

Chemical Bonding and Molecular Structure

CHAPTER

ANSWERS

1. Cl^- ions are much larger in size than F^- ions. Therefore, lattice enthalpy of MgCl₂ is much smaller than MgF₂.

- 2. H:Q:N::O: or H-Q-N=O:
- **3.** 3.35×10^{-30} C m
- **4.** CIF₃
- 5. Bent
- **6**. π2*ρ_x*

7. (a) : Smaller is the size of ion and greater is charge density. Hence, more is the lattice energy.

8. (c) : More the charge density of cation (*i.e.*, smaller size and high magnitude of charge) more is the covalent character.

Order of charge density and thus the covalent character is $CCl_4 > BCl_3 > BeCl_2 > LiCl.$

9. (**b**) : NH_3 : Hybridisation $\rightarrow sp^3$

 $[PtCl_4]^{2-}$: Hybridisation $\rightarrow dsp^2$

 PCl_5 : Hybridisation $\rightarrow dsp^3$ or sp^3d

 BCl_3 : Hybridisation $\rightarrow sp^2$

10. (d) : Bond order in $H_2 = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = 1$

B.O. in
$$H_2^+ = \frac{1}{2}(1-0) = \frac{1}{2}$$

B.O. in $H_2^- = \frac{1}{2}(2-1) = \frac{1}{2}$

Although H_2^+ and H_2^- have the same bond order, H_2^- has longer bond length than H_2^+ because of the presence of one electron in the anti-bonding orbital which repels the two H-atoms from coming close.

Further because of larger bond order, H_2 molecule has the shortest bond length. Thus, the actual order is : $H_2^- > H_2^+ > H_2$.

11. (a)

12. (c) : In ionic compounds, ions are tightly held together by strong electrostatic forces of attraction.

13. (d) : Molecular nitrogen is less reactive than molecular oxygen.

14. (b) : The lone pair-bond pair repulsions are less if it occupies equatorial position than if it occupies axial position. As a result, energy is less and stability is more.

15. Formal charge (F.C) of an atom in a polyatomic ion/ molecule is defined as the difference between the number of valence electrons of that atom in a free state and the number of electrons assigned to that atom in the Lewis structure. On an atom in a Lewis structure.

F.C. = (Total no. of valence electrons to the free atoms) – (Total no. of non-bonding electrons) $-\frac{1}{2}$ (total no. of bonding electrons)

The lowest energy structure (stable one) is the one with the smallest formal charges on the atoms.

OR

(a) (b) The nitrite ion structure is $[: \mathbf{O} - \mathbf{N} = \mathbf{O}:]^-$ The formal charge on oxygen atom marked (a) is

$$6 - 6 - \frac{1}{2} \times 2 = -1$$

The formal charge on oxygen atom marked (b) is

$$6 - 4 - \frac{1}{2} \times 4 = 0$$

The formal charge on nitrogen atom is $5-2-\frac{1}{2}\times 6=0$

16. Fluorine atom contains 9 electrons. So, fluorine molecule contains 18 electrons. The electronic configuration of F_2 molecule is

σ1s² σ*1s², σ2s² σ*2s² σ2p²_z (π2p²_z = π2p²_y)(π*2p²_x = π*2p²_y)

As all MO are fully filled, there is no unpaired electron present. Therefore, F_2 molecule is diamagnetic.

17. The hybridisation of O atom in OF₂ is :
Hybridisation (H) =
$$\frac{1}{2}$$
 [Number of valence

electron on O atom + Number of monovalent F atoms attached – Charge on cation + Charge on anion]

$$=\frac{1}{2}\left[6+2-0+0\right]=4$$

i.e., it is sp^3 hybridised and since it involves sp^3 hybridisation so its shape is tetrahedral.

18. Only $SnCl_2$ has the same shape as $SO_2.SO_2$ and $SnCl_2$ both are AX_2L type molecule. Both have bent structure. While CO_2 and BeH_2 are AX_2 type molecule with linear shape.



- (i) Ionic, SrO
- (ii) Covalent, CBr₄
- (iii) Ionic, GaF₃

21.

(iv) Covalent, NBr₃

19. (a) A = 32, N = 40, S = N - A = 40 - 32 = 8where A = Total number of electrons available in the valence shell of all the atoms

N = Total number of electrons needed by all atoms to achieve noble gas configuration

S = Total number of electrons shared



(b)
$$\begin{bmatrix} : \ddot{\mathbf{0}} : : \mathbf{1} : \ddot{\mathbf{0}} : \mathbf{H} \end{bmatrix}$$
 or $\begin{bmatrix} : \ddot{\mathbf{0}} \leftarrow \mathbf{I} - \ddot{\mathbf{0}} - \mathbf{H} \end{bmatrix}$

- (c) A = 10, N = 18, S = N A = 18 10 = 8H··C:N: or H-C=N
- **20.** M.O. configuration of Ne₂ :

(*KK*) $\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 (\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^2 = \pi^* 2p_y^2)\sigma^* 2p_z^2$ B.O. = $\frac{8-8}{2} = 0$, diamagnetic

N₂:
$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 (\pi 2p_x^2 = \pi 2p_y^2) \sigma 2p_z^2$$

B.O. = $\frac{1}{2}(10 - 4) = 3$, diamagnetic

	Molecule	Structure	Sigma bond	pi-bond
(i)	C ₂ H ₃ Cl	H H H H H - C = C - CI	5	1
(ii)	CH ₂ Cl ₂	H H-C-CI CI	4	0
(iii)	H ₃ C−CH=CH−C≡CH	$ \begin{array}{cccc} H & H \\ I & I \\ H-C-C=C-C\equiv C-H \\ I & I \\ H & H \end{array} $	10	3

22. (i) BF₃ has trigonal planar structure hence, it has zero dipole moment. Both H₂S and H₂O have bent structures but electronegativity of oxygen is more than that of sulphur. Hence, the dipole moment of H₂O is more than H₂S. Thus, increasing order is : BF₃ < H₂S < H₂O

(ii) The size of the anion in increasing order is $CI^- < Br^- < I^-$. Hence, LiCl is least covalent and Lil is most. The order is LiCl < LiBr < Lil.

(iii) Cation size in decreasing order is $Na^+ > Mg^{2+} > Al^{3+}$ The covalent character is $NaCl < MgCl_2 < AlCl_3$.

Hence, the order of ionic character is $AICI_3 < MgCI_2 < NaCI$

23. (a) The dipole moment of hydrogen halides decreases from HF to HI as the electronegativity of halogens decreases from F to I. Hence, polar nature of the bond decreases.

(b) NaCl is an ionic compound and hence gives Cl⁻ ions in

the solution which combine with Ag^+ ions given by $AgNO_3$ to form a white precipitate of AgCI. But CCI_4 is a covalent compound and does not give CI^- ions.

(c) It is not necessary for the non-polar molecules to have always non-polar bonds. For example, BF_3 molecule is non-polar but all the three B — F bonds are polar. BF_3 is a non-polar molecule as it has symmetrical structure and the resultant polarity is zero.

24. (a) *p*-Nitrophenol has higher boiling point because there is intermolecular H-bonding while in *o*-nitrophenol, there is intramolecular H-bonding.

(b) These compounds contain polar –OH bonds which can form H-bonds with water.

(c) The lattice energy of $BaSO_4$ is very high in comparison to its hydration energy.

OR

(a) It is the hypothetical phenomenon of intermixing of orbitals of same atom with slightly different energies resulting in the formation of same number of new orbitals with equal energies and shape.

Hybridisation of S in $SF_6 : sp^3d^2$

Hybridisation of C in $CCl_4 : sp^3$

Hybridisation of Ni in $[Ni(CO)_{4}]$: sp^{3}

- Hybridisation of B in BF_3 : sp^2
- (b) H: 1s¹
- C (ground state) : $1s^22s^22p^2$





25. Formation of PCI_5 (*sp*³*d* hybridisation)



The shape of the molecule is trigonal bipyramidal and all the bond angles are not equal. Three P—CI bonds lie in one plane with 120° angle and are called equatorial bonds while two P—CI bonds which lie above and below the equatorial bonds are called axial bonds. Since axial bonds suffer more repulsion from equatorial bond pairs, they are slightly longer than the equatorial bonds.





It has a regular octahedral geometry.

26. (a) Types of overlapping :

(i) **s-s overlapping :** In this case, there is overlap of two half filled *s*-orbitals along the internuclear axis as shown :



(ii) *s-p* **overlapping :** This type of overlap occurs between half filled *s*-orbitals of one atom and half filled *p*-orbitals of another atom.



(iii) *p-p* **overlapping** : This type of overlap takes place between half filled *p*-orbitals of the two approaching atoms.



(ii) BF₃ : 120°

27. (i) (a) Since the covalent bond depends on the overlapping of orbitals between different orbitals, the geometry of the molecule is different. The orientation of overlap is the factor responsible for their directional nature. (b) Due to presence of two lone pairs of electrons on oxygen atom in H₂O the repulsion between *lp-lp* is more. CO_2 undergoes *sp* hybridisation resulting in linear shape (O = C = O) while H₂O undergoes *sp*³ hybridisation resulting in distorted tetrahedral or bent structure.



(c) In ethyne molecule carbon undergoes *sp* hybridisation with two unhybridised orbitals. One *sp* hybrid orbital of one carbon atom overlaps axially with *sp* hybrid orbital of the other carbon atom to form C—C sigma bond while the other hybridised orbital of each carbon atom overlaps axially with *s* orbitals of hydrogen atoms forming σ bonds. Unhybridised orbitals form π bonds.



(ii) CO_3^{2-} is represented by more than one electronic arrangement to explain all the properties. The actual structure of the ion is intermediate of the various structures and is known as resonance hybrid. Various electronic arrangements are known as resonating structures or canonical structures.



28. (i) Important conditions for hybridisation :

(a) The orbitals present in the valence shell of the atom are hybridised.

(b) The orbitals undergoing hybridisation should have almost equal energy.

(c) Promotion of electron is not essential condition of hybridisation.

(d) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

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

29. (a) Water has higher dipole moment than CO_2 , because H_2O has irregular geometry and possess dipole moment but CO_2 has regular geometry. Thus, possess zero dipole moment.



(b) (i) He₂ molecule does not exist in nature, because electron-electron repulsion is more than nucleus-electron attraction and fully filled outermost shell orbital does not take part in overlapping according to V.B. Theory.

(ii) The M.O. electronic configuration of N₂⁺ (total electrons = 13) is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 (\pi 2p_x^2 = \pi 2p_y^2) \sigma 2p_z^1$

As one unpaired electron is present in $\sigma 2p_z$ MO, N₂⁺ cannot be diamagnetic, it is paramagnetic in nature.

(iii) The bond dissociation energy is directly related to the bond order.

The bond order of H_2^+ is $\frac{1}{2}$ and the bond order of H_2^+ ($\sigma 1s^2\sigma^* 1s^1$) is also $\frac{1}{2}$. As bond order is same, the bond dissociation energy of H_2^+ is almost same as that of He_2^+ .

OR

(a) $p_x - p_y$ will not result in bond formation due to different axis which results in zero overlapping. In first figure, the + + overlap cancels the + - overlap and net overlap is zero.

- (b) Linear molecules BeCl₂, HOCl Non-linear molecules — H₂O, Cl₂O
- (c) The compounds formed with hydrogen

$$\begin{array}{rcrcr} X & - & XH_4 \\ Y & - & YH_3 \\ Z & - & ZH \end{array}$$

ZH will have highest dipole moment due to maximum difference in electronegativity of atoms.

30. (i) Charge =
$$\frac{\text{Dipole moment}}{\text{Bond lengh}} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}}$$

= $1.2 \times 10^{-10} \text{ esu}$

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

(ii) Greater the electronegativity of the halogen, more will be the dipole moment of the molecule.

Thus, increasing order is : $\rm CH_3 I < \rm CH_3 Br < \rm CH_3 CI < \rm CH_3 F$

(iii) Coulomb meter (C m)

(iv) CO_2 has a linear structure while SO_2 has bent structure.

$$0 \underset{\mu=0}{\longleftarrow} C \underset{\mu=0}{\longrightarrow} 0 \qquad 0 \underset{\mu=1.6 \text{ D}}{\longleftarrow} 0$$

(v) OCS will have a higher dipole moment than CS₂ although both are linear in shape. This is due to difference in electronegativity of O and S. In OCS, two dissimilar atoms are bonded to the central C atom.

$$\begin{array}{c} \overleftarrow{\mu_1} + \overleftarrow{\mu_2} \\ S = C = S \end{array} \qquad \begin{array}{c} \overleftarrow{\mu_1} + \overleftarrow{\mu_2} \\ O = C = S \end{array}$$
$$\mu_{net} = 0 \qquad \mu_{net} \neq 0$$
$$r \quad \mu_1 = \mu_2 \quad \text{or} \quad \mu_1 > \mu_2 \end{array}$$

0

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