= \frac{4}{3}\pi \times [(1.23 \times 10^{-8})^3 - (0.76 \times 10^{-8})^3]$

$= \frac{4}{3}\pi \times 1.422 \times 10^{-24}$

$\therefore$ % Volume occupied by 2*s* '*e*'

$$= \frac{\frac{4}{3}\pi \times 1.422 \times 10^{-24} \times 100}{\frac{4}{3}\pi \times (1.23 \times 10^{-8})^3}$$

$= 76.45$

33. Total strength of all hydrogen bonds

$= 30.8 - 14.4 = 16.4$ kJ/mol

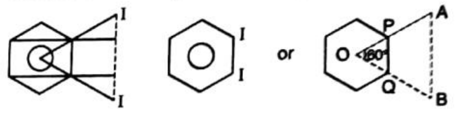
There are 6 nearest neighbours, but each hydrogen bond involves 2 ammonia molecules.

$\therefore$ Strength of each H-bond in solid NH_3

$= \frac{16.4}{3} = \mathbf{5.5\ kJ/mol}$

34. (a) ***o*-di-iodobenzene:**

The distance between two I atoms $AB = AO = OB$, because ΔAOB is equilateral triangle.



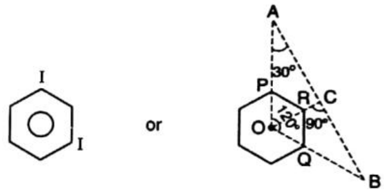
$\therefore$ $AB = OP + PA$

$\therefore$ $AB = OP +$ covalent radius of C + covalent radius of I

$= OP + 1.33 + 0.77 = 1.40 + 1.33 + 0.77$

$AB = \mathbf{3.50}$ **Å** ($OP = OQ = PQ$, because ΔOPQ is also equilateral triangle and $PQ =$ C—C bond length)

(b) ***m*-di-iodobenzene:**



The distance between two I atoms is

$AB = AC + BC = 2AC$ $(\because AC = BC)$

$= 2AO \cos 30° = 2(AP + OP) \cos 30°$

$= 2(AP + PR) \cos 30°$

$(OP = PR \because \Delta POR$ is equilateral)

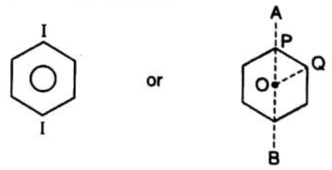
$= 2(2.10 + 1.40) \times 0.866$

$= \mathbf{6.06}$ **Å**

[$\because$ AP = covalent radius of C + covalent radius of I $= 0.77 + 1.33 = 2.10$ Å and

PR = covalent bond length of C—C = 1.40]

(c) ***p*-di-iodobenzene:**



$\therefore$ $AB = OA + OB = 2OA$

$= 2(OP + PA)$

$= 2 \times (PQ + PA)$

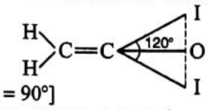
$(\because OP = PQ; \Delta OPQ$ is equilateral)

$= 2\,(PQ + \text{covalent radius of C} + \text{covalent radius of I})$

$= 2 \times (1.40 + 0.77 + 1.33) = \mathbf{7.0\ Å}$

35. $CH_2 = CI_2$ has sp^2-hybridised carbon and thus ICI bond angle is 120°.

$\therefore \quad \frac{IO}{CI} = \sin 60°$



[In Δ $ICO \angle ICO = 60°$ and $\angle IOC = 90°$]

or $\quad IO = CI \sin 60° = 2.10 \times 0.866 = 1.8186\ Å$

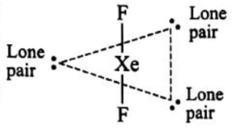
$\therefore$ I—I distance $= 2 \times 1.8186 = \mathbf{3.64\ Å}$

36. (a) sp (b) sp^2 (c) sp^3d^2 (d) sp^2 (e) sp (f) sp^2 (g) sp^3 (h) sp^3d^2 (i) sp^3d (j) sp^2 (k) sp^3 (l) sp^3d^2 (m) sp^3 (n) sp^3 (o) sp^3d (p) sp^3 (q) sp^2.

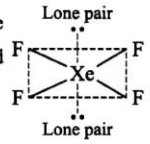
37. (a) sp^2, sp, sp^2 (b) sp^2, sp, sp, sp^2

(c) sp^3; sp^2 on all four carbon of CN.

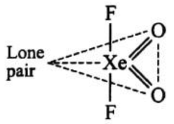
38. $\mathbf{XeF_2}$ **:** Xe is in sp^3d-hybridised state having three lone pair of electrons located equationally and thus, shape is linear.



$\mathbf{XeF_4}$ **:** Xe is in sp^3d^2-hybridised state having two lone pair of electrons located axially and thus, shape is square planar.

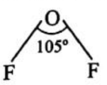


$\mathbf{XeO_2F_2}$ **:** Xe is in sp^3d^3-hybridised state having one lone pair of electron at equatorial position and thus, shape is distorted trigonal pyramidal.



39. The structure of OF_2 is V-shape due to sp^3-hybridisation of oxygen with two lone pair of electrons on it.

Oxidation number of O and F are +2 and −1 respectively.



40. MO configuration of $O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_y^1, \pi^* 2p_z^1$.

Bond order $= \frac{1}{2}$ [No. of bonding electron − No. of antibonding electron]

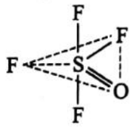
$= \frac{1}{2}[10 - 6] = 2$

Also O_2 is paramagnetic as it has two unpaired electrons.

41. (a) sp^3 and sp, (b) sp^3, sp^2 and sp^2

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

42. S atom in OSF_4 shows sp^3d^2-hybridisation leading to trigonal bipyramidal geometry but distorted due to S=O bond. The F atoms are at axial and equatorial positions whereas oxygen being less electronegative occupies one of the three equatorial positions.



43. The MO configuration of O_2, O_2^+ in $O_2[AsF_4]$ and O_2^- in $K^+O_2^-$ are:

$$O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{matrix} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{matrix}$$

$$O_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \pi^* 2p_y^1$$

$$O_2^- : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{matrix} \pi^* 2p_y^2 \\ \pi^* 2p_z^1 \end{matrix}$$

Thus, bond orders and bond length are:

Species	O_2	O_2^+	O_2^-
Bond order	2	2.5	1.5
Bond length	$O_2^+ < O_2 < O_2^-$		

Higher is the bond order, lesser is bond length.

44. Mole of AgCl obtained

= mole of Cl^- ions ionised from $\frac{2.665}{266.5}$ mole of $CrCl_3 \cdot 6H_2O$

= 0.01 (molar mass of $CrCl_3 \cdot 6H_2O = 266.5$)

$\therefore \quad$ Mole of Cl^- ionised $= \frac{2.87}{143.5} = 0.02$

Thus, 0.01 mole of complex $CrCl_3 \cdot 6H_2O$ gives 0.02 mole of Cl^- on ionisation.

Now, since co-ordination number of Cr is six and only one Cl ion is attached to Cr by co-ordinate bond or secondary valency and therefore, complex is $[CrCl \cdot (H_2O)_5]Cl_2 \cdot H_2O$.

$$[CrCl \cdot (H_2O)_5]Cl_2 \cdot H_2O \longrightarrow [CrCl(H_2O)_5]^{2+} + 2Cl^- + H_2O$$

$$2Cl^- + 2AgNO_3 \longrightarrow 2AgCl + 2NO_3^-$$

45. Molar mass of $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O = 266.5$

$\therefore \quad$ Mole of complex $= \frac{1}{266.5}$

Note : 1 mole of $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ will give 2 mole of Cl^- ions or 2 mole of HCl.

Thus, $\quad$ mole of HCl formed $= \frac{2 \times 1}{266.5}$

$\therefore \quad N_{HCl} = \frac{2 \times 1}{266.5 \times 1} = \mathbf{0.0075}$

46. The Cl atoms out side the co-ordination sphere will be ionised to produce acid HCl.

Thus, Meq. of Cl^- ions outside = Meq. of HCl formed

= Meq. of NaOH used

$= 28.5 \times 0.125 = 3.56$

$\frac{0.319}{266.5}$ mole or 1.197 *m* mole of complex produce 3.56 Meq. or millimole small of Cl^-.

Thus, 1 mole of complex will give 3 mole of Cl^-, *i.e.*, all the three Cl atoms are outside the co-ordination sphere.

Thus, complex is $\mathbf{[Cr(H_2O)_6]Cl_3}$.

47. $M(CO)_x$

In $Fe(CO)_x$: EAN = At. no. of Fe + 2 × No. of ligands, *i.e.*, CO

$\therefore \quad 36 = 26 + 2 \cdot x$

$\therefore \quad x = 5$

∴ Formula of iron carbonyl is $\mathbf{Fe(CO)_5}$

Similarly, $\mathbf{Cr(CO)_6}$ and $\mathbf{Ni(CO)_4}$.

48. Complex $Cr(NH_3)_4Cl_2Br$ has two isomers. Since, co-ordination number of Cr is six and thus, two forms may be :

$$\underset{(B)}{[Cr(NH_3)_4Cl_2]Br} \xrightarrow{AgNO_3} [Cr(NH_3)_2Cl_2]^+ + NO_3^- + AgBr\downarrow$$

yellow ppt. soluble partially in conc. NH_3, *i.e.*, $[Ag(NH_3)_2]Br$

and $$\underset{(A)}{[Cr(NH_3)_4Br\cdot Cl]Cl} \xrightarrow{AgNO_3} [Cr(NH_3)_4ClBr]^+ + NO_3^- + AgCl\downarrow$$

white ppt. soluble in dil. NH_3, *i.e.*, $[Ag(NH_3)_2]Cl$

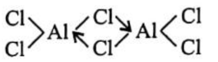
Hybridisation of Cr in (*A*) and (*B*) is d^2sp^3 having 3 unpaired electrons ($3d^3$).

Magnetic moment $= \sqrt{n(n+2)}$ B.M.

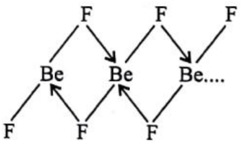
$= \sqrt{3(3+2)} = \mathbf{3.87\ B.M.}$

49. Cu^{2+} has coordination number four $[Cu(H_2O)_4]\cdot SO_4 \cdot H_2O$.

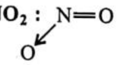
50. In solid state $AlCl_3$ exists as Al_2Cl_6 and has co-ordination number four.



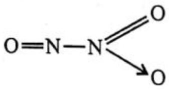
51. In solid state BeF_2 exists as $(BeF_2)_n$. The hybridisation in $(BeF_2)_n$ is sp^3.



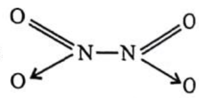
52. N_2O, N_2O_3, N_2O_4, $\mathbf{N_2O}$: N≡N→O, **NO**: N=O, $\mathbf{NO_2}$:



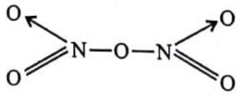
$\mathbf{N_2O_3}$:



, $\mathbf{N_2O_4}$:

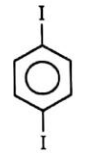


$\mathbf{N_2O_5}$:



• SINGLE INTEGER ANSWER PROBLEMS •

1. Number of σ bonds in $C(CN)_4$ are ......
2. Number of equitorial bonds in PCl_5 are ......
3. The ratio of s-character in sp and sp^3 hybridization is ......
4. Number of lone pair of electrons in $XeOF_4$ are ......
5. Number of shell in which valence electrons of iodine lies ......
6. Number of electron pairs in SF_6 at the corners of octahedron are ......
7. Number of electron pairs in XeF_4 at the corners of square are ......
8. Bond order of BN is ......
9. Maximum number of atoms which can be attached on N-atom is ......
10. Assuming C_6H_6 ring a regular hexagon and C—I bond lies on the line through the centre of hexagon. If the distance between adjacent carbon is 1.40 Å and covalent radius of iodine and carbon atoms are 1.33Å and 0.77Å. The I—I distance in Å is ......



11. The dipole moment of AB is 1.6×10^{-30} C-m. If intermolecular distance is 2.0×10^{-10} m, the % ionic character of AB is ......
12. Bond order for CO is ......
13. Ratio of bond pair-lone pair electrons in $XeOF_2$ is ......
14. Number of unpaired electrons in $O_2[AsF_4]$ is ......
15. Bond order of NO^+ is ......
16. Number of lone pairs of electrons on central iodine atom of I_3^- ion is ......
17. AX_n possess trigonal bipyramidal shape. If A has no lone pair, the value of n is ......
18. XeO_4 shows maximum oxidation state (+8). If Xe reacts with fluorine atom, the maximum oxidation state shown by Xe is + ...
19. Ratio of number of bond pair and lone pair in IF_4^- is ......
20. Number of hybridised orbitals populated with bonding electron pairs in ICl_2^- are ......
21. Ratio of σ and π bonds in OSF_4 is ......
22. Number of nearest neighbours of NH_3 molecules round each molecule in solid NH_3 are ......
23. Based on VSEPR theory, number of 90 degree F—Br—F bonds in BrF_5 is ...... **(IIT 2010)**
24. The ratio of shielding constant for Ne and Na^+ is.....
25. Bond order of CO is.....
26. The ratio of bond order in O_2^{2+} and O_2^- is.....
27. The number of anti bonding electrons in N_2^- is.....
28. The ratio of p-character and s-character in solid BeF_2 is.....
29. The number of σ -bonds in C $(CN)_4$.....
30. Number of lone pair of electrons on central atom of I_3^-.....
31. The ratio of σ and π-bonds in tetracyano methane is.....
32. Number of 90° F—Xe—F bond angles in XeF_4 is.....
33. Number of 90° F—I—F bond angles in IF_5 is.....
34. Number of covalent bonds in Al_2Cl_6 is ......
35. The number of three centre two electrons bonds in a molecule of diborane is ......
36. The ratio of σ -bond and π-bond in tetracyano methane is ......
37. Number of S–S bonds in cyclic trimer of SO_3 is ......
38. Ratio of number of σ -bonds and S–O–S bonds in trimer of SO_3 is ......
39. Number of π -bonds in trimer of SO_3 is ......
40. $H_2S_5O_6$ a polythionic acid on decomposition gives sulphur molecules equal to ......
41. The ratio of P—O and P $=$ O bonds in P_4O_{10} is ......
42. Number of S—S bonds in $H_2S_5O_6$ is ......
43. Number of identical Cr – O bonds in $Cr_2O_7^{2-}$ ion is ......
44. The ratio of σ and π-bonds in benzene is ......

ANSWERS

1. Eight	2. Three	3. Two	4. One	5. Five	6. Six	7. Four	8. Two	9. Four	10. Seven	11. Five	12. Three
13. Two	14. One	15. Three	16. Three	17. Five	18. Six	19. Two	20. Two	21. Five	22. Six	23. Zero	24. One
25. Three	26. Two	27. Five	28. Three	29. Eight	30. Three	31. One	32. Four	33. Eight	34. Six	35. Two	36. One
37. Zero	38. Four	39. Six	40. Three	41. Three	42. Four	43. Six	44. Four				

OBJECTIVE PROBLEMS (One Answer Correct)

1. Shielding constant σ for Ne is 4.15. The effective nuclear charge on Na^+ and F^- are respectively :
(a) 4.85, 6.85 (b) 5.85, 6.85
(c) 6.85, 4.85 (d) 4.85, 4.85

2. Electron gain enthalpy and ionisation energy of an atom are $-a$ and $+b$ eV respectively. The electronegativity of that atom on Mulliken scale is given by :
(a) $a-b$ (b) $\frac{b-a}{2}$
(c) $a+b$ (d) $\frac{a+b}{2}$

3. The atomic radii of Li is 1.23 Å and ionic radius of Li^+ is 0.76 Å. The fraction of the volume occupied by 2*s* electron in Li is :
(a) 0.764 (b) 0.184
(c) 0.595 (d) 0.236

4. Photons of monochromatic light having just sufficient energy to ionise Ar-atom are incidented over the mixture of inert gases He, Ne, Ar, Kr and Xe. The mixture will contain:
(a) He, Ne, gases; Ar^+, Kr^+, Xe^+ ions
(b) He^+, Ne^+ ions; Ar, Kr, Xe gases
(c) He^+, Ne^+, Ar^+, Kr^+ and Xe^+ ions
(d) He^+, Ne^+, Ar^+ ions and Kr, Xe gases

5. If EA_1 and EA_2 for oxygen atom are -142 kJ mol^{-1} and $+844$ kJ mol^{-1}. The energy released to form $2O + 2e \longrightarrow 2O^-$ will be : (in kJ mol^{-1})
(a) 986 (b) 702
(c) 284 (d) 1688

6. Dipole moment of K^+Cl^- is 3.336×10^{-29} cm and it is 80% ionic in nature. The inter ionic distance between K^+ and Cl^- is :
(a) 1.30 Å (b) 2.60 Å
(c) 3.9 Å (d) 1.20 Å

7. Bond order for CO^+ and NO^+ are respectively :
(a) 3.5, 3.0 (b) 2.5, 3.0
(c) 2.5, 2.5 (d) 3.0, 2.5

8. Bond order for N_2^+ and N_2^- are same. Which relation is correct for N_2^+ and N_2^-?
(a) Bond energy of N_2^+ = Bond energy of N_2^-
(b) Bond energy of N_2^+ > Bond energy of N_2^-
(c) Bond energy of N_2^+ < Bond energy of N_2^-
(d) Bond energy of $N_2^+ \gtrless$ Bond energy of N_2^-

9. The electron gain enthalpy of fluorine atom is 333 kJ mol^{-1} and dissociation energy of F_2 is 158.8 kJ mol^{-1}. Energy released during formation of 2 g F^- from 2 g F_2 (atomic mass 40) is :
(a) 33.3 kJ (b) 7.94 kJ
(c) 25.36 kJ (d) 41.24 kJ

10. The ionisation energy of lithium is 5.40 eV. If ionisation energy of H-atom is 13.6 eV, the effective charge acting upon outermost shell of Li is :
(a) 1.26 (b) 2.52
(c) 0.63 (d) 3.0

11. Which of the molecule is hypovalent but has complete octet?
(a) $AlCl_3$ (b) PH_3
(c) PCl_3 (d) SF_4

12. Which of the molecule does not possess hypervalent nature?
(a) IF_7 (b) SF_4
(c) BF_3 (d) SF_6

13. The species not having same bond order is :
(a) N_2^+ (b) O_2^+
(c) NO (d) NO^+

14. Least basic trihalide is :
(a) NF_3 (b) NCl_3
(c) NBr_3 (d) NI_3

15. Least acidic trihalide is :
(a) BF_3 (b) BCl_3
(c) BBr_3 (d) BI_3

16. During the reaction : $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$; the hybridised state of carbon changes from :
(a) sp^2 to sp (b) sp to sp^2
(c) sp^3 to sp (d) sp to sp^3

17. Which of the following is T-shaped?
(a) $XeOF_2$ (b) XeO_3
(c) $XeOF_4$ (d) XeF_4

18. Number of sigma bonds and double bonds in P_4O_{10} are respectively :
(a) 12, 4 (b) 6, 4
(c) 8, 2 (d) 10, 4

19. Which of the following is not correct for P_4O_{10} and P_4O_6?
(a) Both are acidic anhydride
(b) Both have sp^2-hybridised P-atoms
(c) Both have P — O — P bonds
(d) Both have six P — O — P bonds

20. A planar molecule has AB_X structure with six pairs of electrons around A and one lone pair. The value of X is :
(a) 2 (b) 4
(c) 6 (d) 7

21. Among the following species, identify the isostructural pairs:
$NF_3, NO_3^-, BF_3, H_3O^+, HN_3$
(a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$
(b) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
(c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
(d) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

22. The two carbon atoms in calcium carbide are held by which of the following bonds :
(a) three sigma bonds
(b) ionic bonds
(c) two pi and one sigma bonds
(d) ionic and covalent bonds

23. Arrange the following compounds in order of increasing dipole moment : Toluene (I); *m*-dichlorobenzene (II); *o*-dichlorobenzene (III); *p*-dichlorobenzene (IV)
(a) I<IV<II<III (b) IV<I<II<III
(c) IV<I<III<II (d) IV<II<I<III

24. 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

25. Which contains both polar and non-polar bonds :
(a) NH_4Cl (b) HCN
(c) H_2O_2 (d) CH_4

26. Which has sp^2-hybridization :
(a) CO_2 (b) SO_2
(c) N_2O (d) CO

27. The critical temperature of water is higher than that of O_2 because the H_2O molecule has :
(a) fewer electrons than O_2
(b) two covalent bonds
(c) V-shape
(d) dipole moment

28. The geometry and the type of hybrid orbitals present about the central atom in BF_3 is :
(a) linear, *sp* (b) trigonal planar, sp^2
(c) tetrahedral sp^3 (d) pyramidal, sp^3

29. The geometry of H_2S and its dipole moment are :
(a) angular and non-zero (b) angular and zero
(c) linear and non-zero (d) linear and zero

30. In compounds of type ECl_3, where E = B, P, As and Bi the angles Cl — E — Cl for different E are in the order :
(a) B> P = As = Bi (b) B> P > As > Bi
(c) B< P = As = Bi (d) B< P < As > Bi

31. In the compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type :
(a) sp-sp^2 (b) sp^3-sp^3
(c) sp-sp^3 (d) sp^2-sp^3

32. Which of the following shows biggest jump in II and III ionisation energy:
(a) $1s^2, 2s^2 2p^6, 3s^2$
(b) $1s^2, 2s^2 2p^6, 3s^2 3p^2$
(c) $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 4p^2$
(d) $1s^2, 2s^2$

33. Which of the following possesses highest second ionisation energy:
(a) $1s^2, 2s^2 2p^6, 3s^2$ (b) $1s^2, 2s^2 2p^6, 3s^1$
(c) $1s^2, 2s^2 2p^3$ (d) $1s^2, 2s^2 2p^4$

34. EA_1 of element is:
(a) always exothermic
(b) always endothermic
(c) may be exothermic or endothermic
(d) always zero

35. Element having highest I.E. but zero electron gain enthalpy:
(a) H (b) F
(c) He (d) B

36. The second electron gain enthalpy of O and S (in $kJ\ mol^{-1}$) respectively are :
(a) –844, +590 (b) +590, +844
(c) +844, +590 (d) –590, +844

37. Which factor is responsible to make Li as a powerful reducing agent:
(a) Electronegativity (b) Ionisation energy
(c) Electron gain enthalpy (d) Hydration energy

38. The first electron gain enthalpy of which pair is not correctly represented by:
(a) O > S (b) Cl > F
(c) N > P (d) B > C

39. Which of the following factors does not influence the covalent character in molecule:
(a) size of cation
(b) size of anion
(c) pseudo inert gas configuration of cation
(d) bond energy

40. If the formation of O^{2-} from O^- atom is shown below
$$O(g) + e \rightarrow O^-(g);\ \Delta H = -142\ kJ\ mol^{-1}$$
$$O^-(g) + e \rightarrow O^{2-}(g);\ \Delta H = +844\ kJ\ mol^{-1}$$
then which of the following statements are correct:

(a) $O(g) \rightarrow O^{2-}(g)$; $\Delta H = 702$ k J mol^{-1}
(b) O^- ion opposes further addition of electron
(c) EA_2 of O > EA_1 of O
(d) All of these

41. The correct order of II ionisation energy shown in correct order is:
(a) F > O > N > C (b) C > N > O > F
(c) O > N > F > C (d) O > F > N > C

42. The correct order of increasing electron affinity of the following is:
(a) O < S < F < Cl (b) O < S < Cl < F
(c) S < O < F < Cl (d) S < O < Cl < F

43. Shielding constant of Ne is 4.15, the shielding constant of Na^+ would be:
(a) 4.15 (b) 3.70
(c) 5.20 (d) 6.20

44. First ionisation energy of Li and K are 5.4 and 4.3 eV respectively, approximate ionisation energy of Na will be:
(a) 8.7 eV (b) 1.1 eV
(c) 4.9 eV (d) 2.2 eV

45. Which of the following has the highest electron releasing tendency:
(a) F^- (b) OH^-
(c) NH_2^- (d) CH_3^-

46. The compound which contains both ionic and covalent bonds is:
(a) CH_4 (b) H_2
(c) KCN (d) KCl

47. The octet rule is not valid for the molecule:
(a) CO_2 (b) H_2O
(c) O_2 (d) CO

48. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be:
(a) X^+Y^- (b) X^-Y^+
(c) $X - Y$ (d) $X \rightarrow Y$

49. Which of the following compounds are covalent?
(a) H_2 (b) CaO
(c) KCl (d) Na_2S

50. The total number of electrons that take part in forming the bond in N_2 is:
(a) 2 (b) 4
(c) 6 (d) 10

51. Which of the following is soluble in water:
(a) CS_2 (b) C_2H_5OH
(c) CCl_4 (d) $CHCl_3$

52. If a molecule MX_2, has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are:
(a) pure p (b) sp hybrid
(c) sp^2 hybrid (d) sp^3 hybrid

53. The ion that is isoelectronic with CO is:
(a) CN^- (b) O_2^+
(c) O_2^- (d) N_2^+

54. Among the following, the molecule that is linear is:
(a) CO_2 (b) NO_2
(c) SO_2 (d) ClO_2

55. Carbon tetrachloride has no net dipole moment because of:
(a) its planar structure
(b) its regular tetrahedral structure
(c) similar sizes of carbon and chlorine
(d) similar electron affinities of carbon and chlorine

56. Which one among the following does not have the hydrogen bond?
(a) phenol (b) liquid NH_3
(c) water (d) liquid HCl

57. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only:
(a) electrovalent and covalent
(b) electrovalent and coordinate covalent
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent

58. On hybridization of one s and one p orbitals we get:
(a) two mutually perpendicular orbitals
(b) two orbitals at 180°
(c) four orbitals directed tetrahedrally
(d) three orbitals in a plane

59. The molecule having one unpaired electron is:
(a) NO (b) CO
(c) CN^- (d) O_2

60. The hydration energy of Mg^{2+} is greater than that of:
(a) Al^{3+} (b) Na^+
(c) Be^{2+} (d) Mg^{2+}

61. The bonds present in N_2O_5 are:
(a) only ionic (b) covalent and coordinate
(c) only covalent (d) covalent and ionic

62. The bond between two identical non-metal atoms has a pair of electrons:
(a) unequally shared between the two
(b) transferred fully from one atom to another
(c) with identical spins
(d) equally shared between them

63. The hydrogen bond is strongest in:
(a) O – H...... S (b) S – H...... O
(c) F – H...... F (d) F – H...... O

64. The hybridisation of sulphur in sulphur dioxide is:
(a) sp (b) sp^3
(c) sp^2 (d) dsp^2

65. Hydrogen bonding is maximum in:
(a) Ethanol (b) Diethylether
(c) Ethyl chloride (d) Triethylamine

66. The first ionisation potential (in electron volt) of nitrogen and oxygen atoms are respectively:
(a) 14.6, 13.6 (b) 13.6, 14.6
(c) 13.6, 13.6 (d) 14.6, 14.6

67. Atomic radii of fluorine and neon (in Å) are respectively:
(a) 0.72, 1.60 (b) 1.60, 1.60
(c) 0.72, 0.72 (d) 1.60, 0.72

68. The correct increasing order of electronegativity is:
(a) $C < N < Si < P$ (b) $N < Si < C < P$
(c) $Si < P < C < N$ (d) $P < Si < N < C$

69. Which of the following has zero dipole moment?
(a) 1, 1-dichloro ethane
(b) *cis*-1, 2-dichloro ethene
(c) *trans*-1, 2-dichloro ethene
(d) none of the above

70. The bond between carbon atom (1) and carbon atom (2) in $N \equiv C - CH = CH_2$ involves hybridisation:
(a) sp^2, sp^2 (b) sp^3, sp
(c) sp, sp^2 (d) sp, sp

71. The correct order for IE_1 is:
(a) $Na < Mg > Al < Si$ (b) $Na > Mg > Al > Si$
(c) $Na < Mg < Al > Si$ (d) $Na > Mg > Al < Si$

72. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is:
(a) PH_3 (b) NH_3
(c) CH_3^+ (d) SbH_3

73. The molecule that has linear structure is:
(a) CO_2 (b) NO_2
(c) SO_2 (d) SiO_2

74. The molecule which has zero dipole moment is:
(a) CH_2Cl_2 (b) BF_3
(c) NF_3 (d) ClO_2

75. The molecule which has pyramidal shape is:
(a) PCl_3 (b) SO_3
(c) CO_3^{2-} (d) NO_3^-

76. The compound in which carbon use its sp^3 hybrid orbitals for bond formation is:
(a) $H\overset{*}{C}OOH$ (b) $(H_2N)_2\overset{*}{C}O$
(c) $(CH_3)_3\overset{*}{C}OH$ (d) $CH_3\overset{*}{C}HO$

77. Which of the following is paramagnetic:
(a) O_2 (b) CN
(c) CO (d) NO^+

78. Which has highest ionisation energy:
(a) $[Ne]\,3s^2 3p^1$ (b) $[Ne]\,3s^2 3p^3$
(c) $[Ne]\,3s^2 3p^2$ (d) $[Ar]\,3d^{10}, 4s^2 4p^3$

79. The hybridisation of carbon atom in C–C single bond of $HC \equiv C - CH = CH_2$ is:
(a) $sp^3 - sp^3$ (b) $sp^2 - sp^2$
(c) $sp - sp^2$ (d) $sp^3 - sp$

80. The type of hybrid orbitals used by the chlorine atom in ClO_3^- is:
(a) sp^3 (b) sp^2
(c) sp (d) none of these

81. The maximum possible number of hydrogen bonds a water molecule can form is:
(a) 2 (b) 4
(c) 3 (d) 1

82. The cyanide ion, CN^- and N_2 are isoelectronic. But in contrast to CN^-, N_2 is chemically inert, because of:
(a) low bond energy
(b) absence of bond polarity
(c) unsymmetrical electron distribution
(d) presence of more number of electrons in bonding orbitals

83. Allyl isocyanide has:
(a) 9σ and 4π bonds
(b) 8σ and 5π bonds
(c) 9σ, 3π bonds and 2 non bonding electrons
(d) 8σ, 3π bonds and 4 non bonding electrons

84. Which one is most ionic:
(a) P_2O_5 (b) CrO_3
(c) MnO (d) Mn_2O_7

85. Number of paired electrons in O_2 molecule is:
(a) 7 (b) 8
(c) 16 (d) 14

86. Which of the following statement is true about $CsBr_3$:
(a) It is a covalent compound
(b) It contains Cs^{3+} and Br^- ions
(c) It contains Cs^+ and Br_3^- ions
(d) It contains Cs, Br^- and lattice Br_2 molecule

87. KF combines with HF to form KHF_2. The compound contains:
(a) K^+, F^- and H^+ (b) K^+, F^- and HF
(c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F^-

88. Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is:
(a) H_2CO_3 (b) SiF_4
(c) BF_3 (d) $HClO_2$

89. Which one of the following compounds has sp^2 hybridisation?
(a) CO_2 (b) SO_2
(c) N_2O (d) CO

90. The incorrect statement is:
(a) IE_1 of Al < IE_1 of Mg (b) IE_2 of Mg > IE_2 of Na
(c) IE_1 of Na < IE_1 of Mg (d) IE_3 of Mg < IE_3 of Al

91. The geometry and type of hybridisation about central atom of BF_3 is:

(a) linear, *sp* (b) trigonal planar sp^2
(c) tetrahedral sp^3 (d) pyramidal, sp^3

92. The correct order of increasing C – O bond length of CO, CO_3^{2-}, CO_2 is:

(a) $CO_3^{2-} < CO_2 < CO$ (b) $CO_2 < CO_3^{2-} < CO$
(c) $CO < CO_3^{2-} < CO_2$ (d) $CO < CO_2 < CO_3^{2-}$

93. Ionic radii of:

(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^- < ^{37}Cl^-$
(c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$

94. In the compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type:

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

95. The correct order of radii is: **(IIT2000)**

(a) $N < Be < B$ (b) $F^- < O^{-2} < N^{3-}$
(c) $Na < Li < K$ (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

96. Molecular shape of SF_4, CF_4 and XeF_4 are: **(IIT 2000)**

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

97. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are: **(IIT 2000)**

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

98. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is: **(IIT 2000)**

(a) H_2O because of H-bonding
(b) H_2Te because of higher molar mass
(c) H_2S because of H-bonding
(d) H_2Se because of lower molar mass

99. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is: **(IIT 2001)**

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

100. The common features among the species CN^-, CO and NO^+ are: **(IIT 2001)**

(a) bond order 3 and isoelectronics
(b) bond order 3 and weak field ligands
(c) bond order 2 and π-acceptor
(d) isoelectric and weak field ligands

101. The set representing the correct order for first ionisation potential **(IIT 2001)**

(a) $K > Na > Li$ (b) $Be > Mg > Ca$
(c) $B > C > N$ (d) $Ge > Si > C$

102. Specify the coordination geometry around and hybridization of N and B complex of NH_3 and BF_3: **(IIT 2002)**

(a) N : tetrahedral, sp^3; B : tetrahedral, sp^3
(b) N : pyramidal, sp^3; B : pyramidal, sp^3
(c) N : pyramidal, sp^3; B : planar, sp^3
(d) N : pyramidal, sp^3; B : tetrahedral, sp^3

103. The least stable amongst the following is: **(IIT 2002)**

(a) Li^- (b) Be^-
(c) B^- (d) C^-

104. Which of the following molecular species has unpaired electrons: **(IIT 2002)**

(a) N_2 (b) F_2
(c) O_2^- (d) O_2^{2-}

105. The nodal plane is the π-bond of ethene is located in:

(a) the molecular plane
(b) a plane parallel to molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon sigma and at right angles
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon sigma bond

106. Among the following the molecule with the highest dipole moment is: **(IIT 2003)**

(a) CH_3Cl (b) CH_2Cl_2
(c) $CHCl_3$ (d) CCl_4

107. Which of the following are isoelectronics and isostructural:

$$NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$$

(IIT 2003)

(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

108. Which of the following represents the given mode of hybridization sp^2-sp^2-*sp*-*sp* from left to right: **(IIT 2003)**

(a) $CH_2 = CH - C \equiv CH$
(b) $CH \equiv C - C \equiv CH$
(c) $CH_2 = C = C = CH_2$
(d) $CH_2 = CH - CH = CH_2$

109. Total number of lone pair of electrons in $XeOF_4$ is : **(IIT 2004)**
(a) 0 (b) 1
(c) 2 (d) 3

110. Which statement is correct about O_2^+ : **(IIT 2004)**
(a) Paramagnetic and bond order < O_2
(b) Paramagnetic and bond order > O_2
(c) Diamagnetic and bond order < O_2
(d) Diamagnetic and bond order > O_2

111. Which species has the maximum number of lone pair of electrons on the central atom : **(IIT 2005)**
(a) $[ClO_3]^-$ (b) XeF_4
(c) SF_4 (d) $[I_3]^-$

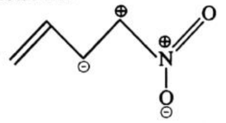
112. If the bond length of C—O bond in carbon monoxide is 1.128 Å, then what is the value of C—O bond length in $Fe(CO)_5$: **(IIT 2006)**
(a) 1.15 Å (b) 1.128 Å
(c) 1.72 Å (d) 1.118 Å

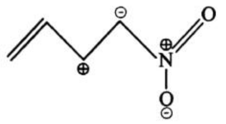
113. The species having different bond order that of CO is : **(IIT 2007)**
(a) NO (b) NO^+
(c) CN^- (d) N_2

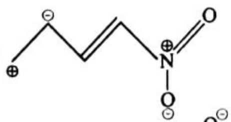
114. Among the following the paramagnetic compound is : **(IIT 2007)**
(a) Na_2O_2 (b) O_3
(c) N_2O (d) KO_2

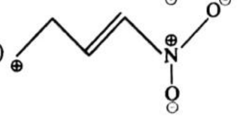
115. The percentage of *p*-character in the orbitals of P_4 forming P—P bond is : **(IIT 2007)**
(a) 25 (b) 33
(c) 50 (d) 75

116. Among the following, the least stable resonance structure is: **(IIT 2007)**

(a) 

(b) 

(c) 

(d) 

117. Among the following statement, the correct statement about PH_3 and NH_3 is : **(IIT 2008)**
(a) NH_3 is a better electron donor because the lone pair of electron occupies spherical *s*-orbital and is less directional.
(b) PH_3 is a better electron donor because the lone pair of electron occupies sp^3-orbital and is more directional
(c) NH_3 is a better electron donor because the lone pair of electron occupies sp^3-orbital and more directional.
(d) PH_3 is a better electron donor because the lone pair of electron occupies spherical *s*-orbital and is less directional.

118. The correct stability order of the following resonating structures is : **(IIT 2009)**
(i) $H_2C=\overset{+}{N}=\overset{-}{N}$ (ii) $H_2\overset{+}{C}-N=\overset{-}{N}$
(iii) $H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (iv) $H_2\overset{-}{C}-N=\overset{+}{N}$
(a) (i) > (ii) > (iv) > (iii) (b) (i) > (iii) > (ii) > (iv)
(c) (ii) > (i) > (iii) > (iv) (d) (iii) > (i) > (iv) > (ii)

119. The species having pyramidal shape is : **(IIT 2010)**
(a) SO_3 (b) BrF_5
(c) SiO_3^{2-} (d) OSF_2

120. Assuming that Hund's rule is violeted, the bond order and magnetic nature of diatomic molecule of B_2 is : **(IIT 2010)**
(a) 1 and diamagnetic (b) zero and diamagnetic
(c) 1 and paramagnetic (d) zero and paramagnetic

121. In allene (C_3H_4), the type(s) of hybridization of the carbon atoms is/are : **(IIT 2012)**
(a) *sp* and sp^3 (b) *sp* and sp^2
(c) only sp^2 (d) sp^2 and sp^3

122. The shape of XeO_2F_2 molecule is : **(IIT 2012)**
(a) trigonal bipyramidal (b) square planar
(c) tetrahedral (d) see-saw

123. Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[JEE (Main) 2013]**
(a) O_2 (b) S_2
(c) C_2 (d) N_2

124. In which of the following pairs of molecules/ions, both the species are not likely to exist ? **[JEE (Main) 2013]**
(a) H_2^{2+}, He_2 (b) H_2^-, He_2^{2+}
(c) H_2^+, He_2^{2-} (d) H_2^-, He_2^{2-}

125. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar? **[JEE (Main) 2013]**
(a) Ba < Ca < Se < S < Ar (b) Ca < Ba < S < Se < Ar
(c) Ca < S < Ba < Se < Ar (d) S < Se < Ca < Ba < Ar

126. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of: **[JEE (Main) 2013]**

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

127. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be : **[JEE (Main) 2013]**

(a) −10.2 eV (b) +2.55 eV
(c) −2.55 eV (d) −5.1 eV

SOLUTIONS (One Answer Correct)

1. (c) $_{10}Ne: 1s^2, 2s^2 2p^6$ $_{11}Na^+: 1s^2 2s^2 2p^6$
$_{12}F^-: 1s^2, 2s^2 2p^6$
All have same shielding constant.
Also, $Z_{eff} = Z - \sigma$ $\therefore Z_{eff\,Na} = 11 - 4.15 = 6.85$
and $Z_{eff\,F^-} = 9 - 4.15 = 4.85$

2. (d) $EN = \frac{IE + EA}{2}$ and $EA = -E_{ga}$

3. (a) $V_{Li} = \frac{4}{3} \times 3.14 \times (1.23)^3 = 7.79\,(Å)^3$

$V_{Li^+} = \frac{4}{3} \times 3.14 \times (0.76)^3 = 1.84\,(Å)^3$

Volume occupied by 2s-electron
$= 7.79 - 1.84 = 5.95\,(Å)^3$

$\therefore$ Fraction of volume occupied by 2s-electron
$= \frac{5.95}{7.79} = 0.764$

4. (a) IE_1 decreases down the gp. Thus Ar, Kr and Xe will show ionisation.

5. (c) $O + e \longrightarrow O^-$; $\Delta H = -144$ kJ
$\therefore 2O + 2e \longrightarrow 2O^-$; $\Delta H = 2 \times (-142) = -284$ kJ

6. (b) $\mu = \delta \times d$

$3.336 \times 10^{-29} = \frac{1.602 \times 10^{-19} \times 80}{100} \times d$

$\therefore \quad d = \frac{3.336 \times 10^{-29} \times 100}{1.602 \times 10^{-19} \times 80}$
$= 2.60 \times 10^{-10}$ m $= 2.60$ Å

7. (a) $NO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2$

$\therefore$ BO $= \frac{1}{2}[10 - 4] = 3$

$CO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_x^2, \pi 2p_y^2; \pi 2p_z^2, \sigma^* 2s^1$

$\therefore$ BO $= \frac{1}{2}[10 - 3] = 3.5$

8. (b) $N_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2$

In N_2^+ : one bonding electron is less but in N_2^- one antibonding electron is more.
$\therefore$ N_2^+ is more stable than N_2^-.

9. (c) $F_2 \longrightarrow 2F$; $\Delta H = 158.8$ kJ mol^{-1}
$F + e \longrightarrow F^-$; $E_{ga} = -333$ kJ mol^{-1}

$2\,g\,F_2 = \frac{2}{40}$ mol F_2

$\therefore \Delta H = \frac{158.8 \times 2}{40} = 7.94$ kJ mol^{-1}

Also, $\frac{2}{40}$ mol $F_2 = 2 \times \frac{2}{40}$ g-atom of F
$= \frac{1}{10}$ g-atom of F

$\therefore E_{A(T)} = 333 \times \frac{1}{10} = 33.3$

$\therefore \Delta H$ for 2 g ($F_2 \longrightarrow 2F^-$) $= -33.3 + 7.94$
$= -25.36$ kJ

10. (a) $Li: 1s^2, 2s^1$ $n = 2$

$E_{Li} = \frac{Z^2}{n^2} \times E_H$, where Z is effective charge.

$\therefore Z = n\sqrt{\frac{E_{Li}}{E_H}} = 2 \times \sqrt{\frac{5.40}{13.6}} = 1.26$

11. (a) $AlCl_3$ is hypovalent but $AlCl_3$ completes its octet by coordinate bond forming Al_2Cl_6.

12. (c) Except BF_3 all have expanded octet.

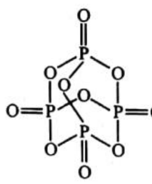
13. (d) Bond order for N_2^+, O_2^+ and NO is 2.5. For NO^+ it is 3.

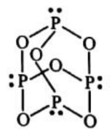
14. (a) Due to more +ve charge on N on account of more electronegativity of F.

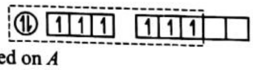
15. (a) Due to back bonding.

16. (a) C_2H_4 has sp^2-hybridised carbon and CO_2 has sp-hybridization.

17. (a) $XeOF_2$ has sp^3d-hybridization with two lone pairs of electrons leading trigonal by pyramid shape in T-shaped molecule.

18. (a) P_4O_{10} is  sp^2-hybridised P

19. (b) P_4O_6 is  sp^3-hybridised P

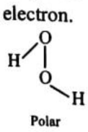
20. (c) A :  sp^3d^3 six B are attached on A

21. (c) NF_3 and H_3O^+ have sp^3-hybridization; NO_3^- and BF_3 have sp^2-hybridization.

22. (c) $\overline{C} \equiv \overline{C}$ bonding in CaC_2.

23. (b) p-dichlorobenzene is non-polar ($\mu = 0$), o-isomer has maximum dipole moment cos $\alpha = 60°$.

24. (c) KO_2 has $K^+O_2^-$ structure having one unpaired electron.

25. (c)  non-planar.

Polar

26. (b) S in SO_2 has sp^2-hybridization.

27. (d) More is dipole moment, more is attraction among molecules, more will be T_C.

28. (b) B in BF_3 has sp^2-hybridization and trigonal planar.

29. (a) S in H_2S shows sp^3-hybridization with angular V-shape due to the presence of two lone pairs on S-atom. Also, $\mu \neq 0$.

30. (b) BCl_3 is s^2-hybridised (120°); Rest all are sp^3-hybridised. Also angle decreases from P to Bi.

31. (d) $\overset{1}{\underset{sp^2}{CH_2}} = \overset{2}{\underset{sp^2}{CH}} - \overset{3}{\underset{sp^3}{CH_2}} - \overset{4}{\underset{sp^3}{CH_2}} - \overset{5}{\underset{sp}{CH}} \equiv \overset{6}{\underset{sp}{CH}}$

32. (d) In all biggest jump will be in $_4Be$ as 1s is closest to nucleus.

33. (b) After removal of I electron, next electron will be removed from $2p^6$.

34. (c) First *EA* are exothermic however in alkaline earth metals these are endothermic.

35. (c) He has completely filled 1s orbital.

36. (c) In O^- and S^-, EA_2 will be +ve because addition of electron is opposed by anionic sphere in each. Also repulsion will be more predominant in O^-.

37. (d) $Li_{(g)} \rightarrow Li^+_{(g)} + e$; IE = less +ve

$Li^+_{(g)} + Aq. \rightarrow Li^+_{aq}$; ΔH_h = more –ve due to small size of cation

$Li_{(g)} + Aq. \rightarrow Li^+_{aq}$; $\Delta H = -$ ve

38. (a) EA_1 of S > O; EA_1 of Cl > F ; EA_1 of N > F and EA_1 of B > EA_1 of C

39. (d) Rest all influence polarisation of anion.

40. (d) Addition of electron in anion is opposed by ionic sphere.

41. (d) After the removal of one electron in oxygen, it acquires half filled configuration, *i.e.*, O^+ $1s^2, 2s^2sp^3$

42. (a) Follow text.

43. (a) Ne : $1s^2, 2s^2 2p^6$

$Na^+ : 1s^2, 2s^2 2p^6$ Shielding effect will be same.

44. (c) $IE\ \text{Na} = \dfrac{IE\ \text{K} + IE\ \text{Li}}{2}$

45. (d) The basic nature is $CH_3^- > NH_2^- > OH^- > F^-$

46. (c) K^+ and $[C \equiv N]^-$

47. (b) H–O–H; H has duplet of electron.

48. (a) X^+Y^- as *X* loses electron

49. (a) H — H

50. (c) $:N \equiv N:$

51. (b) Due to H-bonding

52. (b) *eg.* CO_2 or BeF_2

53. (a) CN^- and CO both have 14 electrons.

54. (a) *sp*-hybridisation O = C = O

55. (b) Net μ = 0 due to regular tetrahedron geometry.

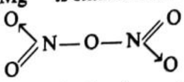
56. (d) H-bonding is observed if H is attached on N, O or F atoms.

57. (c) $[Cu(H_2O)_4]^{2+} \cdot SO_4 \cdot H_2O$

58. (b) *sp*-hybridisation has 180° angle.

59. (a) NO has 15 electrons

60. (b) Mg^{2+} is smaller than Na^+ and has more charge

61. (b) 

62. (d) Non polar bond *e.g.*, H–H

63. (c) F–H > O–H > N–H

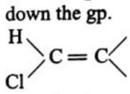
64. (c) $O = \underset{sp^2}{S} = O$

65. (a) Diethyl ether, ethyl chloride and triethyl amine do not show H-bonding.

66. (a) IE_1 of N > IE_1 of O due to half filled nature of orbitals in N.

67. (a) F has covalent radius whereas Ne has van der Waals' radius. Covalent radius is smaller.

68. (c) Electronegativity increases along the period, decreases down the gp.

69. (c)  $\mu = 0$

70. (c) $N \equiv \overset{1}{\underset{sp}{C}} - \overset{2}{\underset{sp^2}{CH}} = \overset{3}{\underset{sp^2}{CH_2}}$

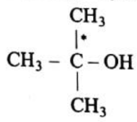
71. (a) Ionisation energy order ; *IE* of Al < *IE* of Mg due to ellipticity.

72. (c) CH_3^+ has sp^2-hybridisation.

73. (a) Due to *sp*-hybridisation

74. (b) μ_{Total} = 0 due to coplanar (sp^2) geometry.

75. (a) Due to sp^3-hybridisation with one lone pair on P atom.

76. (c)  , $C^\bullet$ has 4σ-bonds.

77. (a) O_2 is paramagnetic has two unpaired electrons.

78. (b) Half filled nature. Also *IE* decreases down the gp

79. (c) $H\overset{4}{C} \equiv \overset{3}{\underset{sp}{C}} - \overset{2}{\underset{sp^2}{CH}} = \overset{1}{CH_2}$

80. (a) Cl in ClO_3^- has sp^3-hybridisation.

81. (b) $\overset{4}{H} - \underset{2}{\overset{1}{\ddot{\underset{\cdot\cdot}{O}}}} - \overset{3}{H}$

82. (b) CN^- is polar; N_2 is non polar.

83. (c) $CH_2 = CH - CH_2 - C \equiv N$; 9σ, 3π and 2 non bonding electrons on N.

84. (c) Lowest oxidation states of metals are more ionic.

85. (d) O_2 has 16 electrons out of which two are unpaired.

86. (c) $CsBr_3$ has Cs^+ and Br_3^- ions

87. (c) KHF_2 has K^+ and $[HF_2]^-$ ions

88. (a) $HO-\underset{sp^2}{\overset{\overset{\displaystyle O}{||}}{C}}-OH$ and polar

89. (b) $O=S=O$

90. (b) Removal of 2nd electron from 3*s* in Mg and 2*p* in Na (more closer)

$\therefore$ IE_2 of Na > IE_2 of Mg

91. (b) sp^2 leads to coplanar trigonal geometry of BF_3

92. (d) Follow resonance

93. (d) Due to more effective nuclear charge on P^{5+}, the radii decreases.

94. (d) $\underset{sp^2}{\overset{1}{CH_2}}=\underset{sp^2}{\overset{2}{CH}}-\underset{sp^3}{\overset{3}{CH_2}}-\underset{sp^3}{\overset{4}{CH_2}}-\underset{sp}{\overset{5}{C}}\equiv\underset{sp}{\overset{6}{CH}}$

95. (b) Each has 10 electrons. The size of isoelectronic decreases along the period

96. (d) SF_4 has sp^3d-hybridization with one lone pair, CF_4 has sp^3-hybridization with no lone pair and XeF_4 has sp^3d^2-hybridization with two lone pairs.

97. (b) The hybridised states of N in NO_2^+, NO_3^- and NH_4^+ are *sp*, sp^2 and sp^3 respectively.

98. (a) It is a reason for given fact.

99. (b) N in NH_3 (sp^3), Pt in $[PtCl_4]^{2-}$ (dsp^2), P in PCl_5 (sp^3d) and B in BCl_3 (sp^2).

100. (a) Each possesses 14 electrons with bond order 3.

101. (b) The IE_1 decreases down the gp

102. (a) $\underset{sp^3}{NH_3}+\underset{sp^2}{BF_3}\longrightarrow[\underset{sp^3}{H_3N}\longrightarrow\underset{sp^3}{BF_3}]$

103. (b) $Li^-: 1s^2, 2s^2$ (EA_1 = –ve)

$Be^-: 1s^2, 2s^2 2p^1$ (EA_2 = +ve)

104. (c) O_2^- has one unpaired electron.

105. (a) A π-bond nodel plane passing through the two bonded nuclei, *i.e.*, molecular plane.

106. (a) $\mu_{CCl_4}=0, \mu_{CHCl_3}=1.0\,D, \mu_{CH_2Cl_2}=1.6\,D,$

$\mu_{CH_3Cl}=1.8\,D$

107. (a) Both NO_3^- and CO_3^{2-} have 32 electrons and central atom in each is sp^2-hybridized.

108. (a) $\underset{sp^2}{CH_2}=\underset{sp^2}{CH}-\underset{sp}{C}\equiv\underset{sp}{CH}$

109. (b) Xe in $XeOF_4$ shows sp^3d^2-hybridization with one lone pair on Xe-atom.

110. (b) Both O_2^+ and O_2 are paramagnetic : Bond order of $O_2=2$, Bond order $O_2^+=2.5$.

111. (d) I_3^-, XeF_4, SF_4 and ClO_3^- have 3, 2, 1, 1 lone pair of electrons respectively.

112. (a) Due to synergic bond formation between CO and metal, C—O bond length increases.

113. (b) Bond order of CO is 3 and of NO^+ is 2.5.

114. (d) It has O_2^{-1} in having one unpaired electron.

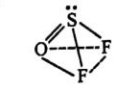
115. (d) P_4 has sp^3-hybridization: *s*-character 25%, *p*-character 75%

116. (a) Follow text

117. (c) Basic character of hydrides $NH_3 > PH_3$.

118. (b) Follow characteristics of resonance

119. (d) Due to sp^3-hybridisation of *S* and one lone pair.



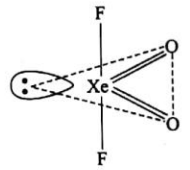
120. (a) In absence of Hund's rule, molecular orbital diagram of B_2 will be :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2$$

121. (b) The different hybridization in C_3H_4 ($H_2C=C=CH_2$) are :

$$\underset{}{\overset{sp^2}{H_2C}}=\overset{sp}{C}=\overset{sp^2}{CH_2}$$

122. (d) Xenon in XeO_2F_2 shows sp^3d-hybridization having one lone pair of electron



sp^3d-hybridization (see-saw)

123. (c,d) Both (C_2 and N_2) are diamagnetic as both have no unpaired electron

M.O. configuration of

$$C_2: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}$$

M.O. configuration of

$$N_2: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \sigma 2p_x^2$$

O_2 and S_2 both have two unpaired electrons.

124. (a) Both H_2^{2+} and He_2 ($\sigma 1s^2 \sigma^* 1s^2$) have bond order zero.

125. (a) Ionisation enthalpy increases along the period but decreases down the group.

126. (d) Bond order for Li_2, Li_2^+ and Li_2^- are 1, 0.5, 0.5 respectively. However Li_2^+ (one antibonding electron) is more stable than Li_2^- because Li_2^- has three antibonding electrons.

127. (d) $Na(g)\longrightarrow Na^+(g)+e$; IE = 5.1eV

$Na^+(g)+e\longrightarrow Na(g)$; $EA=-IE=-5.1$ eV

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statements :
   (a) Ionisation energy increases for each successive electron removal.
   (b) The greatest increase in ionisation enthalpy is experienced on removal of electron from the case of noble gas.
   (c) End of valence electrons is marked by a big jump in ionisation enthalpy.
   (d) Removal of electron from orbitals bearing lower *n* values is easier than from orbital having higher *n* value.
2. Which of the following compounds have electrovalent, covalent and coordinate bonds but do not have hydrogen bond?
   (a) $CaCl_2 \cdot 2H_2O$ (b) $CuSO_4 \cdot 5H_2O$
   (c) $FeSO_4 \cdot 7H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$
3. Which are correct about the structure of trimer of SO_3, *i.e.*, S_3O_9?
   (a) It has cyclic structure
   (b) It has two S—S bonds
   (c) It has three S—O—S bonds
   (d) It has sp^2-hybridization of S and 12σ and 6π-bonds
4. Which are correct for white phosphorus molecule?
   (a) It exists as P_4
   (b) P—P bond length equal to 2.21 Å
   (c) P—P bond angle is 109°28′
   (d) It has sp^3-hybridization and tetrahedron structure
5. Which of the following are correct about bond angles?
   (a) $OSF_2 < OSCl_2 < OSBr_2$
   (b) $SbI_3 < AsI_3 < PI_3$
   (c) $PF_3 > PCl_3 < PBr_3 < PI_3$
   (d) $NO_2^- < NO_2 < NO_2^+$
6. Which of the following are correct for CO^+, N_2^+ ?
   (a) Both have 13 electrons
   (b) N_2^+ has bond order 2.5 whereas CO^+ has bond order 3.5
   (c) Both have same M.O. configuration
   (d) Bond length of N—N in N_2^+ is greater than N_2 but bond length of CO^+ is shorter than CO
7. Which facts are correctly represented?
   (a) Bond length : $NO^+ < NO^{2+} < NO < NO^-$
   (b) Bond order : $NO^+ > NO^{2+} = NO > NO^-$
   (c) Bond length : $NO^+ < NO^{2+} = NO < NO^-$
   (d) Bond order : $NO^+ > NO^{2+} > NO > NO^-$
8. In which of the following H-atom attached on carbon atom shows H-bonding?
   (a) $CCl_3 \cdot CH(OH)_2$
   (b) $CHCl_3$ in acetone
   (c) $CH_3 \cdot CO \cdot CH_3$
   (d) $CH_3 \cdot CO \cdot CH_2COOC_2H_5$
9. Which of the following are correct?
   (a) PH_5 and $BiCl_5$ does not exist
   (b) SeF_4 and CH_4 have same geometry
   (c) $p\pi - d\pi$ bonds are present in SO_2
   (d) Nodal plane in the π-bonds of ethane are located in molecular plane
10. Select the correct statements :
    (a) IE_1 of deuterium is more than IE_1 of H
    (b) maximum electron affinity exists for F
    (c) maximum *IE* stands for He
    (d) *trans*-pent-2-ene is polar
11. Select the correct statements :
    (a) There are two π-bonds in N_2 molecule
    (b) Delocalisation involving sigma bonds orbitals is called hyperconjugation
    (c) Dipole moment of CH_3F is greater than CH_3Cl
    (d) C_2H_2, CO_2, $SnCl_2$ all are linear molecules
12. Resonance molecule should have:
    (a) identical arrangement of atoms
    (b) nearly same energy content
    (c) the same number of paired electrons
    (d) identical bonding
13. Dipole moment is shown by:
    (a) 1, 4-dichloro ethane
    (b) *cis*-1,2-dichloro ethane
    (c) *trans*-1 2-dichloro ethane
    (d) 1, 2-dichloro-2-pentene
14. CO_2 is isostructural with:
    (a) $HgCl_2$ (b) $SnCl_2$
    (c) C_2H_2 (d) NO_2
15. Which of the following are correct:
    (a) The ionisation potential of oxygen is less than that of nitrogen
    (b) The ionisation potential of nitrogen is greater than that of oxygen
    (c) The two ionisation potential values are comparable
    (d) The differences between the two ionisation potential values is too large
16. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because:

(a) The hydration energy of Na_2SO_4 is more than its lattice energy
(b) The lattice energy of $BaSO_4$ is more than its hydration energy
(c) The lattice energy has no role is solubility
(d) The hydration energy of Na_2SO_4 is less than its lattice energy

17. The linear structure is assumed by:
(a) $SnCl_2$ (b) NCO^-
(c) CS_2 (d) NO_2^+
(e) SO_2

18. Which of the following have identical bond order?
(a) CN^- (b) O_2^-
(c) NO^+ (d) CN^+

19. The molecules that will have dipole moment are:
(a) 2, 2-dimethylpropane
(b) *trans*-2-pentene
(c) *cis*-3-hexene
(d) 2,2,3,3-tetramethylbutane

20. Pick out the isoelectronic structrues from the following:
I CH_3^+ II H_3O^+
III NH_3 IV CH_3^-
(a) I and II (b) III and IV
(c) I and III (d) II, III and IV

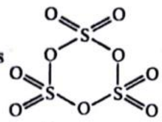
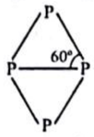
21. *A, B* and *C* are hydroxy compounds of the elements *X, Y* and *Z* respectively. *X, Y* and *Z* are in the same period of periodic table. A gives an aqueous solution of pH less than 7. *B* reacts with both strong acid and strong base. *C* gives an aqueous solution which is strongly basic. Which of the following statements is/are true?
(a) The three elements are non-metal
(b) The electronegativities decrease from *X* to *Z*
(c) The atomic radius decreases in the order $Z > Y > X$
(d) *X, Y* and *Z* may be phosphorous, aluminium and potassium respectively

22. Which of the following statement is incorrect?
(a) O_2 is paramagnetic, O_3 is also paramagnetic
(b) O_2 is paramagnetic N_2^{2+} is also paramagnetic
(c) B_2 is paramagnetic, C_2 is also paramagnetic
(d) Different observation is found in their bond length when $NO \longrightarrow NO^+$ and $CO \longrightarrow CO^+$

23. Which of the following statement(s) is/are correct?
(a) The removal of one electron from $Na^+(g)$ ion requires more energy than that from $Mg^+(g)$
(b) The hydration energy of Na^+ ion is more than that of K^+ ion
(c) Ionic radii follows the order for three elements (*X, Y, Z*) of same period belonging to group 1, 2 and 3 (*i.e.,* IA, IIA and IIIA) in the periodic table is $X^+ > Y^{2+} > Z^{3+}$.
(d) With the increasing electronegativity (which increases with increasing positive charge), the basic strength of any elemental oxide decreases

24. Which of the following shows same hybridized state :
(a) central N atom of azide ion (N_3^-)
(b) N atom in NO_2F
(c) central O atom of ozone
(d) N atoms in N_2F_2

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c) Lower is the value of n higher is the energy.
2. (a,c,d) $CuSO_4 \cdot 5H_2O$ has $[CuSO_4 \cdot H_2O]4H_2O$.
3. (a,c,d) S_3O_9 has 
4. (a,b,d) P_4 is  The molecule is under strain and active in nature due to bond angle 60°
5. (a,b,c,d) Follow concepts of bonding (in concepts of physical chemistry by P. Bahadur, Prakash Publications, Muzaffarnagar).
6. (a,b,d) $N_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}, \sigma 2p_x^2$

$$CO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}, \sigma^* 2s^1$$

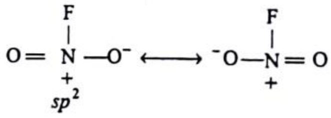
$2s$-orbital of O-atom has lower energy than $2s$-orbital of C-atom. When they mix to form $\sigma 2s$ an $\sigma^* 2s$-orbitals, the latter has so high energy that it goes above $\sigma 2p_x$ as well as $\pi 2p_y$ and $\pi 2p_z$.

7. (a,b) NO^{2+} has one antibonding electron less than NO and thus bond length in NO is more

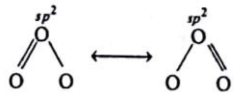
$$NO : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \sigma 2p_x^2, \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}, \pi^* 2p_y^1$$

8. (a,b) Due to increasing charge density of carbon on account of higher electronegativity of Cl.
9. (a,c,d) SeF_4 (sp^3d), CH_4 (sp^3)
10. (a,b,c,d) Follow concepts.
11. (a,b,c) $SnCl_2$ is angular due to sp^2-hybridization.
12. (a,b,c) These are characteristics of resonance.
13. (b,d) μ for $(a) = 0$ and μ for $(c) = 0$.
14. (a,c) Both has sp-hybridization
15. (a,b,c) These are facts.
16. (a,b) These are facts.
17. (b,c) Both are linear.
18. (a,c) Bond order for both is 3.
19. (b,c) μ for $(a) = 0$, μ for $(d) = 0$ due to symmetry.
20. (b,d) These have sp^3-hybridization.
21. (b,c) X is non metal. (*e.g.*, O_3Cl—OH—acidic)
    Y is amphoteric (*e.g.*, $Al(OH)_3$ —amphoteric)
    Z is metal (*e.g.*, KOH—basic)
22. (b,d) Follow text.
23. (a,b,c,d) —do—
24. (b,c,d) The central atom of azide ion has sp-hybridisation.

$$^-N = \overset{sp}{N} \overset{\rightarrow}{=} N;$$



$$F - \underset{sp^2}{N} = \underset{sp^2}{N} - F$$



COMPREHENSION BASED PROBLEMS

Comprehension 1 : Dipole moment of a bond is a vector and physical quantity to calculate the percentage ionic character in a covalent bond. It is expressed as :

$$\text{Dipole moment } (\mu) = \overrightarrow{\partial \times d}$$

where, δ is dipole moment and d is the bond length

It is usually expressed in terms of CGS unit known as Debye (D) $1\text{ D} = 10^{-18}$ esu cm. In SI unit it is expressed in Coulomb meter. Resultant dipole moment (μ_R) of two bond moments (μ_1 and μ_2) acting at an angle θ, is given by :

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

If $\mu_1 = \mu_2$, Also if $\cos\theta = -1$, *i.e.*, $\theta = 180°$ then $\mu = 0$. (molecule is non polar)

If $\mu \neq 0$ molecule is polar.

Dipole moment plays an important role in deciding the stability order of alkanes, *i.e.*, a more stable alkane has less dipole moment. The dipole moment of a molecule can predict the geometrical and position isomers as well as orientations in benzene nucleus and polarity of molecule.

[1] Dipole moment of HCl molecule is found to be 0.816 D. Assuming HCl bond length to be equal to 1 Å, the % ionic character of HCl molecule is:
(a) 10% (b) 17%
(c) 27% (d) 37%

[2] The correct increasing order of dipole moment of the following compounds is,
I Toluene; II *o*-dichlorobenzene;
III *m*-dichlorobenzene; IV *p*-dichlorobenzene
(a) I<II<III<IV (b) IV<I<III<II
(c) I<IV<III<II (d) IV<I<II<III

[3] Dipole moment of
(1) *p*-dinitrobenzene (2) *p*-dichlorobenzene and
(3) *p*-dimethoxybenzene are in the order:
(a) 3 > 2 > 1 (b) 3 = 2 > 1
(c) 3 = 2 = 1 (d) 3 > (2 = 1)

[4] Match the compounds in list-I with their correct values of dipole moment in list-II :

List-I Compound	List-II Dipole moment (D)	
1. *o*-nitrophenol	(A)	0.05
2. *o*-dichlorobenzene	(B)	1.00
3. *o*-xylene	(C)	1.20

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

[5] Identify the correct increasing order of the stability of the following alkenes, I *cis*-2-butene; II *trans*-2-butene; III isobutene:
(a) II<III<I (b) I<III<II
(c) I<II<III (d) III<II<I

[6] Which of the following species is non polar?
(a) Ammonia (b) Sulphur dioxide
(c) Water (d) Sulphur trioxide

[7] The increasing order of dipole moment of bond in halogen acids is:
(a) HF > HCl > HBr > HI (b) HI > HCl > HBr > HF
(c) HCl > HBr > HI > HF (d) HI > HBr > HF > HCl

[8] Which molecule is non polar?
(a) *trans*-Pent-2-ene (b) *cis*-Pent-2-ene
(c) *cis*-1-chloropropene (d) SF_6

[9] Which species is polar?
(a) *trans*-Hex-3-ene (b) *trans*-But-2-ene
(c) PCl_5 (d) XeF_6

SOLUTIONS

Comprehension 1

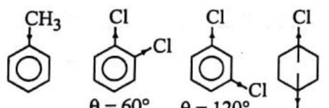
[1]. (b) $\mu_m = \overrightarrow{\delta \times d}$

$0.816 \times 10^{-18} = \delta \times 10^{-8}$

$\therefore \delta = 0.816 \times 10^{-10}$ esu

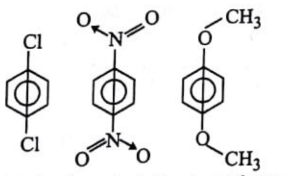
$\therefore$ % ionic character $= \dfrac{0.816 \times 10^{-10}}{4.803 \times 10^{-10}} \times 100 = 16.9\%$

[2]. (b)



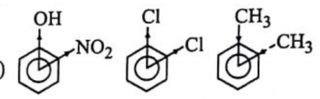
θ = 60° θ = 120° θ = 180°

[3]. (d)

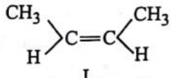


Notice the orientation in methoxy group.

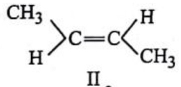
[4]. (c)



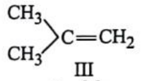
[5]. (d)



I
μ = Less than III



II
$\mu = 0$



III
μ = Max

The stability order is
cis-2-butene > *trans*-2-butene > isobutene

[6]. (d) SO_3 has sp^2-hybridization and three equal vectors acts at 120°.

[7]. (a) The electronegativity order is F > Cl > Br > I.

[8]. (d) SF_6 has octahedral geometry having $\mu = 0$.

[9]. (d) XeF_6 has sp^3d^3-hybridization and pentagonal pyramidal nature.

STATEMENT-EXPLANATION PROBLEMS

In each sub question given below a statement (**S**) and explanation (**E**) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but **E** is wrong
(b) S is wrong but **E** is correct
(c) Both S and **E** are corect and **E** is correct explanation of **S**
(d) Both S and **E** are correct but **E** is not correct explanation of S

1. S : Cs and F_2 reacts violently.
E : Cs is most electropositive and F_2 is most electronegative.

2. S : Transition elements exhibit horizontal and vertical relationship.
E : The shielding effect as well as same outermost shell configuration in transition metals are responsible for their behaviour.

3. S : $BiCl_5$ does not exist.
E : In Bi inert pair effect is predominant.

4. S : Bond order for CO^+ is more than bond order in CO whereas bond order in N_2^+ is less than N_2 whereas both are isoelectronics.
E : Both have same bond order.

5. S : Bond order for N_2^+ and N_2^- are same but N_2^+ is more stable than N_2^-.
E : Antibonding electrons are more in N_2^-.

6. S : The bond angles in NO_2^+, NO_2 and NO_2^- are 180°, 134° and 115° respectively.
E : Bond angles in a molecule also depends upon the presence of lone electron as well as lone pair of electron.

7. S : Bond angle of $PF_3 > PCl_3$ but bond angle of $PCl_3 < PBr_3$.
E : The bond angles show an increase on decreasing electronegativity of attached other atom on central atom but in PF_3 $p\pi - d\pi$ bonding results in an increase in bond angle.

8. S : Although carbon in HCHO is sp^2-hybridized and all the three bond angles are 120°C.
E : In HCHO, presence of multiple bond gives rise two bond angle. < HCO is 122° and < HCH is 116°.

9. S : N_2O is represented by (i) $N=N=O$ and (ii) $N \equiv N \rightarrow O$ but later is more stable.
E : The form (ii) shows resonance.

10. S : CS_2 is linear whereas H_2S is non-linear.
E : C in CS_2 is *sp*-hybridized whereas S in H_2S is sp^3-hybridized.

11. S : Nitric oxide, though an odd electron molecule is diamagnetic in liquid state.
E : There occurs only partial dimerisation of NO to N_2O_2.

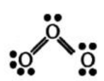
12. S : All the Al—Cl bonds in Al_2Cl_6 are equivalent.
E : The terminal Al—Cl bonds are different from bridge Al—Cl bonds.

13. S : Bond dissociation energy of F_2 is lesser than Cl_2.
E : An additional π-bond formation is created by donor-acceptor mechanism in Cl_2 in which an unshared electron of one Cl-atom overlaps with a free 3*d*-orbital electron of another Cl-atom.

14. S : LiCl is predominantly a covalent compound.
E : Electronegativity difference between Li and Cl is too small.

15. S : The electronic structure of O_3 is:

E :



structure of O_3 is not allowed.

16. S : Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.
E : Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}

17. S : Helium and Beryllium have similar outer electronic configuration.
E : Both are chemically inert.

18. S : The size decreases as $Pb > Pb^{2+} > Pb^{4+}$.
E : The nuclear charge/electron increases, *i.e.*, the force of attraction towards nucleus increases.

19. S : The S—S—S bond angle in S_8 molecule is 105°.
E : S_8 has V-shape.

20. S : O—O bond length in H_2O_2 is shorter than that of O_2F_2.
E : H_2O_2 is a covalent compound.

21. S : Fluorine molecule has bond order one.
E : The number of electrons in antibonding molecular orbitals is two less than in bonding molecular orbitals.

22. S : The dipole moment helps to predict whether molecule is polar or non-polar.
E : The dipole moment helps to predict the geometry of molecules.

23. S : All F—S—F bond angles in SF_4 are greater than 90° but lesser than 180°.
E : The lone pair-bond pair repulsion is weaker than bond pair-bond pair repulsion.

24. S : N_2 and NO^+ both are diamagnetic substances.
E : NO^+ is isoelectronic to N_2.

25. S : The bond angle of PBr_3 is greater than PH_3 but the bond angle of NBr_3 is lesser than NH_3.
E : Electronegativity of P-atom is less than that of N-atom.

26. S : CaF_2 is soluble in water but CaI_2 not.
E : CaF_2 is more ionic than CaI_2.

27. S : O_3 and NO_2^- are isoelectronic.
E : Bond angles of O_3 and NO_2^- are 116.8° and 115° respectively.

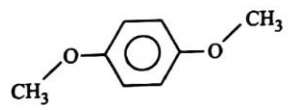
28. S : NO_2 is readily dimerised to N_2O_4.
E : NO_2 has one unpaired electron and two such electrons with opposite spin in two NO_2 molecules forms bond between two N-atoms readily.

29. S : Both Cu^+ and Na^+ have almost same radii.
E : Cu^+ possesses more power to polarise an anion.

30. S : IE_1 for He is maximum and EA_1 for Cl is more than EA_1 of F.
E : He possesses paired electrons in 1*s* sub-shell, closest to nucleus, whereas electron density in F is maximum which exerts more electron-electron repulsion.

31. S : If difference of electronegativity between two atoms is zero the resultant molecule will be non-polar covalent.
E : The shared pair of electron lies just in the middle of two atoms.

32. S : *p*-dimethoxy benzene is polar molecule.
E : The two methoxy groups at para positions are located as



33. S : The lattice energy of silver halides is
AgF > AgCl > AgBr > AgI.
E : AgF is water soluble

34. S : The molecule *cis*-1-chloropropene is more polar than *trans*- 1-chloropropene.
E : The magnitude of resultant vector in *trans*-1-chloro- propene is non-zero.

35. S : IF_7 is super octet molecule.
E : Central atom of I in IF_7 has 14 electrons.

36. S : $FeCl_2$ is more covalent than $FeCl_3$ because electronegativity of $Fe^{3+} > Fe^{2+}$.
E : Higher is the charge on cation, more is deformation of anion, more is covalent character.

37. S : MO configuration of CO is
$\sigma 1s^2, \sigma^* 1s^2\, \sigma 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \sigma^* 2s^2$.
E : The bond energy level $\sigma^* 2s^2$ possesses higher energy because then only bond length order for CO (more) and CO^+ (less) can be explained.

38. S : The dipole moment of NH_3 is less than NF_3.
E : The lone pair present on N shows additive nature to N—H vector whereas it is subtractive to N—F vector.

39. S : The bond energy of P—Cl bond in PCl_3 and PCl_5 are different.
E : In $PCl_3, sp^3 - p$ overlapping whereas in $PCl_5, sp^3d - p$ overlapping is noticed.

40. S : SF_4 has lone pair of electron at equatorial position in preference to apical position in the overall trigonal bipyramidal geometry
E : If lone pair is at equatorial position then only repulsion is minimum.

41. S : BF_3 molecule is planar with an angle of 120°C.
E : BF_3 has bond pair-lone pair electron ratio 1 : 3.

42. S : N and P show a maximum covalency of five.
E : P can expand the outer shell of electrons beyond an octet by involving *d*-orbitals present in its valence shell.

43. S : All molecules with polar bond have dipole moment.
E : Dipole moment is a vector quantity.

44. S : PCl_5 conducts current in solid state.
E : PCl_5 exists as $[PCl_4]^+$ and $[PCl_6]^-$ ions.

45. S : EA_2 for halogens is endothermic.
E : Halogens have ns^2np^5 configuration and can accommodate only one electron.

46. S : F atom has less electron affinity than Cl atom.
E : Additional electrons are repelled more effectively by 3*p*-electrons in Cl atom than by 2*p*-electrons in F atom.

47. S : The ionisation energy of ${}_1H^2$ is more than ionisation energy of ${}_1H^1$.
E : This is due to isotopic effect.

48. S : Solubility of NaOH in water increases with rise in temperature, although it is exothermic dissolution.
E : Changes showing exothermic nature occurs in backward direction if temperature is raised.

49. S : Solubility of NaCl in D_2O is less than, H_2O.
E : Higher viscosity of D_2O is responsible for low solubility of NaCl.

50. S : NH_3 and CH_3^- both have pyramidal shape.
E : N in NH_3 and C in CH_3^- both have sp^3-hybridisation with one lone pair of electron on each.

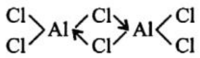
51. S : The bond angle in H_2O is greater than H_2S.
E : H-bonding does not occur in H_2S due to low electronegativity of S.

52. S : The bond angle in BF_3 is smaller than that in BF_4.
E : BF_3 has sp^2-hybridisation, whereas BF_4^- has sp^3-hybridisation.

53. S : The first ionisation energy of N is greater than O.
E : N atom has half filled *p*-orbitals.

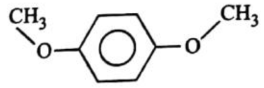
54. S : The first ionisation energy of Be is greater than that of B. **[IIT 2000]**
E : 2*p*-orbital is lower in energy than 2*s*-orbital.

ANSWERS (Statement Explanation Problems)

1. (c) Explanation is correct reason for statement.
2. (c) —do—
3. (c) —do—
4. (a) Both N_2 and CO have different MO configuration but bond order is same which results a change in N_2^+ and CO^+ configuration and thus, bond order of N_2^+ and CO^+ are different.
5. (c) Explanation is correct reason for statement.
6. (c) —do—
7. (c) —do—
8. (b) It is a fact.
9. (a) Form II is more stable due to lesser formal charge on N-atom.
10. (c) Explanation is correct reason for statement.
11. (b) It is an experimental fact.
12. (b) Al_2Cl_6 has the structure. 
13. (c) Explanation is correct reason for statement.
14. (a) LiCl is covalent due to high polarising power of Li^+.
15. (d) Both are correct.
16. (d) $BaSO_4$ is insoluble. $MgSO_4$ is soluble.
17. (a) Be is reactive metal.
18. (c) Explanation is correct reason for statement.
19. (a) S_8 has puckered ring structure.
20. (b) O—O bond is H_2O_2 and O_2F_2 are same.
21. (c) Explanation is correct reason for statement.
22. (c) Explanation is correct reason for statement.
23. (a) Bond angles in $SF_4(sp^3d^2)$ are 116°.
24. (d) Both statements are correct.
25. (d) —do—
26. (b) CaF_2 is insoluble in water but more ionic having high lattice energy due to small size of F^-.
27. (d) Both are correct. The difference in bond angle is due to lone pair-bond pair repulsion in O_3 and lone electron-bond pair repulsion in NO_2^-.
28. (c) Since the process does not require any rearrangement and thus energy of activation for dimerisation of NO_2 is low.
29. (d) The more power of Cu^+ to polarise an anion is due to its pseudo noble gas structure.

$$r_{Cu^+} = 0.96Å; r_{Na^+} = 0.95Å$$

30. (c) Explanation is correct reason for statement.
31. (c) Explanation is correct reason for statement.
32. (a) *p*-dimethoxy benzene is polar due to orientation of CH_3 group as, the resultant vector is not zero.



33. (d) Inspite of higher lattice energy AgF is soluble because F^- is extensively hydrated and heat of hydration predominates over lattice energy.
34. (b) Both *cis*-and *trans*-forms are polar. *Trans* is more polar due to higher value of dipole moment due to additive nature of CH_3 and Cl vectors.
35. (c) Explanation is correct reason for statement.
36. (b) This is Fajans' rule. $FeCl_3$ is more covalent.
37. (c) Explanation is correct reason for statement.
38. (b) That is why $\mu_{NH_3} > \mu_{NF_3}$.
39. (c) Explanation is correct reason for statement.
40. (c) Explanation is correct reason for statement.
41. (d) BF_3 is planar due to sp^2-hybridisation.Also in BF_3, three bond pair on boron atom and 9 lone pairs of electrons on F atoms.
42. (b) N shows maximum covalence of +3 along with one coordinat bond whereas P shows maximum covalence of +5 due to given explanation.
43. (b) Molecules having polar bonds may (*e.g.*, ClF_3 polar) or may not (*e.g.*, BF_3) have dipole moment. The resultant vector of bond moment decides the net dipole moment in molecule.
44. (b) Solid ionic compounds conduct current only in fused state. PCl_5 in solid state exists as $[PCl_6]^-[PCl_4]^+$.
45. (b) Halogens can have only EA_1 value because they can accommodate only one electron (ns^2np^5 to ns^2np^6): No scope for further addition, thus EA_2 for halogens is zero.
46. (a) Electron affinity of F < Electron affinity of Cl. Due to more 2*p*-test electron repulsion in F atom.
47. (c) Explanation is correct reason for statement.
48. (d) Assertion is an experimental fact observed against Le Chatelier principle.
49. (c) Explanation is correct reason for statement.
50. (c) Explanation is correct reason for statement.
51. (d) The bond angle in H_2S is smaller because S atom has bigger size than O.Also H_2S does not show H-bonding.
52. (b) In sp^2-hybridisation bond angle is 120°. In sp^3 it is 109°28′.
53. (c) Removal of electron from N atom requires more energy due to half filled *p*-orbital in N atom.
54. (a) Energy level of 2*s* is lesser than 2*p*-orbital.

MATCHING TYPE PROBLEMS

Type I : Only One Match Are Possible

1.

List A	List B
(A) Melting point	(i) $O^{2-} < O^- < O < O^+$
(B) Thermal stability	(ii) $F^- < Cl^- < Br^- < I^-$
(C) Polarisability	(iii) $HI < HBr < HCl < HF$
(D) Electron affinity	(iv) $XeF_6 < XeF_4 < XeF_2$

2.

List A	List B
(A) SO_2Cl_2	(i) Paramagnetic
(B) Ice	(ii) Refrigerant
(C) $CuSO_4$ (anhy.)	(iii) Testing NH_3
(D) $K_2HgI_4 + NaOH$	(iv) Testing H_2O
(E) Fluorocarbons	(v) H-bonding
(F) NO	(vi) Tetrahedral

Type II : More Than One Match Are Possible

3.

List A	List B
(A) B_2	(p) Paramagnetic
(B) N_2	(q) Undergoes oxidation
(C) O_2^-	(r) Undergoes reduction
(D) O_2	(s) Bond order ≥ 2
	(t) Mixing of s and p-orbitals

[IIT 2009]

4.

List A	List B
(A) sp^3-hybridisation	1. NH_3
(B) Lone pair effect	2. Diethyl ether
(C) Heteromolecular species	3. H_2O
(D) Paramagnetism	4. N_2O
(E) Dipole moment	5. O_2
(F) H-bonding	6. N_2^-

Type III : Only One Match From Each List

5.

List A	List B	List C
A. See-saw	1. I_3^-	a. ClF_3
B. T-shaped	2. e^{-2}	b. CS_2
C. Linear	3. IF_4^+	c. 0.14
D. Ratio of probable density of electron at $r = a_0$ and $r = 0$	4. $XeOF_2$	d. 0.018
E. Ratio of probable density of electron at $r = 2a_0$ and $r = 0$	5. e^{-4}	e. SF_4

6.

List A	List B	List C
A. Electrovalent bonding	a. Kossel and Lewis	1. Ions
B. Covalent bonding	b. Lewis	2. Polarity
C. Singlet linkage	c. Sugden	3. One sided sharing of 'e'
D. Co-ordinate bonding	d. Menzies	4. One sided sharing of 'e' pair
E. Valence bond theory	e. Heitlor and London	5. Hybridization
F. Molecular orbital theory	f. Hund -Mulliken	6. Paramagnetism

7.

List A	List B	List C
A. PCl_5	a. sp^3d	1. Linear
B. $BeCl_2$	b. sp	2. Trigonal bipyramids
C. NH_3	c. sp^3	3. Pyramidal
D. XeF_4	d. sp^3d^2	4. Square planar
E. XeF_6	e. sp^3d^3	5. Pentagonal pyramid

8.

List A	List B	List C
A. XeF_4	1. sp^3d^2	a. V-shaped
B. $HgCl_2$	2. sp^3d	b. See-saw
C. I_3^-	3. sp	c. T-shaped
D. NO_2^-	4. sp^2	d. Tetrahedral
E. ClO_4^-	5. sp^3	e. Linear
F. $XeOF_3$		f. Square planar
G. ICl_4^-		
H. ICl_2^-		
I. $TeCl_4$		

ANSWERS

1. A – iv; B – iii; C – ii; D – i
2. A – (vi); B – (v); C – (iv); D – (iii); E – (ii); F – (i)
3. A–p, q, r, t; B–q, r, s, t; C–p, q, r, t; D–p, q, r, s, t
4. A – 1, 2, 3; B – 1, 2, 3; C – 1, 2, 3, 4; D – 4, 5, 6; E – 1, 2, 3, 4; F – 1, 3
5. A – 3 – e; B – 4 – a; C – 1 – b; D – 2 – c; E – 5 – d
6. A – a – 1; B – b – 2; C – c – 3; D – d – 4; E – e – 5; F – f – 6
7. A – a – 2; B – b – 1; C – c – 3; D – d – 4; E – e – 5
8. A – 1 – f; B – 3 – e; C – 2 – e; D – 4 – a; E – 5 – d; F – 2 – c; G – 1 – f; H – 2 – e; I – 2 – b