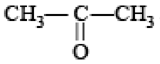
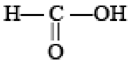
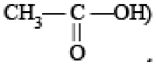
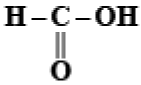
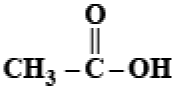
Fill Ups of Chemical Bonding and Molecular Structure

Q.1. The angle between two covalen t bonds is maximum in .... (CH_4, H_2O, CO_2) (1981 - 1 Mark)

Ans. Sol. CO_2; Bond angle in CH_4 is 109°.28’, in H_2O it is 105 and in CO_2 it is 180°. So it is maximum in case of CO_2

Q.2. Pair of molecules which forms strongest intermolecular hydrogen bond is ....

(SiH_4 and SiF_4,  $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ **and $CHCl_3$,**  $H-\underset{\underset{O}{\|}}{C}-OH$ **and**  $CH_3-\underset{\underset{O}{\|}}{C}-OH)$ **(1981 - 1 Mark)**

Ans. Sol.  $H-\underset{\underset{O}{\|}}{C}-OH$ and  $CH_3-\overset{\overset{O}{\|}}{C}-OH$ form strongest hydrogen bonds because of largest difference in electronegativities of bonded atoms.

Q.3. There are .... π bonds in a nitrogen molecule. (1982 - 1 Mark)

Ans. Sol. 2; $N \equiv N$ (N_2) has 1σ and 2π bonds. (A triple bond consists of 1σ and 2π bonds)

Q.4. .... hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. (1982 - 1 Mark)

Ans. Sol. sp^3; Hybridisation (H)= **1/2** [No. of valence electron in centralatom + No. of monovalent atoms – Charge on cation + Charge on anion]

For N in NH^{4+}, hybridisation (H) = **1/2** (5 + 4 – 1 + 0) = 4
∴ sp^3 hybridisation.

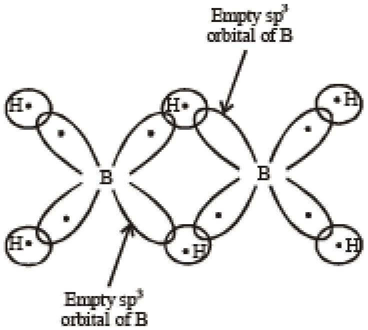
Q.5. The shape of $[CH_3]^+$ is .... (1990 - 1 Mark)

Ans. Sol. Planar; $^+CH_3$ is a carbocation and such a species has aplanar shape.

Q.6. The two types of bonds present in B_2H_6 are covalent and .... (1994 - 1 Mark)

Ans. Sol. Three centred two electron bonds or banana bond;

NOTE : The formation of three centred two electron bond is due to one empty sp^3 orbital of one of the B atom, 1s orbital of the bridge hydrogen atom and one of the sp^3 (filled) orbital of the other B-atom. This forms a delocalized orbital covering the three nuclei giving the shape of a banana. Thus also known as banana bonds.



Q.7. When N_2 goes to N^+_2 , the N–N bond distance ..., and when O_2 goes to O^+_2 the O–O bond distance.... (1996 - 1 Mark)

Ans. Sol. Increases, decreases;

∴ Bond order in N_2 = 3 and Bond order in N^{2+} = 2.5

Thus conversion of N_2 to N^+_2 decreases bond order (from 3 to 2.5) and hence

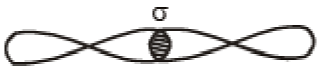
increases the N – N bond distance. [∵ Bond distance increases with decrease in B.O.) Bond order in O_2 = 2 and Bond order in O^+_2 = 2.5

NOTE : Thus conversion of O_2 to O^+_2 increases bond order (from 2 to 2.5) hence decrease O – O bond distance.

True False of Chemical Bonding and Molecular Structure

Q.1. Linear overlap of two atomic p-orbitals leads to a sigma bon d. (1983 - 1 Mark)

Ans. Sol. True : Sigma bond is formed by the overlapping of two s-orbitals or one s and one p or the two p orbitals of the two different atoms. Thus linear overlap of two p-orbitals results in formation of a σ– bond.



Axial p-p overlapping

Q.2. All molecules with polar bonds have dipole moment. (1985 - ½ Mark)

Ans. Sol. False : Symmetrical molecules with polar bonds have zero dipole moment.

Q.3. $SnCl_2$ is a non-linear molecule. (1985 - ½ Mark)

Ans. Sol. True : $SnCl_2$ has 2 bond pairs and one lone pair of electrons.
It is sp^2 hybridised and is trigonal planar in shape.

Q. 4. In benzene, carbon uses all the three p -orbitals for hybridisation. (1987 - 1 Mark)

Ans. Sol. False : Only two orbitals are used since C in benzene is in sp^2 hybridised state.

Q.5. sp^2 hybrid orbitals have equal s and p character. (1987 - 1 Mark)

Ans. Sol. False : sp^2 hybrid orbitals do not have equal s and p character.
They have 33.3% s-character and 66.7% p-character

Q.6. The presence of polar bonds in a poly-atomic molecule suggests that the molecule has non-zero dipole moment. (1990 - 1 Mark)

Ans. Sol. False : The presence of polar bonds in a polyatomic molecule does not always lead to a definite dipole moment. This is because the dipole moment is a vector quantity and when the bond moment of one bond is cancelled by the equal but opposite bond moment due to other bond(s), the molecule has zero dipole moment, e.g. CO_2, CH_4, CCl_4 etc.

Q.7. The dipole moment of CH_3F is greater than that of CH_3Cl. (1993 - 1 Mark)

Ans. Sol. False : The C – F distance is less than the C – Cl, although the former involves more charge separation. However, here bond distance has more dominating effect causing dipole moment of CH_3Cl to be more than that of CH_3F.

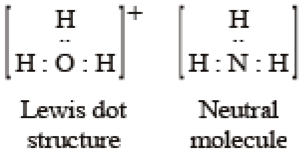
Subjective questions of Chemical Bonding and Molecular Structure

Q.1. Water is liquid while H_2S is a gas at room temperature. (1978)

Ans. Sol. H_2O molecules are held together by hydrogen bonding which is stronger force of attraction but H_2S molecules are held together by vander waals forces of attraction, which are weaker forces. As a result water molecules come closer and exist in liquid state.

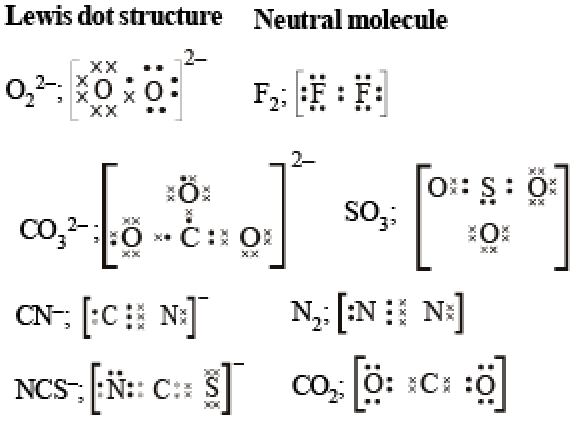
Q.2. Write the Lewis dot structural formula for each of the following. Give, also, the formula of a neutral molecule, which has the same geometry and the same arrangement of the bonding electrons as in each of the following. An example is

given below in the case of H_3O^+ :



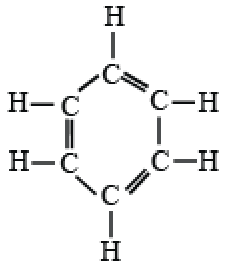
(i) O_2^{2-} ; (ii) CO_3^{2-} ; (iii) CN^-; (iv) NCS^- (1983 - 1 × 4 = 4 Marks)

Ans. Sol.



Q.3. How many sigma bonds and how many pi-bonds are present in a benzene molecule? (1985 - 1 Mark)

Ans. Sol.

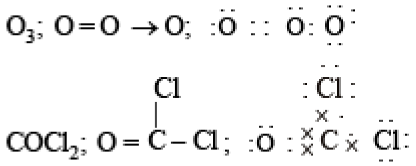


∴ It has 12σ and 3π bonds.

(6σ C–C bonds and 6σ C–H bonds)

Q.4. Write the Lewis dot structure of the following : O_3, $COCl_2$ (1986 - 1 Mark)

Ans. Sol.



Q.5. Arrange the following : (i)N_2, O_2, F_2, Cl_2 in increasing order of bond dissociation en ergy. (1988 - 1 Mark)

(ii) Increasing strength of hydrogen bonding (X–H–X) : (1991 - 1 Mark)

O, S, F, Cl, N

(iii) In the decreasing order of the O – O bond length present in them (2004 - 4 Marks)

O_2, KO_2 and O_2 [AsF_4]

Ans. Sol. (i) Increasing order of bond dissociation energy.

$F_2 < Cl_2 < O_2 < N_2$

NOTE : Fluorine-fluorine bond energy is less than the Cl–Cl because of larger repulsion between the nonbonded electrons of the two smaller fluorine atoms (chlorine atoms are larger in size; hence their lone pair of electrons exert less repulsion than fluorine). Oxygen having two pairs of lone pair of electrons on each atom exert less repulsion than that of chlorine or fluorine each having three lone pairs of electrons. Nitrogen having only one lone pair of electrons exert minimum repulsion, hence it is the most stable.

(ii) H-bonding is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N). Further, higher the electronegativity and smaller the size of the atom, the stronger is the hydrogen bond.

NOTE : Although Cl has the same electronegativity as nitrogen, it does not form effective hydrogen bonds.

This is because of its larger size than that of N with the result its electrostatic attractions are weak. Similarly, sulphur forms a very weak hydrogen bond due to its low electronegativity, although oxygen present in the same group forms a strong hydrogen bond.

Hence the order is S < Cl < N < O < F

(iii) In KO_2, O_2 is present as O_2^-, while in $\overset{+1}{O_2}(\overset{+3}{As}\overset{-4}{F_4})$, O_2 is present as O_2^+. Write down the MO configuration of O_2, O_2^- and O_2^+.

$O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \{\pi 2p_y{}^2, = \pi 2p_z{}^2,$
$\{\pi^* 2p_y{}^1 = \pi^* 2p_z{}^1.$

Thus the bond order $= \frac{10-6}{2} = 2$

O_2^- : Same as above except $\pi^* 2p_y^2, \pi^* 2p_z^1$ in place of $\pi^* 2p_y^1, \pi^* 2p_z^1$.

Thus the bond order in $O_2^- = \frac{10-7}{2} = 1.5$

O_2^+ : Same as in O_2 except $\pi^* 2p_y{}^1 = \pi^* 2p_z{}^0$ in place of

$\pi^* 2p_y^1, \pi^* 2p_z^1$.

∴ Bond order in $O_2^+ = \frac{10-5}{2} = 2.5$

∴ Bond order in the three species is $O_2^+ > O_2 > O_2^-$ or $O_2[AsF_4] > O_2 > KO_2$

Q.6. The dipole moment of KCl is 3.336 × 10^{-29} Coulomb meters 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 the percentage ionic character of KCl. (1993 - 2 Marks)

Ans. Sol. Dipole moment, $\mu = e \times d$ coulombs metre For KCl $d = 2.6 \times 10^{-10}$ m

For complete separation of unit charge (electronic charge) (e) = 1.602×10^{-19} C

Hence $\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$ Cm $\mu KCl = 3.336 \times 10^{-29}$

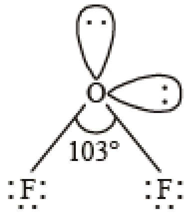
Coulomb meter (given)

$$\therefore \% \text{ Ionic character of KCl} = \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100$$

$= 80.09\%$

Q.7. Using the VSEPR theory, identify the type of hybridization and draw the structure of OF_2. What are the oxidation states of O and F ? (1994 - 3 Marks)

Ans. Sol. The structure of OF_2 is similar to H_2O and involves sp^3 hybridization on O atom. The bond angle in F – O – F is not exactly 109º28’, but distorted (103º) due to presence of lone pair of electrons on O as well as F leading to V shape or tetrahedral positions with two positions occupied by lone pair of electrons of the molecule.



Oxidation number of F = –1

∴ Oxidation number of O = +2

Q. 8. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. (1997 - 2 Marks)

Ans. Sol. Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM

where n → number of unpaired electrons m = 1.73
BM for vanadium ion 1.73 BM = $\sqrt{n(n+2)}$ So, $(1.73)^2 = n(n + 2)$

$3.0 = n^2 + 2n$ or $n^2 + 2n - 3 = 0$

$n^2 + 3n - n - 3 = 0$

∴ $n(n + 3) - 1 (n + 3) = 0$ $(n - 1) (n + 3) = 0$

Correct value of n = 1 Thus no. of unpaired electrons in vanadiumion = 1

$_{23}V = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^2$

It will have one unpaired electron if it will lose two electrons from 4s and two from 3d.

∴ Vanadium (IV) has one unpaired electron.

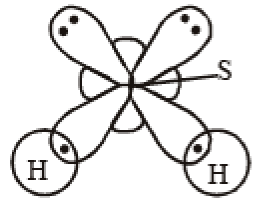
$V_4^+ = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$

Q. 9. Interpret the non-linear shape of H_2S molecule and nonplanar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. (Atomic numbers : H = 1, P = 15, S = 16, Cl = 17.) (1998 - 4 Marks)

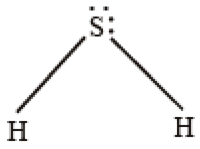
Ans. Sol. In H_2S, no. of hybrid orbitals = $\frac{1}{2}(6+2-0+0)=4$

Hence here sulphur is sp^3 hybridised, so

$$_{16}S = 1s^2, 2s^2 2p^6, \underbrace{3s^2 3p_x^2 3p_y^1 3p_z^1}_{sp^3 \text{ hybridisation}}$$



or

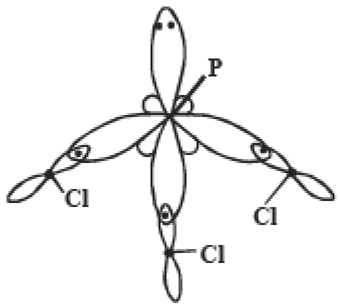


NOTE : Due to repulsion betwen lp **-** lp; the geometry of H_2S is distorted from tetrahedral to V-shape.

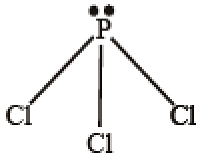
In PCl_3, no. of hybrid orbitals = **1/2** [5 + 3 **-** 0 + 0] = 4

Hence, here P shows sp^3 – hybridization

$${}_{15}P = 1s^2, 2s^2 2p^6, \underbrace{3s^2 3p_x^1 3p_y^1 3p_z^1}_{sp^3 \text{ hybridisation}}$$



or



Thus due to repulsion between lp - bp, geometry is distorted from tetrahedral to pyramidal.

Q.10. Write the M.O. electron distribution of O_2. Specify its bond order and magnetic property. (2000 - 3 Marks)

Ans. Sol. MO configuration of O_2 :

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

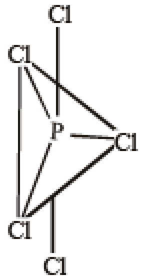
$$\{\pi^* 2p_y^1 = \pi^* 2p_z^1$$

Bond order = **1/2** (10 **-** 6) = 2

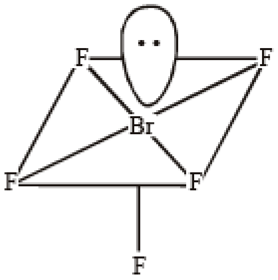
Since O_2 molecule has two unpaired electrons, it is paramagnetic.

Q.11. Using VSEPR theory, draw the shape of PCl_5 and BrF_5. (2003 - 2 Marks)

Ans. Sol.



PCl_5 : sp^3d Trigonal bipyramidal



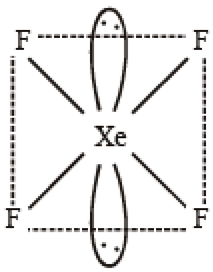
BrF_5 : sp^3d^2 Square pyramidal

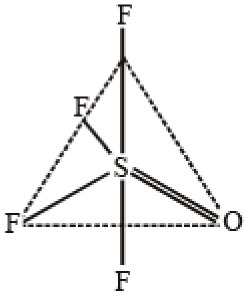
Q. 12. Draw the structure of XeF_4 and OSF_4 according to VSEPR theory, clearly indicating the state of hybridisation of the central atom and lone pair of electrons (if any) on the central atom. (2004 - 2 Marks)

Ans. Sol. First determine the total number of electron pairs around the central atom.

$$XeF_4 = \frac{N}{2} = \frac{8+4}{2} = 6$$

Thus in XeF_4, Xe is sp^3d^2 hybridised. The structure of the molecule is octahedral and shape is square planer with two lone pair of electrons.



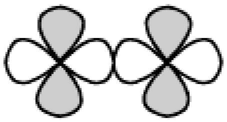
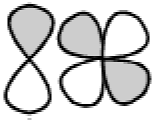
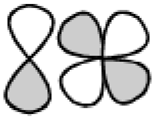
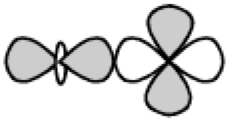


For OSF_4 : $\frac{N}{2} = \frac{6+4}{2} = 5$

Thus the central atom (S) is sp^3d hybridised leading to trigonal bipyramidal structure with no lone pair of electrons.

Match the following of Chemical Bonding and Molecular Structure

Q.1. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. (JEE Adv. 2014)

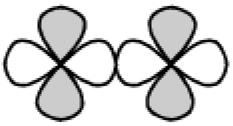
List-I		**List-II**
P.		**1. p – d (π antibonding)**
Q.		**2. d – d (σ bonding)**
R.		**3. p – d (π bonding)**
S.		**4. d – d (σ antibonding)**

Code:

	P	**Q**	**R**	**S**
(a)	2	1	3	4
(b)	4	3	1	2
(c)	2	3	1	4
(d)	4	1	3	2

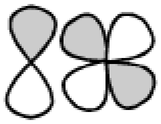
Ans. Sol. (c)

P.



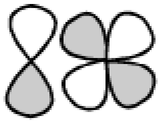
d – d (σ bonding)

Q.



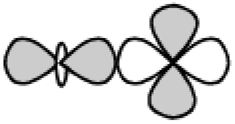
p – d (π bonding)

R.



p – d (π antibonding)

S.



d – d (σ antibonding)

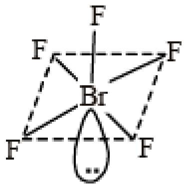
Integer Type ques of Chemical Bonding and Molecular Structure

Q.1. Based on VSEPR theory, the number of 90 degree F–Br–F angles in BrF_5 is (2010)

Ans. (0)

Sol. According to VSEPR theory, number of electron pairs around central atom (Br) are 6.

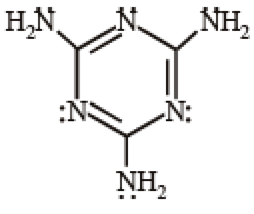
$\frac{N}{2} = \frac{7+5}{2} = 6.$ (Five are bond pairs and one is lone pair) Its geometry is octahedral but due to lone pair –bond pair repulsion, the four fluorine atoms at corner are forced towards the upper fluorine atom thus reducing F–Br–F angle from 90° to 84.8°.



Q.2. The total number of lone-pairs of electrons in melamine is (JEE Adv. 2013)

Ans. (6)

Sol. Structure of melamine is as follows :



Total no. of lone pairs of electron is '6'.

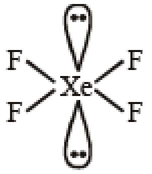
Q.3. A list of species having the formula XZ_4 is given below.

XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is (JEE Adv. 2014)

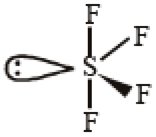
Ans. (4)

XeF_4 :



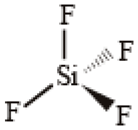
Square planar (sp^3d^2)

SF_4 :



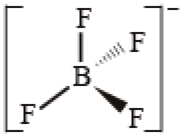
See-saw (sp^3d)

SiF_4 :



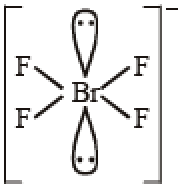
Tetrahedral (sp^3)

BF_4^- :



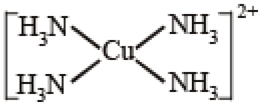
Tetrahedral (sp^3)

BrF_4^- :



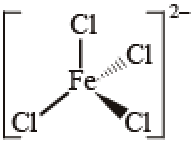
Square planar (sp^3d^2)

$[Cu(NH_3)_4]^{2+}$:



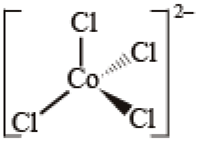
Square planar (dsp^2)

$[FeCl_4]^{2-}$:



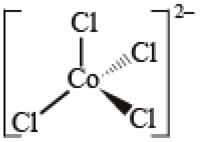
Tetrahedral (sp^3)

$[CoCl_4]^{2-}$:



Tetrahedral (sp^3)

$[CoCl_4]^{2-}$:



Tetrahedral (sp^3)

4. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is [Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54] (JEE Adv. 2015)

Ans. (4)

Sol.

$Cl-Be-Cl$

Hybridization *sp*

Structure linear

$N\equiv N-\ddot{\underset{\cdot\cdot}{N}}:^{-}$

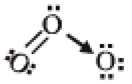
Hybridisation *sp*

Structure linear

$O=\overset{+}{N}\rightarrow O$

Hybridisation *sp*

Structure Linear



Hybridisation sp^2

Structure Trigonal planar

Hybridisation sp^3

Structure Angular

$[Cl-\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot}{I}}-Cl]^{-}$

Hybridisation sp^3d

Structure linear

$[I-\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot}{I}}-I]^{-}$

Hybridisation sp^3d

Structure Linear

$F-\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot}{Xe}}-F$

Hybridisation sp^3d

Structure Linear

$\overset{-}{N}=\overset{+}{N}=O$

Hybridisation *sp*

Structure Linear

Only $BeCl_2$, N_3^-, N_2O and NO_2 are linear with sp-hybridisation.