Chemical Bonding and Molecular Structure

Case Study Based Questions

Read the following passages and answer the questions that follow:

1. Electron dot structures or Lewis dot formulas can be drawn if the molecular formula of the compound is known. It defines the nature of bond and position of atoms of the molecule which are connected in the molecule. The representation of molecules in Lewis electron dot structure or just a Lewis structure is in honour of the American chemist Gilbert Newton Lewis. Lewis dot structures also called electron dot structures are diagrams that describe the chemical bonding between atoms in a molecule. They also display the total number of lone pairs present in each of the atoms that constitute the molecule. Lewis dot structures are commonly referred to as electron dot structures or Lewis structures. Lewis defined a base as an electron pair donor and an acid as an electron pair acceptor. Lewis dot structures reflect the electronic structures of the elements, including how the electrons are paired. Lewis structures are a useful way to summarize certain information about bonding and may be thought of as "electron bookkeeping". In the Lewis dot structure, each dot represents an electron. A pair of dots between chemical symbols for atoms represents a bond.

(A) Which of the following conditions doesn't apply to Lewis dot structure?

(1) Each bond is created as a result of the atoms sharing an electron pair.

(II) Only one atom from the two atoms contributes combining electron(s) to the shared pair.

(III) The sharing of electrons allows the atoms to achieve the outer shell noble gas structures. Options:

(a) (1) and (III)

(b) (II) and (III)

(c) Only (II)

(d) Only (III)

(B) The structure with the..... formal charges on the atoms has the lowest energy.

(a) smallest

(b) highest

(c) zero
(d) negative

(C) Identify the group valence of atoms in the halogen family.

(a) 2
(b) 1
(c) 9
(d) 7

(D) Which rule is followed by sharing or transfer of electrons from one atom to the other to attain a stable octet configuration?

(a) Duet rule
(b) Triplet rule
(c) Octet rule
(d) Septet rule

(E) For which molecule octet rule is not valid?

(a) H_2O
(b) CO
(c) CO_2
(d) 0_2

Ans. (A) (c) (II) only

Explanation: To form covalent bonds we need two atoms at least so that sharing of electrons can take place. Thus, (II) is not appropriate for the Lewis structure.

(B) (a) smallest

Explanation: The structure with the least formal charge on the atoms has the lowest energy.

(C) (b) 1

Explanation: The group valance can be calculated from Lewis symbols either by subtracting it from eight (more than 4) or having it equal (less than 4). The halogen family has 7 electrons in their outer orbit. So 87 = 1. Therefore, the valency of the halogen family is 1.

(D) (c) Octet rule

Explanation: As per the electronic theory of chemical bond that's put forth by Lewis and Kossel states that the atoms follow the octet rule by sharing or transfer of electrons from one atom to the other to attain a stable octet configuration.

(E) (b) CO

Explanation: In CO molecule, the carbon atom contains only six valence electrons whereas eight electrons are required to fulfill its octet. Hence, CO molecule does not have an octet. The Octet rule is not valid for CO molecule.

2. Lattice energy is a measure of the strength of the ionic bonds in an ionic compound. It provides insight into several properties of ionic solids including their volatility, their solubility, and their hardness. The lattice energy of an ionic solid cannot be measured directly. However, it can be estimated with the help of the Born-Haber cycle. Generally, this quantity is expressed in terms of kilojoules per mole (kJ/mol). Lattice energy can be defined as the energy required to convert one mole of an ionic solid into gaseous ionic constituents. Alternately, it can be defined as the energy that must be supplied to one mole of an ionic crystal in order to separate it into gaseous ions in a vacuum via an endothermic process. Therefore, this quantity always holds a positive value. Some sources define lattice energy in the opposite manner, i.e. the amount of energy released when an ionic solid is formed from its gaseous ionic constituents via an exothermic process. According to this definition, lattice energy must always hold a negative value due to the electrostatic forces between them, the individual ions in an ionic lattice are attracted to each other. The strength of the electrostatic force of attraction is directly proportional to the magnitude of the charge held by the constituent ions, i.e. the greater the charge, the stronger the force of attraction and the stronger the lattice. For example, the lattice energy of calcium chloride is greater than that of potassium chloride despite the similarity in the crystal arrangements of these compounds. This is because the magnitude of the positive charge held by the calcium cation (+2) is greater than that held by the potassium cation (+1). As a consequence of this, the electrostatic forces of attraction are stronger in calcium chloride (than those in potassium chloride). Therefore, the lattice energy of $CaCl_2$ is greater than that of KCL

(A) AlCl3 has a higher lattice enthalpy than $MgCl_2$. Explain.

(B) List the lattice energies of lithium halides in decreasing order.

(C) Which of the two salts, NaCl or CsCl, has the higher lattice energy and why?

Ans. (A) As charge is higher and size is smaller of Al^{3+}. Charge is directly proportional and size is inversely proportional to lattice energy. Hence, $AlCl_3$ has higher lattice enthalpy than $MgCl_2$.

(B) LiI< LiBr< LiCl < LIF

(C) Lattice energy is proportional to ion charge and inversely proportional to atom radius. Now, between NaCl and CsCl, the radius of Cs^+ is far greater than that of Nat^+ even though CsCl is more ionic, the radius is greater, and thus, the lattice energy is lower.

3. Bond energy is the amount of energy required to break any bond in a molecule. It is observed that the shorter the bond length greater is the bond energy. Bond energy increases with the increasing bond order. It also decreases with the increase in lone pairs on the bonded atom due to the electrostatic repulsion of lone pairs on the two bonded atoms. Bond energy is affected by the resonance. In the case of similar molecules, down the group, the bond energy decreases. According to the concept of resonance, when a single Lewis structure cannot define a molecule properly then a number of structures with the almost same energy and the same position of nuclei are taken as a canonical structures. Resonance stabilizes the molecule as the energy of the resonance hybrid is less and lies between the canonical structure. As the result of resonance, the bond order changes in many molecules or ions.

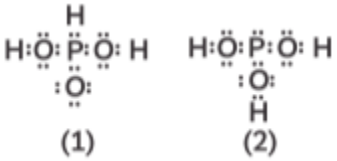
(A) Arrange these in the bond energy order.

C≡C

C=C

C—C

(B) H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not, give reasons for the same.



(1) (2)

(C) Answer the following questions:

(i) Compare the bond energy in Cl_2, N_2, and O2.

(ii) Find the average bond energy of O-H bond in H_2O molecule.

Ans. (A) The order of bond energy is

C≡C > C=C > C—C

Multiple bonds have more bond energy than the single bond.

(B) As the position of atoms has been changed in the given structures, thus these cannot be taken as the canonical forms of the resonance hybrid of H3PO3.

(C) (i) The bond energy in Cl_2, N_2 and O_2 can be calculated by the presence of a number of lone pairs.

$$\text{Bond energy} \propto \frac{1}{\text{Bond order}}$$

CL-CL has one bond.
O-O has two bond order.
N-N has three bond order.
So, the order of bond energy will be:
N-N>O-O> CL-CL
(ii) In H_2O molecule:
$H\text{-}O\text{-}H_{(g)} \rightarrow 2H_{(g)} + O_{(g)}$; $\Delta H = 926\ kJmol^{-1}$ The average bond energy of the O-H bond

$$= \frac{926}{2}$$

$$= 463\ kJmol^{-1}$$

4. The bond angle of a molecule depends on hybridisation, lone pair repulsion and electronegativity of a molecule. The lone pair of a molecule always tries to repel the bonded pair of electrons. Because of this, a slight increase is seen in the angle of the respective atom. The bond angle increases with a decrease in the electronegativity if the central atom is the same for different molecules. It also depends on the state of hybridisation of the central atom. The geometry of a molecule is also predicted by the dipole moment. A symmetrical molecule shows zero dipole moment. Molecules having zero dipole moments are called non-polar molecules and the molecules having μ0 are called polar molecules.

(A) The actual bond angle of NH_3 is:

(a) 105°
(c) 110.95°
(b) 106.7°
(d) 102°

(B) Compare the bond angle between NH_3, PH_3 and AsH_3.

(a) $NH_3 > PH_3 > ASH_3$
(b) $NH_3 < PH_3 < ASH_3$
(c) $NH_3 < AsH_3 < PH_3$
(d) $PH_3 < AsH_3 < NH_3$

(C) Identify the correct statement regarding NH_3 and BF_3.

(a) Both are Lewis acid

(b) Both are isostructural

(c) Both are Lewis base

(d) Have different values of dipole moment

(D) The SCL_2 molecule has a bent shape and is not linear because of:

(a) presence of two lone pairs at sulphur atom

(b) presence of four lone pairs at sulphur atom

(c) do not have a bent shape

(d) the size of sulphur atom is smaller than chlorine

(E) The bond angle with the decrease in electronegativity.

(a) increases

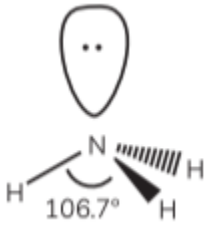
(b) decreases

(c) first increases then decrease

(d) remains constant

Ans. (A) (b) 106.7°

Explanation: The actual bond angle of NH3 is 106.7°.



(B) (a) NH3> PH3> ASH3

Explanation: The bond angle depends upon the electronegativity of the central atom. Bond angle decreases with the decrease in electronegativity.

NH_3> PH_3> AsH_3

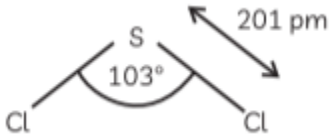
107° 93° 91.48°

(C) (d) Have different values of dipole moment.

Explanation: NH_3 is a Lewis base as it has lone pair of electrons to donate while BF_3 is a Lewis acid as its octet is not complete and it is ready to accept the electrons. NH_3 is trigonal pyramidal due to the presence of a lone pair while BF_3 is trigonal planar. BF_3 has zero dipole moment as it has a symmetrical structure while NH_3 has a dipole moment of 1.4 D.

(D) (a) presence of two lone pairs at sulphur atom.

Explanation: The SCl_2 molecules have a bent shape and are not linear because of the presence of two lone pairs of electrons at the sulphur atom. The chlorine atoms and lone pairs repel each other. This gives a bent shape to SCl_2 molecule.



(E) (a) increases

Explanation: The bond angle is inversely proportional to the substituents' electronegativity. A more electronegative substituent attracts electrons, lowering the charge density on the central atom. As a result, the bond angle decreases.

5.The simplest case to consider overlapping is the hydrogen molecule, H2. When we say that the based on earlier work by other scientists that incorporated a consideration of electron pairs in predicting three-dimensional structures. The valence shell is the outermost electron- occupied shell of an atom. The valence shell holds the electrons that are involved in bonding and are the electrons shown in a Lewis structure. The acronym VSEPR stands for the valence-shell electron pair repulsion model. The model states that electron pairs will repel each other such that the shape of the molecule will adjust, so that the valence electron- pairs stay as far apart from one another as possible. Molecules can be systematically classified according to the number of bonding pairs of electrons; as well as the number of nonbonding, or lone pairs, around the central atom. For the purposes of the VSEPR model, a double or triple bond is no different in terms of repulsion than a single bond. A few molecules are given below, answer the following questions based on these molecules, CH_4, PCL_5, SF_6 H_2O and XeF_4

(A) Identify the molecules which don't have a lone pair of electrons and give the number of bond pairs present in them.

(B) Identify the molecule having four bond pairs and determine its geometry.

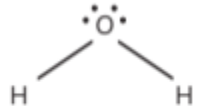
(C) Find the molecules which are having lone pairs of electrons and draw their structures.

Ans. (A) The molecules which do not have lone pairs of electrons are SF_6, CH_4 & PCLs. The valence electrons present in the central atom S is 6 that are satisfied by the 6 fluorine atoms, so no lone pairs are there. The valence electrons in carbon are 4 which are all satisfied by 4-H atoms so no more lone pair is there and the valence electrons present in the P are 5 which are all satisfied by 5 Cl atoms. So, it also does not have a

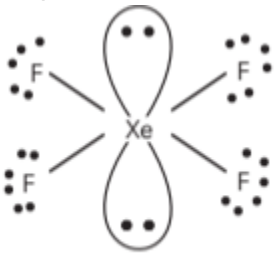
lone pair of electrons.

(B) The CH4 (methane) molecule is having four bond pairs where the four valencies of carbon are satisfied by four hydrogen atoms. So, four bond pairs are present. The methane molecule is in a tetrahedral geometry.

(C) Among the given options H_2O and XeF_4 have both lone pairs and bond pairs. Both the molecules have 2 lone pairs on central atom.



Structure of H_2O molecule



Structure of XeF_4

6. The attractive force which holds the two atoms together is called a chemical bond. A covalent bond is formed by an equal sharing of electrons. A coordinate bond is also known as the dative bond is formed when an atom donates both of its electrons in a covalent bond. An ionic bond is formed by the transfer of electrons from one atom to another. Octet rule, although very useful, is not universally applicable. According to valence bond theory, a covalent bond is formed by overlapping half- filled atomic orbitals which form new orbitals of lower energy and more stability. The number of bonds between the two atoms in a molecule is called bond order. The higher the bond order more will be stability and bond dissociation enthalpy but the smaller the bond length. The polarity of a covalent bond depends upon the difference in electronegativity. The covalent character of a bond depends upon polarizing
power. The smaller the cations and bigger the anions more will be the polarizing power. VSEPR theory helps to predict the shapes of molecules.

(A) Draw the structure of XeO_4.

(B) On the basis of hybridisation, draw the shape of methane CH_4.

(C) Explain the non-linear shape of H2S and non-planar shape of PCl_3 using valence shell electron pair repulsion theory.

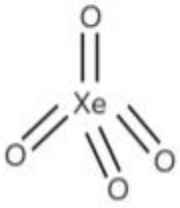
Ans. (A) For XeO_4,

$$H = \frac{(8+0)}{2} = 4$$

Total bond pairs: 4

Total lone pair: (4 – 4) = 0

Hybridisation of XeO_4 is sp^3 with no lone pair, so the shape is tetrahedral.



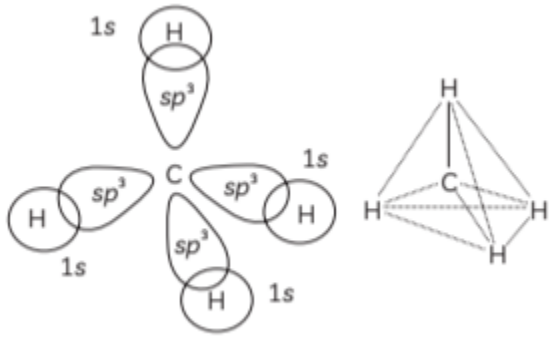
Tetrahedral (sp^3)

(B) Atomic number of C = 6

Its electronic configuration in the ground state is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$

The electronic configuration of C in the excited state is $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

One 2s and three 2p orbitals undergo sp^3 hybridisation to form four sp^3 h-orbitals which are arranged tetrahedrally at an angle of 109.5° to each other.



Formation and structure of methane

(C) In H_2S, S is the main atom which has 2 lone pairs. These lone pairs cause repulsion and move the H-S bond away causing a non-linear shape.

The valency of P is 5 in PCl_3, P has 3 single bonds and 1 lone pair (pair of unshared is non-planar due to lone pair-bond pair interactions.

7. Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitals combine to form two molecular orbitals called bonding molecular orbital (BMO) and antibonding molecular orbital (ABMO). The energy of the antibonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding

orbital is lower than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order:

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

And for oxygen an elements after oxygen order of energy of molecular orbitals is given below:

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

Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head- on, the molecular orbital is called
'Sigma, (a) and if the overlap is lateral, the molecular orbital is called 'pi, (r). The molecular orbitals are filled with electrons according to the same rules as followed for the filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

(A) Which of the following statements is correct?

(a) In the formation of dioxygen from oxygen atoms, ten molecular orbitals will be formed.
(b) All the molecular orbitals in the dioxygen will be completely filled.
(c) Total number of bonding molecular orbitals will not be the same as
the total number of anti-bonding orbitals in dioxygen.
(d) Number of filled bonding orbitals will be the same as the number of filled anti-bonding orbitals.

(B) Which of the following molecular orbitals has a maximum number of nodal planes?

(a) $\sigma 1s$ (b) $\overset{*}{\sigma} 2p_z$
(c) $\sigma 2p_x$ (d) $\overset{*}{\pi} 2p_y$

(C) Which of the following chemical species is most stable?

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

(D) Which of the following order of energies of molecular orbitals is correct for C_2

molecule?

(a) $(\pi 2p_x) \approx (\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(b) $(\pi 2p_x) \approx (\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(c) $(\pi 2p_x) \approx (\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(d) $(\pi 2p_x) \approx (\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(E) Diamagnetic species are those which contain no unpaired electrons. Which among the following is diamagnetic?

(a) C_2 (b) N_2^{2-}

(c) O_2 (d) O_2^{2-}

Ans. (A) (a) In the formation of dioxygen from oxygen atoms, ten molecular orbitals will be formed.

Explanation: Applying MOT in dioxygen molecule:

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

$$= \pi 2p_y^2\, \overset{*}{\sigma} 2p_z^0$$

Clearly, ten molecular orbitals are involved. All molecular orbitals are not completely filled.

Total Number of bonding molecular orbitals will be the same as the number of anti-bonding molecular orbitals. Number of filled bonding orbitals will not be the same as the number of filled anti-bonding molecular orbitals.

(B)

(b) $\overset{*}{\sigma} 2p_z$

Explanation:

$\sigma 1s$ has 1 nodal plane.

$\overset{*}{\sigma} 2p_z$ has 2 nodal planes.

$\sigma 2p_x$ has 1 nodal plane.

$\overset{*}{\pi} 2p_y$ has 1 nodal plane.

(C)

(b) O_2^+,

Explanation: O_2:

O_2: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma^* 2p_z)^2$
$(\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$

O_2^+: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 =$
$(\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^1$

O_2^-: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 =$
$(\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^1$

O_2^{2-}: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2$
$= (\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

The most stable is O_2^+ due to least electrons in antibonding orbital.

(D)

(d) $(\pi 2p_x) = (\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) = (\pi^* 2p_y)$

Explanation: Molecules like B_2, C_2 and N_2. Energy of o_2p, molecular orbital is greater than that of $_2$px and $_2$py molecular orbitals.

(d) O_2^{2-}

Explanation:

The MOT diagram for O_2^{2-} is
$(\sigma 1s)^2(\overset{*}{\sigma} 1s)^2(\sigma 2s)^2(\overset{*}{\sigma} 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2$
$= \pi 2p_y^2)(\overset{*}{\pi} 2p_x^2 = \overset{*}{\pi} 2p_y^2)$
as there are no unpaired electron thus, it has diamagnetic character.

8. When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces. Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment.

(A) Identify the hydride which has the lowest boiling point.

(a) NH_3

(b) PH_3

(c) SbH_3

(d) AsH_3

(B) The hydrogen bonding is strongest in:

(a) O-H-------S

(b) S-H-------O
(c) F-H--------F
(d) F-H-------O

(C) What is the reason behind the higher boiling point of water?

(a) Covalent bonding
(b) Co-ordinate bonding
(c) Hydrogen bonding
(d) Electrostatic force of attraction

(D) The boiling increases with increase in ..... of a substance.

(a) intramolecular hydrogen bonding
(b) molecular mass
(c) intermolecular hydrogen bonding
(d) both (b) and (c)

(E) H-bonding couldn't affect the boiling point of:

(a) HI
(b) NH_3
(c) H_2O
(d) CH_3OH

Ans. (A) (b) PH_3
Explanation: As the hydrogen bonding is absent in PH_3 molecule in a liquid state, it has the lowest boiling point.
(B) (c) F-----H-F
Explanation: The hydrogen bonding is strongest in F-----HF because of high electronegativity of fluorine.
(C) (c) Hydrogen bonding
Explanation: In H**2**O molecule, the central oxygen atom is covalently linked to two H-atoms. Each H-atom can form a hydrogen bond. In addition to these two hydrogen bonds, the central oxygen atom also forms two hydrogen bonds with the neighbouring molecules. Therefore the reason behind the higher boiling point of water is hydrogen bonding.
(D) (d) both (b) and (c)
Explanation: Due to intermolecular hydrogen bonding molecules associate which increases the boiling point of substance.

(E) (a) HI

Explanation: Hydrogen bonding exists only when a compound has electronegative atoms like N, O, F atoms. Atoms which are larger in size don't show hydrogen bonding because they don't have high electron density.

9. Highly electronegative atoms like N, O, F cannot completely remove the valence electron from hydrogen and form an ion because there are no core electrons in hydrogen. Removing the hydrogen's 1s electron would produce a subatomic particle, the proton, whose small size results in a high charge density that would pull back the electron. So it will not happen. The result is that hydrogen forms polar covalent bonds when attached to an electronegative atom and does not form ions. The electronegative atoms pull on the valence electron "Deshields" the hydrogen's proton resulting in a large 8+ charge over a small area. A highly electronegative atom has a large &- charge and if it has a lone pair of electrons, they are strongly attracted to the "deshielded proton" of another hydrogen and create a hydrogen bond. It should also be noted that the small size of the hydrogen allows it to move in real close, resulting is a strong bonding interaction.

(d) both (b) and (c)

Explanation: Due to intermolecular hydrogen bonding molecules associate which increases the boiling point of substance.

(E) (a) HI

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size of the hydrogen allows it to move in real close, resulting is a strong bonding interaction.

(A) Answer the following questions:

(i) Will all H atoms form H-bonds?

(ii) Why is H-bond strength more in peroxide than water?

(B) How chloroform makes hydrogen bond with acetone?

(C) How many numbers of hydrogen bonds are present in H_3O^+? Draw structure also.

Ans. (A) (1) A molecule that has a hydrogen atom attached to some electronegative atom will form hydrogen bonding.

(ii) Due to one additional oxygen atom in peroxide, the strength of the hydrogen bond is more than water.

(B) Due to the presence of three chlorine atoms in chloroform, the carbon atom becomes partially positive, so it pulls away the electron density from the hydrogen atom to balance electron distribution, thereby making the hydrogen atom partially positive. Hence, the oxygen atom of acetone which is partially negative interacts to form hydrogen bonding.

(C) 3 hydrogen bonds are present in H^3O^+.