

CHAPTER 6

CHEMICAL BONDING

TEXT BOOK EXERCISE

Q.1. Select the correct statement.

- i. An ionic compound A^+B^- is most likely to be formed when
 - a. the ionization energy of A is high and electron affinity of B is low.
 - b. the ionization energy of A is low and electron affinity of B is high.
 - c. both the ionization energy of A and electron affinity of B is high.
 - d. both the ionization energy of A and electron affinity of B is low.
- ii. The number of bonds in nitrogen molecule is
 - a. one and one
 - b. one and two
 - c. three sigma only
 - d. two and one
- iii. Which of the following statements is not correct regarding bonding molecular orbitals?
 - a. Bonding molecular orbitals possess less energy than atomic orbitals from which they are formed.
 - b. Bonding molecular orbitals have low electron density between the two nuclei
 - c. Every electron in the bonding molecular orbitals contributes to the attraction between atoms.
 - d. Bonding molecular orbitals are formed when the electron waves Undergo constructive interference.

- iv. Which of the following molecules has zero dipole moment?
- a. NH_3 b. CHCl_3 c. H_2O
d. BF_3
- v. Which of the hydrogen halides has the highest percentage of ionic character?
- a. HCl b. HBr c. HF d. HI
- vi. Which of the following species has unpaired electrons antibonding molecular orbitals?
- a. b. c. B_2 d. F_2

Ans: (i) b (ii) b (iii) b (iv) d (v) c (vi) b

Q.2. Fill in the blanks.

- i. The tendency of atoms to attain maximum of _____ electrons in the valence shell is called completion of octet.
- ii. The geometrical shape of SiCl_4 and PCl_3 can be explained on the basis of _____ and _____ hybridizations.
- iii. The VSEPR theory stands for _____.
- iv. For N_2 molecule, the energy of $(2p)_x$ orbital is _____ than $(2p_y)$ orbital.
- v. The paramagnetic property of O_2 is well explained on the basis of M.O theory in terms of the presence of _____ electrons in two M.O orbitals.
- vi. The bond order of N_2 is _____ while that of Ne_2 is _____.
- vii. The values of dipole moment for CS_2 is _____ while for SO_2 is _____.

Ans: (i) eight (ii) SP^3 , SP^2 (iii) valence shell electron pair repulsion (iv) greater (v) un-pairs electron (vi) zero, zero (vii) zero, 1.61 D

Q.3. Classify the statements as true or false. Explain with reasons.

- i. The core of an atom is the atom minus its valence shell.
- ii. The molecules of nitrogen (N_2) and acetylene ($\text{HC}\equiv\text{CH}$) are not iso-electronic.
- iii. There are four coordinate covalent bonds in CO_3^{2-} ion.
- iv. A $\text{C}\equiv\text{C}$ bond is stronger than $\text{C}=\text{C}$ bond and the electrons of $\text{C}\equiv\text{C}$ bond are more diffused than $\text{C}=\text{C}$ bond.
- v. The bond energy of heteroatomic diatomic molecules increases with the decrease in the electro negativities of the bonded atoms.
- vi. With increases in bond order, bond length decreases and bond strength increases.
- vii. The first ionization energies of the elements rise steadily with increasing atomic number from top to bottom in a group.
- viii. A double bond is stronger than a single bond and a triple bond is weaker than a double bond.
- ix. The bonds formed between the elements having electro negativity difference more than 1.7 are said to be covalent in nature.
- x. The repulsive force between two bonding pairs is less than that between the two lone pairs.
- xi. The number of covalent bonds an atom can form is related to the number of unpaired electrons it has.
- xii. The rules which govern the filling of electrons into the atomic orbitals also govern the filling of electrons into the molecular orbitals.

**Ans: (i) true (ii) false (iii) false (iv) false (v) false (vi) true
(vii) false (viii) true (ix) false (x) false (xi) true (xii) true**

Q.5.a. Define ionization energy and electron affinity. How these qualities change in the periodic table. What factors are responsible for their variation?

b. Explain, what do you understand by the term electro negativity? Discuss its variations in the periodic table. How does it affect the bond strengths?

Ans:

a. Ionization Energy

The minimum energy required to remove an electron from gaseous atom to form positive ion is called ionization energy. The process is called ionization. E.g.

The ionization energy indicates the stability of an isolated atom. Moreover ionization energy is an index to the metallic character.

- i. The elements with low I.E are metals
- ii. The elements with high I.E are non-metals
- iii. The elements with intermediate I.E values are metalloids.

Factors Influencing Ionization Energies:

The I.E depends upon following factors

- i. Atomic radius or atomic size
- ii. Nuclear charge (Proton number) of atom
- iii. Shielding effect of inner electrons
- iv. Nature of orbital

Higher Ionization Energies:

The energy required to remove an electron after the removal of first electron is called second ionization energy. E.g.

The energy required to remove an electron after the removal of second electron is called third ionization energy. E.g.

It is fact that $3^{\text{rd}} \text{ I.E} > 2^{\text{nd}} \text{ I.E} > 1^{\text{st}} \text{ I.E}$

The reason is that after the removal of one or more electrons, the remaining electrons are held tightly by nuclear positive charge. Thus further removal of electrons requires more energy.

Ionization Energy and Valency:

We can guess the valency of an element from gap between first, second, third and higher I.E values. If there is big gap between first and second I.E, then valency of element is one. Similarly if there is big gap between second and third I.E, then valency of element is two. E.g. valency of K is one.

Variation of I.E in Periodic Table:

(a) I.E in a Group:

The ionization energy decreases from top to bottom of a group. The reason is that new shells are added from top to bottom of group. Thus valence electrons are at large distance from the nucleus. So force of attraction between nucleus and outer electron decreases. Therefore I.E decreases down the group.

(b) I.E in a Period:

The I.E increases from left to right of a period. The reason is that in a period nuclear charge increases one by one but no new shell is added so atomic size decreases. Thus force of attraction between nucleus and outer electron increases. Therefore I.E increases in a period.

Electron Affinity

The energy released when an electron is added to the partially filled orbital of a gaseous atom to form negative ion is called electron affinity. E.g.

Electron affinity is the measure of attraction between nucleus of an atom and extra incoming electron.

Factors Influencing Electron Affinity:

Electron affinity depends upon following factors.

- i. Atomic radius
- ii. Nuclear charge

- iii. Shielding effect of inner electrons
- iv. Nature of orbital

In general electron affinity decreases with increase of atomic radius. The reason is that by increasing distance between nucleus and valence electrons, the force of attraction decreases. Hence E.A decreases with increase of atomic radius.

Variation of E.A in Periodic Table:

i. E.A in a Group:

When we go from top to bottom in a group the proton number increases and new electronic shells are introduced. So atomic radius increases. Thus force of attraction between nucleus and valence electrons decreases. Hence E.A decrease from top to bottom in a group.

ii. E.A in a Period:

When we go from left to right in a period, the proton number increases one by one but no new electronic shell is added. So atomic radius decreases. Therefore force of attraction between nucleus and valence electrons increases. Hence E.A increases from left to right in a period.

Exceptional Cases:

The electron affinity of fluorine is less than that of chlorine. The reason is that seven valence electrons of fluorine are present in 2s and 2p sub shells. These sub shells have thick electronic cloud. This thick electronic cloud repels the incoming electron. Hence E.A of fluorine is less than that of chlorine.

Q.7.a. Explain qualitatively the valence bond theory. How does it differ from molecular orbital theory?

b. How the bonding in the following molecules can be explained with respect to valence bond theory? Cl₂, O₂, N₂, HF, H₂S.

Ans: (a) Valence Bond Theory:

According to V.B theory molecule is formed by overlap of two atomic orbitals. In the resulted molecule the atomic orbitals retain their identity. The atomic orbitals are monocentric.

M.O. Theory:

According to M.O. theory a molecule is formed by linear combination of atomic orbitals. Here atomic orbitals are buried into each other and lose their identity. Moreover molecular orbitals are Polycentric.

(b) Cl₂:

The Cl₂ molecule has a sigma bond due to linear overlap of partially filled orbitals.

O₂ Molecule:

O₂ molecule has a double bond (one and one) for other molecules.

Q.9. The molecules NF₃, BF₃ and CIF₃ all have molecular formula of the type XF₃. But they have different structural formulas. Keeping in view VSEPR theory sketch the shape of each molecule and explain the origin of differing in shapes.

Ans:

(i) In BF₃, the central atom boron contains three electron pairs. All three pairs are bonding. Thus shape of BF₃ is triangular planar. Each angle is of 120°. It is shown in fig.

(ii) In NF₃, the central atom Nitrogen contains four electrons

pairs. Three are bonding electron pairs and one is lone pair of electrons. Thus shape of will be tetrahedral.

(iii) In ClF_3 , the central atom Chlorine contains five electron pairs. Three pairs are bonding and two are lone pairs of electrons. Thus according to VSEPR theory the molecule ClF_3 has a T-Shaped structure.

Q.10. The species , NH_3 , have bond angles of 105° , 107.5° and 109.5° respectively. Justify these values by drawing their structures.

Ans:

(i) In , nitrogen atom forms two covalent bonds with two hydrogen atoms. Nitrogen has two lone pairs of electrons. These

lone pairs of electrons repel each other. Thus angle decreases from 109.5° to 105° .

(ii) In , nitrogen forms covalent bonds with three hydrogen atoms. There is one lone pair of electrons on nitrogen atom. The lone pair of electrons on nitrogen atom. The lone pair of electron repels bond pairs of electrons. Thus angle decreases from 109.5° to 107° .

(iii) In , nitrogen forms three covalent bonds and one coordinate bond. There is no lone pair of electrons on

nitrogen. So ion has perfect tetrahedral structure. All bond angles are equal to 109.5° .

a. **Hybridization for PH_3 :**

In PH_3 , phosphorus shows SP^3 hybridization. Four SP^3 hybrid orbitals are resulted. Three SP^3 hybrid orbitals form σ -bonds with 1s orbital of three H-atoms. In fourth SP^3 hybrid orbital one lone pair of electrons is present. Due to repulsion between lone pair and bond pairs, the angle decreases from 109.5° to 107° .

Geometry of CCl_4 :

In CCl_4 , carbon shows SP^3 hybridization. Four SP^3 hybrid orbitals are formed. They overlap with p-

orbitals of four Cl-atoms. So structure of CCl_4 is perfect tetrahedral. Each angle is 109.5° .

Geometry of PCl_3 :

In PCl_3 , phosphorus shows SP^3 hybridization. Four SP^3 hybrid orbitals are formed. They form three σ -bonds with P-orbitals of three Chlorine atoms. In the fourth SP^3 -hybrid orbital a lone pair of electrons is present. Due to lone pair-bond pair repulsion angle decreases from 109.5° to 107.5° .

Geometry of H_2S :

In H_2S , sulphur shows SP^3 hybridization. Four SP^3 -hybrid orbitals are formed. Two SP^3 orbitals overlap with 1s orbitals of two H-

atoms. In the remaining two SP^3 orbitals, two lone pairs of electrons are present. Due to lone pair-lone pair repulsions, angle decreases from 109.5° to 104.5° .

b. (i) When atoms are located at the corners of equilateral triangle, then central atoms SP^2 -hybridization.

(ii) When atoms are located at the corners of regular tetrahedron, then central atom shows SP^3 -hybridization.

(iii) When atoms are located at the corners of a triangular bipyramide, then central atom shows SP^3 -hybridization.

Q.13.a Sketch the molecular orbital pictures of

(i) $2p_y$ and $2p_y$ (ii) O_2 , , (iii) He_2 and Ne_2

(a) **Molecular Orbital Picture of Ne_2 :**

The M.O picture of Ne_2 (Neon molecule) is shown below. The bond order = = 0. Because bond order of Neon is zero. So Ne_2 molecule does not exist.

(b) **Hybrid Orbital of PCl_3 :**

Phosphorous shows SP^3 hybridization in PCl_3 . The four SP^3 hybrid orbitals are formed. Three form bonds with P-

orbitals of three chlorine atoms. In fourth SP^3 -hybrid orbital lone pair of electrons is present.

Hybrid Orbital of SF_6 :

In SF_6 , sulphur shows d^2SP^6 hybridization. Six d^2SP^6 hybrid orbitals are formed. They all six overlap with P-orbitals of six-fluorine atoms.

Hybrid Orbital of $SiCl_4$:

In $SiCl_4$, silicon shows SP^3 hybridization. Four SP^3 hybrid orbitals are formed. They overlap with four P-orbitals of four Chlorine atoms.

Hybrid Orbital of :

In , Nitrogen shows SP^3 hybridization. Nitrogen forms three covalent bond with three covalent bond with three H-

atoms and one
coordinate bond
with H⁺ ion.

Q.14.

b. How do you compare the bond strengths of

(i) Polar and non-polar molecules, (ii) and bonds?

c. Calculate the bond energy of H-Br. The bond energy of H-H is 436 KJ mol⁻¹ and that of Br-Br is 193 KJ mol⁻¹.

b.i. A covalent bond between two alike atoms is called. e.g. Cl-Cl, Br-Br. A covalent bond between two unlike atoms is called polar bond. e.g. , . In a polar bond the shared pair of electrons is slightly shifted towards more electro-negative (E.N) atom. So atoms have partial positive and partial negative charges. Thus atoms are attracted due to extra electrostatic (dipole-dipole) forces. Hence a polar bond is stronger than a non-polar bond.

ii. A bond formed by head to head or linear overlap of two partially filled orbitals is called σ -bond. A bond formed by parallel overlap of two partially filled P-orbitals is called π -bond. In σ -bond, overlapping of orbitals is symmetrical on the bond axis. In a π -bond overlapping of orbitals is spread above and below the bond axis. So σ -bond is stronger than a π -bond.

c. Bond energy of $\text{H-H} = 436 \text{ KJ mol}^{-1}$

$$\text{Bond energy of } \text{H-H} \text{ per molecule} = \frac{436}{6.023 \times 10^{23}} = 7.24 \times 10^{-22} \text{ KJ}$$

$$\text{Bond energy of 1 atom of hydrogen} = \frac{436}{2 \times 6.023 \times 10^{23}} = 3.62 \times 10^{-22} \text{ KJ}$$

$$\text{Bond energy of } \text{Br-Br} = 193 \text{ KJ mol}^{-1}$$

$$\text{Bond energy of } \text{Br-Br} \text{ per molecule} = \frac{193}{6.023 \times 10^{23}} = 3.20 \times 10^{-22} \text{ KJ}$$

$$\text{Bond energy of 1 atom of Bromine} = \frac{193}{2 \times 6.023 \times 10^{23}} = 1.60 \times 10^{-22} \text{ KJ}$$

$$\text{Bond energy of 1 molecule of H-Br} = 3.62 \times 10^{-22} + 1.60 \times 10^{-22} = 5.22 \times 10^{-22} \text{ KJ}$$

Bond energy of per mole = $5.22 \times 10^{-22} \times 6.02 \times 10^{23} = 314.2$
Kj mol⁻¹

Q.15.

b. The bond length of H-Br is 1.4×10^{-10} m. Its observed dipole moment is 0.79D. Find the percentage ionic character of the bond. Unit positive charge = 1.6022×10^{-19} c and $1D = 3.336 \times 10^{-30}$ mc.

b. Bond length of HBr, $r = 1.4 \times 10^{-10}$ m, = 0.79D

Unit positive charge, $q = 1.6022 \times 10^{-19}$ C

%ionic character = ?

$$= q \cdot r = 1.6022 \times 10^{-19} \times 1.4 \times 10^{-10} = 2.24 \times 10^{-29} \text{ cm}$$

$$= \frac{2.24 \times 10^{-29}}{3.336 \times 10^{-30}} = 6.72 \text{ D}$$

%ionic character of H-Br =

$$= \frac{0.79}{6.72} = 11.7 \%$$

Q.16. PF₃ is a polar molecular with dipole moment 1.02 D and thus the P-F bond is polar. Si, is in proximity of P in the periodic table. It is expected that Si-F bond would also be polar, but SiF₄ has no dipole moment. Explain it?

Ans: PF₃ is a
Pyramidal
molecule like NH₃.
All three P-F bonds
are polar. Their
polarity is not
cancelled. So PF₃
has a net dipole
moment of 1.02D.
On other hand SiF₄

is a perfect tetrahedral molecule. All four Si F bonds are polar but their polarity is cancelled out. Hence net dipole moment of SiF_4 is zero.

Q.17. Which of the following molecules will be polar or non-polar, sketch the structures and Justify your answer.

(i) CCl_4 (ii) SO_3 (iii) SF_4 (iv) NF_3 (v)

PF_5

(vi) SO_2 (vii) SF_6 (viii) IF_7

Ans:

i. CCl_4 :
The CCl_4 molecule is perfect tetrahedral. All C Cl bonds are polar. Their polarities cancel each other. Thus net dipole moment is zero. So CCl_4 is a non-polar molecule.

ii. SO_3 :
The SO_3 molecule is plane triangular. All bonds are polar but their polarities cancel each other. Thus net dipole

moment is zero. So SO_3 is a non-polar.

iii. SF_4 :

The molecule SF_4 is trigonal bi pyramidal. All four S F bonds are polar. Their bond moments do not cancel each other. Hence net dipole moment of SF_4 is not zero. Therefore SF_4 is a polar molecule.

iv. NF_3 :

The molecule NF_3 is trigonal pyramidal. All four N F bonds are polar. Their bond moments do not cancel each other. So net dipole moment is not zero. Hence NF_3 is a polar molecule.

v. PF_5 :

The molecule PF_5 is trigonal bi pyramidal. All P F bonds are polar. Their bond moments cancel each other. So net dipole moment is zero. Hence PF_5 is a non polar

molecule.

vi. SO₂:

The molecule SO₂ is a angular V shaped. Two bond moments do not cancel each other. Thus net dipole moment is 1.6D. Hence SO₂ is a polar.

vii. SF₆:

The molecule SF₆ is octahedral. All bond moments cancel one another. Thus net dipole moment is zero. Hence SF₆ is a non-polar molecule.

viii. IF₇:

The molecule IF₇ is Pentagonal bi pyramidal. All I-F bond moments cancel each other. So net dipole moment is zero. Hence IF₇ is a non-polar.

Q.18. Classify the statements as true or false. Explain with reasons.

- i. Bond distance is the compromise distance between two atoms.

- ii. The distinction between a coordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+ , H_3O^+ and BF_4^- .
- iii. The bond angles of H_2O and NH_3 are not 109.5° like that of CH_4 . Although, O and N atoms are sp^3 hybridized.
- iv. H_2O is more diffused than NH_3 .
- v. The abnormality of bond length and bond strength in HI is less prominent than that of HCl.
- vi. Solid sodium chloride does not conduct electricity, but when electric current is passed through molten sodium chloride or its aqueous solution, Electrolysis takes place.
- vii. The melting points, boiling points, heat of vaporization and heats of sublimations of electrovalent compounds are higher as compared with those of covalent compounds.

Ans.

- i. When two atoms come close to make a bond, then their attraction increases and P.E decreases. At a certain distance atomic attraction is maximum and energy is minimum. It is compromise distance between two atoms. Here bond formation takes place. If atoms come further closer, then nuclear repulsions takes place and energy of system increases. Here bond formation does not occur. Hence bond distance is the compromise distance between two atoms.
- ii. In a covalent bond two atoms provide shared pair of electrons. In a coordinate covalent bond one atom provides both electrons and one coordinate bond then there is no difference between their bond length and bond energy. E.g. in NH_4^+ ion all four bonds are taken equally. It is the reason that distinction between covalent and coordinate covalent bond vanishes after their formation.
- iii. In NH_3 and H_2O there is SP^3 hybridization like CH_4 . Four SP^3 hybrid orbitals are formed. The angle between SP^3 orbitals should be 109.5° . But we know that NH_3 has one lone pair and H_2O has two lone pairs of electrons. There is repulsion between lone pairs

- and bonding pairs of electrons. Due to lone pair-bond pair repulsion the bond angles in NH_3 and H_2O are not 109.5° like CH_4 which has no lone pair of electrons.
- iv. Sigma bond is formed by head to head (linear) overlap of two partially filled orbitals. Here electron density is symmetrically spread around the bond axis. The Pi-bond formed by parallel overlap of two partially filled P-orbitals. Here electron density is spread above and below the bond axis. It is the reason that π are more diffused than σ .
 - v. Chlorine has smaller size and higher electro negativity than Iodine. Thus HCl has more polarity than HI . Due to this reason abnormality of bond length and bond strength in HI is less prominent than that of HCl .
 - vi. In solid sodium chloride, the Na^+ and Cl^- ions have strong electrostatic attractions. Thus they are tightly held and occupy fixed positions. But in molten or solution form, ions become free and move towards opposite electrodes. It is the reason that solid NaCl does not conduct electricity but in molten or solution form NaCl conducts electricity.

In electrovalent compounds, the opposite ions have strong electrostatic attractions. Thus they are tightly held and occupy fixed positions. It is the reason that electrovalent compounds have high melting points, boiling points, heat of vaporization and heat of sublimations as compared with those of covalent compounds.