CHEMICAL BONDING

PROBLEM 291 Discuss the bonding of the following species:

CO_2, COS, CO_3^{2-}, $SiCl_4$, PCl_5, NH_4^+, PH_4^+, PCl_4^+, PCl_6^-, SF_6, IF_7.

PROBLEM 292 Discuss the bonding of the following species:

SO_2, NH_3, H_2O, PCl_3, NCl_3.

PROBLEM 293 Discuss the relative bond angles in the following species:

(a) NH_3, PH_3, AsH_3, SbH_3 and BiH_3.

(b) H_2O, H_2S, H_2Se, H_2Te.

PROBLEM 294 Arrange the following species in the increasing order of their bond angles, explaining the reason for your order:

H_2O, NH_3, H_2Se, PH_3, AsH_3.

PROBLEM 295 Discuss the bonding of:

ClF_3, $COCl_2$, Cl_2O, OF_2, ICl_4^-, IF_5, $IOCl_4^-$, $IOCl_4^+$.

PROBLEM 296 Discuss the bonding of:

N_3^-, I_3^-, BrF_5, IF_4^-, BF_4^-, ICl_2^+, ICl_2^- and PF_5.

PROBLEM 297 The energy necessary to break similar bond is not always equal, it varies from molecule to molecule as:

$$NCl_3 \longrightarrow NCl_2 + Cl \quad \Delta H = 375 \text{ kJ/mol}$$

and

$$NOCl \longrightarrow NO + Cl \quad \Delta H = 158 \text{ kJ/mol}$$

Discuss the difference.

PROBLEM 298 Draw the shape of the following species:

AsF_5, AsF_2^+, $SnCl_3^-$, NOF, SO_3^{2-}, TeF_5^-, GeF_3^-, SCl_2, $SbCl_6^-$.

PROBLEM 299 Discuss the bonding of following:

ClF_4^+, $FClO_3$, F_2ClO^+, SeO_3^{2-}.

PROBLEM 300 Discuss the relative polarity of the following species:

(a) SCl_2, BF_3, ICl_3, $POCl_3$, PCl_5.

(b) XeF_2, SF_4, XeO_3, $SnCl_4$, PCl_4F.

PROBLEM 301 Arrange the following compounds in the increasing order of their melting points explaining reason for your order: Li_2O, LiF, Li_3N.

PROBLEM 302 Arrange the following in the increasing order of their thermal stability with suitable explanations:

(a) $CaCO_3$, $BaCO_3$, $MgCO_3$, Na_2CO_3, $Al_2(CO_3)_3$, $BeCO_3$.

(b) $CaCO_3$, $CaSO_4$ and $CaSO_3$.

(c) $MgSO_4$, $BaSO_4$, $Al_2(SO_4)_3$, $SrSO_4$.

(d) CaC_2O_4, $K_2C_2O_4$, FeC_2O_4 and $CaCO_3$.

PROBLEM 303 The molecule XeF_4 has two lone pairs at the central atom, instead the bond angle is 90° as expected from its geometry, explain.

PROBLEM 304 Arrange the following species in the increasing order of their ionic character:
$NaCl, CaCl_2, AlCl_3, BaCl_2, MgCl_2$ and $GaCl_3$.

PROBLEM 305 In the following pairs of molecules, select one, which has greater bond angle, and explain the reason for your answer.

(a) NH_3 or NF_3 (b) PH_3 or PF_3 (c) AsH_3 or AsF_3

(d) AsF_3 or $AsCl_3$ (e) H_2O or F_2O

PROBLEM 306 Arrange the following sets of molecules in increasing order of bond angles providing appropriate explanation for your order:

(a) H_2O, H_2S, NH_3 and PH_3 (b) CH_3^-, SiH_3^- and GeH_3^-

PROBLEM 307 Draw the shape of the following species indicating bond angles and distortion (if present):

(a) PF_3Cl_2 (b) PF_2Cl_3 (c) PCl_2BrF_2 (d) ICl_2^+ (e) ICl_2^-

PROBLEM 308 Considering the molecules in question 223, arrange them in the increasing order of their dipole moments.

PROBLEM 309 Arrange the following molecules in the increasing order of their polarity:
$CH_3Cl, CH_2Cl_2, CHCl_3$ and CCl_4.

PROBLEM 310 Discuss the bonding in the following molecules with respect to hybridisation of central atom, shape and bond angles:

(a) ClF_3O_2 (b) $XeOF_4$ (c) $IOCl_4^-$ (d) I_3^+

PROBLEM 311 Discuss the bonding of PCl_5 in gas phase and in solid phase.

PROBLEM 312 Dimethyl ether has tetrahedral geometry of hybrid orbital at central atom whereas disilyl ether has triangular planar geometry of hybrid orbital at central atom. Explain.

PROBLEM 313 Draw the shape of the following molecules:

(a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_2$

(e) $XeOF_4$ (f) XeO_2F_2 (g) XeO_3F_2 (h) I_2Cl_6 (i) $I_2Br_2Cl_4$

PROBLEM 314 Draw the shape of the following molecules:

(a) $(CH_3)_2P(CF_3)_3$ (b) $(CH_3)_3P(CF_3)_2$

PROBLEM 315 In sp^3d-hybridized phosphorus atom in trigonal bipyramidal molecule, will the atom have a greater electronegativity when bonding through equatorial or axial orbitals? Explain.

PROBLEM 316 B—F bond distance in BF_3 is shorter than the same in BF_4^-, explain.

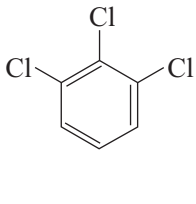
PROBLEM 317 In CCl_4, C—Cl bond length is the sum of the covalent radii of carbon and chlorine whereas in $SiCl_4$, Si—Cl bond distance is smaller than the sum of the covalent radii of Si and Cl, explain.

PROBLEM 318 Arrange the following in increasing order of their Lewis acid strength with proper reasoning. BCl_3, BI_3, BF_3 and BBr_3.

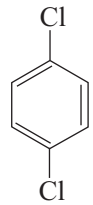
PROBLEM 319 In gas phase, $N(CH_3)_3$ acts as a good Lewis base but $N(SiH_3)_3$ doesn't, explain.

PROBLEM 320 The molecule CHBrCHBr can have two different structures in which one is polar and other is non-polar. Draw the structures labelling them as polar and non-polar.

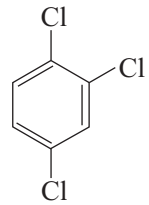
PROBLEM 321 Arrange the following compounds in order of increasing dipole moment:



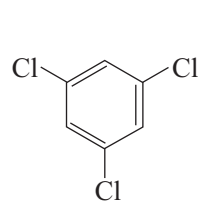
(a)



(b)



(c)



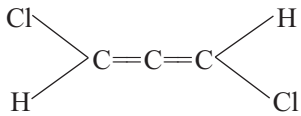
(d)

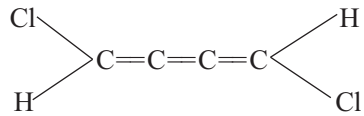
PROBLEM 322 Although both carbon and silicon are in the same group of periodic table, very few Si═Si bonds are known. Account for the instability of Si═Si in general.

PROBLEM 323 Molecule N_2F_2 can acquire two different structures in which one is polar and other is non-polar. Draw them labelling polar and non-polar.

PROBLEM 324 Compound 1,2-dichloro ethane is a non-polar whereas *cis*-1,2-dichloro ethene is polar, explain the difference.

PROBLEM 325 Discuss the dipole moment of the following molecules in view of chemical bonding:



and


PROBLEM 326 Draw all possible structures for the molecule $C_2H_2Cl_2$ and rank them in increasing order of their dipole moment.

PROBLEM 327 Draw shape of a hypothetical molecule N_6 in which nitrogen atoms are part of a six membered ring and has: (a) two pi-bonds, (b) three pi-bonds.

PROBLEM 328 Sodium chloride (NaCl) and sodium fluoride (NaF) both crystallizes in same type of unit cell. Which is expected to have higher lattice energy and why?

PROBLEM 329 The bond energy in NO is 632 kJ mol^{-1} and that of each N—O bond in NO_2 is 469 kJ mol^{-1}. Explain.

PROBLEM 330 In the air, NO can react with NO_2. What is the most likely structure of product?

PROBLEM 331 Draw the Lewis structure of the following species:
(a) SO_2Cl^+, (b) S_2F_4 (contain S—S bond).

PROBLEM 332 The heteronuclear diatomic ion CN^- has an orbital structure similar to that of N_2. How will the fact C has an electronegativity different from that of N affect the energy level diagram.

PROBLEM 333 From the following pair of molecules, select one which will be more soluble in a polar solvent and explain the reason for your choice.
(a) SiF_4 and PF_3, (b) SF_6 and SF_4, (c) IF_5 and AsF_5

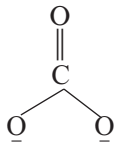
PROBLEM 334 In addition to forming σ- and π-bonds similar to those formed by *p*-orbitals, *d*-orbitals may overlap in δ-bonds with two nodal planes cutting through the internuclear axis. Draw the overlap diagrams showing how *d*-orbitals can overlap in these three ways.

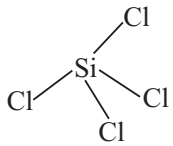
Solutions

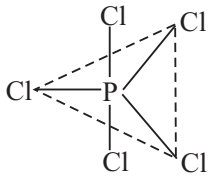
CHEMICAL BONDING

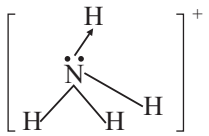
291. CO_2 : O═C═O Linear, non-polar molecule.

COS : S═C═O Linear, polar molecule.

CO_3^{2-} :  Trigonal planar ion with sp^2-hybridized carbon. It exists in three resonating forms.

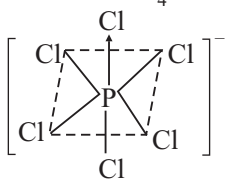
$SiCl_4$:  Tetrahedral molecule with sp^3-hybridized silicon.

PCl_5 :  Pentagonal bipyramidal with sp^3d-hybridized phosphorus. Equatorial bond angle $= 120°$, Axial-equatorial bond angle $= 90°$.

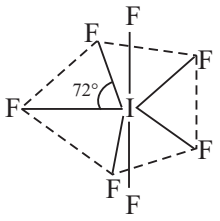
NH_4^+ :  Tetrahedral ion with sp^3-hybridized nitrogen. All bond angles are equal and $109°28'$.

PH_4^+ : Similar to NH_4^+.

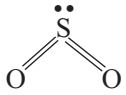
PCl_4^+ : Similar to NH_4^+.

PCl_6^- :  Square pyramidal ion with sp^3d^2-hybridized phosphorus.

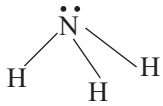
SF_6 : Same as PCl_6^-.

IF_7 : 

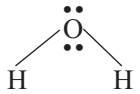
Pentagonal bipyramidal with sp^3d^3-hybridized iodine.

292. SO_2 : 

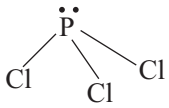
Angular (V-shaped) with sp^2-hybridized sulphur.

NH_3 : 

Trigonal pyramidal with sp^3-hybridized nitrogen.

H_2O : 

Angular (V-shaped) with sp^3-oxygen.

PCl_3 : 

Trigonal pyramidal with sp^3-phosphorus.

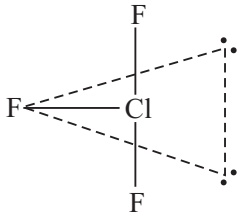
NCl_3 : Same as PCl_3.

293. (a) If every things are same, and central atoms are forms same group, bond angle decreases on descending down the group.

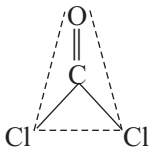
$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(b) $H_2O > H_2S > H_2Se > H_2Te$

294. $AsH_3 < H_2Se < PH_3 < H_2O < NH_3$.

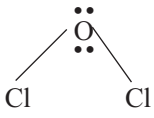
295. ClF_3 : 

T-shaped with sp^3d-hybridized chlorine. (In trigonal bipyramidal geometry, lone pairs are stable at equatorial positions).

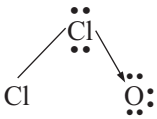
$COCl_2$: 

Triangular planar with sp^2-carbon.

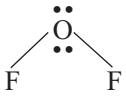
Cl_2O : Two shape can be predicted as :

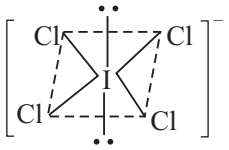


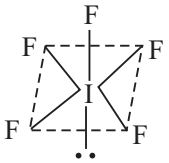
V-shaped with oxygen at centre

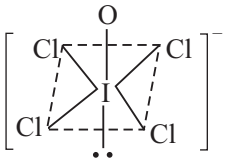


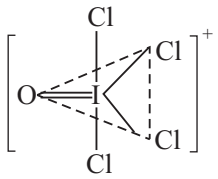
V-shaped with chlorine at centre

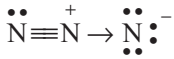
OF_2 :  V-shaped with sp^3-oxygen.

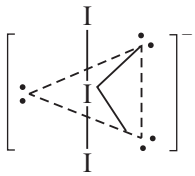
ICl_4^- :  Square planar with sp^3d^2-iodine.

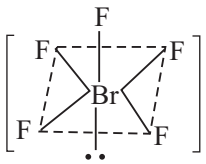
IF_5 :  Square pyramidal sp^3d^2-iodine.

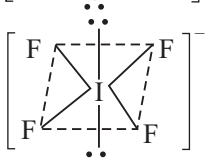
$IOCl_4^-$:  Square pyramidal with sp^3d^2-iodine.

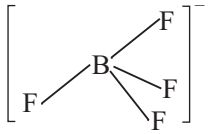
$IOCl_4^+$:  Trigonal bipyramidal with sp^3d-iodine.

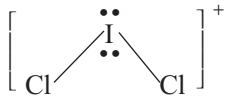
296. N_3^- :  Linear with *sp*-hybridized nitrogen.

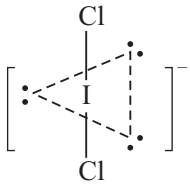
I_3^- :  Linear with sp^3d-hybridized central iodine.

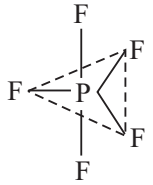
BrF_5 :  Square pyramidal with sp^3d^2-bromine.

IF_4^- :  Square planar with sp^3d^2-iodine.

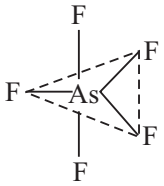
BF_4^- :  Tetrahedral with sp^3-boron.

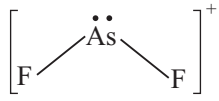
ICl_2^+ :  V-shaped with sp^3-iodine.

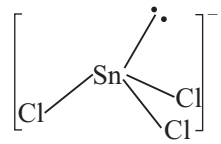
ICl_2^- :  Linear with sp^3d-iodine.

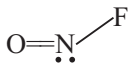
PF_5 :  Trigonal bipyramidal with sp^3d-phosphorus.

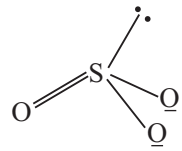
297. Relative electron withdrawing power of nitrogen is more in NCl_3 than in NOCl therefore homolytic cleavage of N—Cl bond would be difficult in NCl_3.

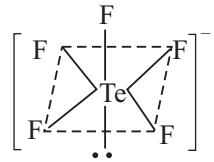
298. AsF_5 : 
Trigonal bipyramidal

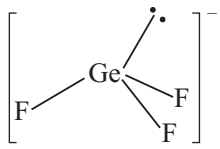
AsF_2^+ : 
V-shaped with sp^2-As

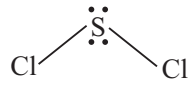
$SnCl_3^-$: 
Trigonal pyramidal with sp^3-Sn

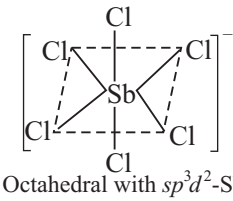
NOF : 
Angular with sp^2-N

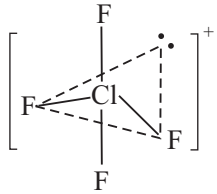
SO_3^{2-} : 
Tetrahedral

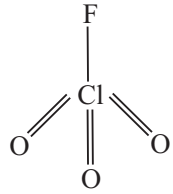
TeF_5^- : 
Square pyramidal with sp^3d^2-Te

GeF_3^- : 
Trigonal pyramidal with sp^3-Ge

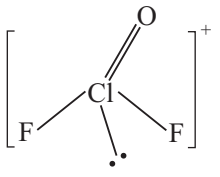
SCl_2 : 
V-shaped with sp^3-S

$SbCl_6^-$: 
Octahedral with sp^3d^2-Sb

299. ClF_4^+ : 
Sea Saw

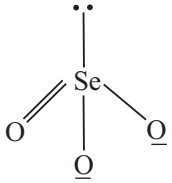
$FClO_3$: 
Tetrahedral with sp^3-Cl

F_2ClO^+ :



Tetrahedral

SeO_3^{2-} :



Trigonal pyramidal

300. (a) $BF_3\,(\mu = 0) = PCl_5\,(\mu = 0) < POCl_3 < SCl_2 < ICl_3$

(b) $XeF_2\,(\mu = 0) = SnCl_4\,(\mu = 0) < PCl_4F < XeO_3 < SF_4$

301. $Li_3N < Li_2O < LiF$ (Fajan's rule)

302. (a) $Al_2(CO_3)_3 < BeCO_3 < MgCO_3 < CaCO_3 < BaCO_3 < Na_2CO_3$

(b) $CaSO_4 < CaSO_3 < CaCO_3$

(c) $Al_2(SO_4)_3 < MgSO_4 < SrSO_4 < BaSO_4$

(d) $FeC_2O_4 < CaC_2O_4 < CaCO_3 < K_2C_2O_4$

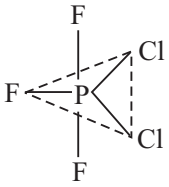
303. Symmetrical repulsion by the two lone pairs from axial positions cancels the effect of one-another and bond angles remains intact.

304. $AlCl_3 < GaCl_3 < MgCl_2 < CaCl_2 < BaCl_2 < NaCl$ (Fajan's rule).

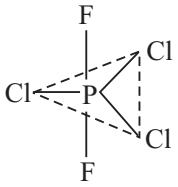
305. (a) NH_3 (b) PF_3 (c) AsF_3 (d) $AsCl_3$ (e) H_2O

306. (a) $H_2S < PH_3 < H_2O < NH_3$ (b) $GeH_3^- < SiH_3^- < CH_3^-$

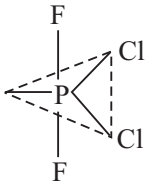
307. (a)



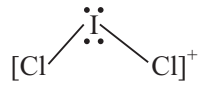
(b)



(c)

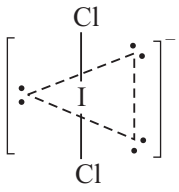


(d)



V-shaped with sp^3-iodine

(e)

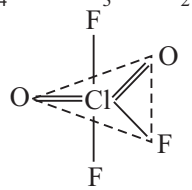


Linear

308. $PCl_3F_2\,(\mu = 0) < PF_3Cl_2 < PBrF_2Cl_2$

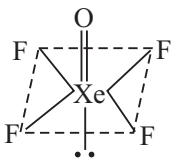
309. $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$

310. (a)

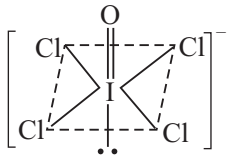


Trigonal bipyramidal with sp^3d^2-Cl

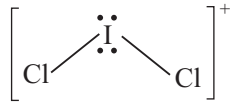
(b)



Square pyramidal with sp^3d^2-Xe

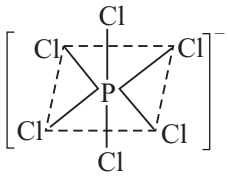
(c) 

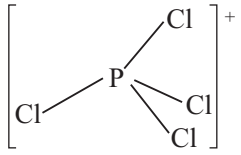
Square pyramidal
with sp^3d^2-I

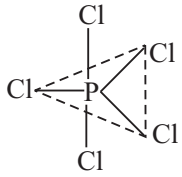
(d) 

V-shaped with sp^3-I

311. In solid state, PCl_5 remains as dipolar ion as $[PCl_6]^-[PCl_4^+]$

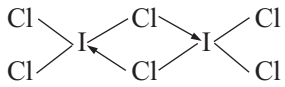


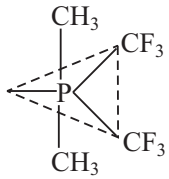
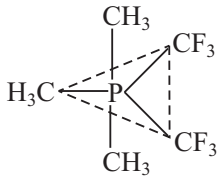


In gas phase PCl_5 remains as isolated gas molecule : 

312. Due to back bonding of a lone pair from *p*-orbital of oxygen to vacant *d*-orbital of Si ($p_\pi - d_\pi$ bonding).

313. (a) Linear (b) Square planar (c) Octahedral (d) T-shaped (e) Square pyramidal

(f) Sea-saw (g) Trigonal bipyramidal (h) 

314. (a)  (b) 

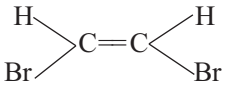
315. Greater electronegativity when bonding through axial positions.

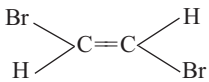
316. $P_\pi - P_\pi$ back bonding in BF_3 gives some double bond character, which is absent in BF_4^-.

317. $P_\pi - d_\pi$ back bonding occurs between Si and Cl, which is absent in CCl_4.

318. $BF_3 < BCl_3 < BBr_3 < BI_3$

319. Lone pair of nitrogen in $N(SiH_3)_3$ is involved in $p_\pi - d_\pi$ back bonding, not available for donation to a Lewis acid.

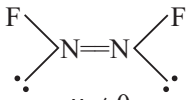
320. 
$\mu \neq 0$


$\mu = 0$

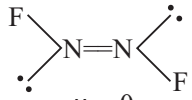
321. $d(\mu = 0) = b(\mu = 0) < c < a$

322. Due to larger size of 3*p*-orbital with Si, there is fewer chance of sidewise overlap giving π-bonds.

323.

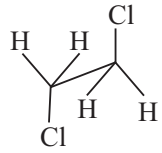


$\mu \neq 0$

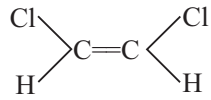


$\mu = 0$

324. Due to free rotation about C—C sigma bond, 1,2-dichloro ethane acquire the anti (most stable) conformation which is non-polar. In dichloroethane, rotation is restricted.



anti conformation of 1,2-dichloro ethane ($\mu = 0$)

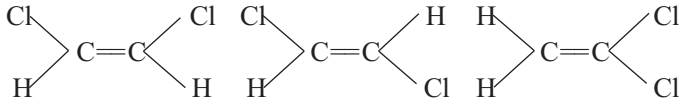


due to restricted rotation, $\mu \neq 0$

325. In ClHC═C═CHCl, the two C—Cl bonds are in perpendicular plane and hence the molecule is polar.

In HClC═C═C═CHCl, the two C—Cl bonds are in the same plane and individual C—Cl dipoles are at 180°, cancelling one another giving zero dipole moment.

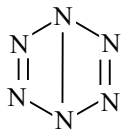
326.



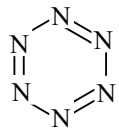
I II III

Dipole moment: II < III < I.

327. (a)

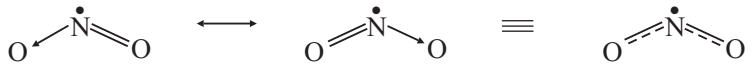


(b)



328. NaF has higher lattice energy than NaCl. Lattice energy is inversely proportional to square of the interionic distance. Since, fluoride ion is smaller in size than chloride ion, NaF will have higher lattice energy.

329. The NO_2 exist in two equivalent resonance form as:



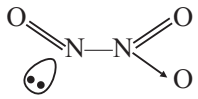
both N—O bonds are identical, therefore equal bond energies.

$\dot{N}$═O It has a one sigma and one pi-bond and bond order is two whereas in NO_2, the N—O bond order is less than two. Therefore, N—O bond energy in NO is greater than in NO_2.

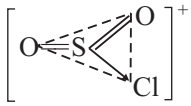
330. Both NO and NO_2 have one odd (unpaired) electron. When the two molecule approach each other, unpaired electron may be shared to form a covalent bond as:

both N have complete octet.

Shape of N_2O_3 :

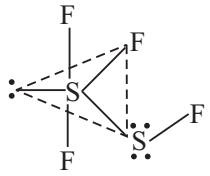


331. (a)



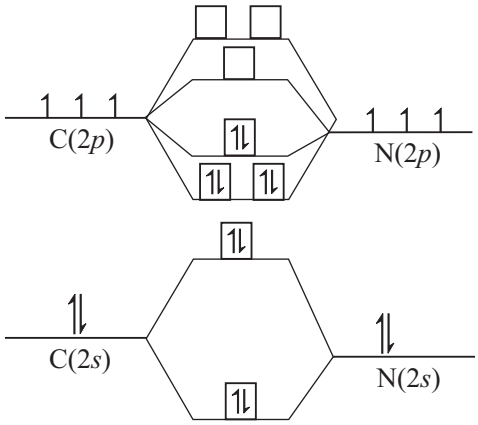
Triangular planar

(b)



One S-is sp^3d and other is sp^3 hybridized.

332. N has higher electronegativity than C, therefore, energy of orbitals of N is less than that of carbon and energy level diagram will be as follows:

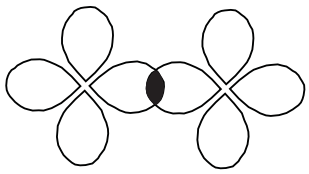


333. (a) SiF_4 is tetrahedral, non-polar molecule while PF_3 is trigonal pyramidal, polar molecule. Therefore, PF_3 will be more soluble in polar solvent.

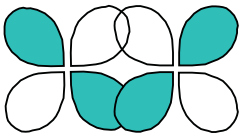
(b) SF_6 is square bipyramidal, non-polar molecule while SF_4 is a seasaw shaped, polar molecule. Therefore, SF_4 will be more soluble in polar solvent.

(c) IF_5 is a square pyramidal, polar molecule while AsF_5 is a trigonal bipyramidal, non-polar molecule. Therefore, IF_5 will be more soluble in a polar solvent.

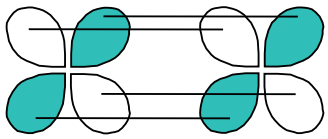
334.



σ-bond



π-bond



δ-bond