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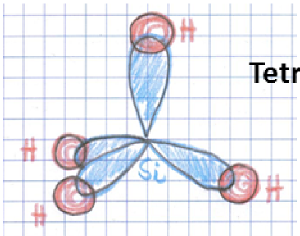
Exercises Topic 2: Molecules

1. Using hybridization concepts and VSEPR model describe the molecular geometry and the spatial distribution of the bonding pairs of the following molecules:
a)SiH_4 b)PF_3 c)XeF_4 d)PF_5

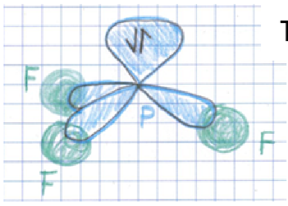
Solution:

a) sp^3 hybridization



Tetrahedral

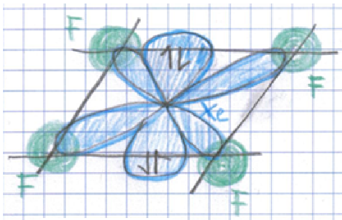
b) sp^3 hybridization $P(Z=15) \xrightarrow{e.e} [Ne]3s^2 3p^3$

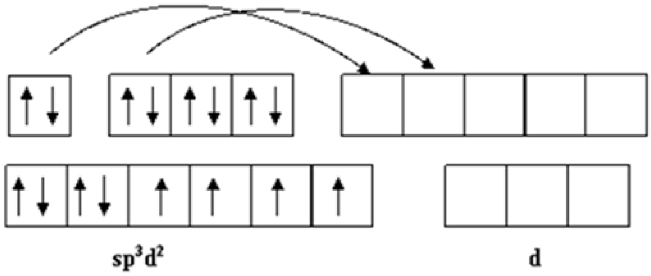


Trigonal pyramidal

c) sp^3d^2 hybridization

$Xe(Z=86) \xrightarrow{e.e} [Kr]5s^2 5p^6 5d^0$

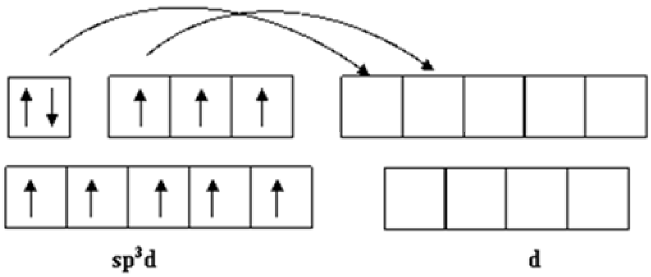


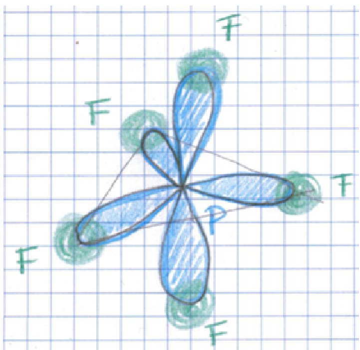


Square

d) sp^3d hybridization

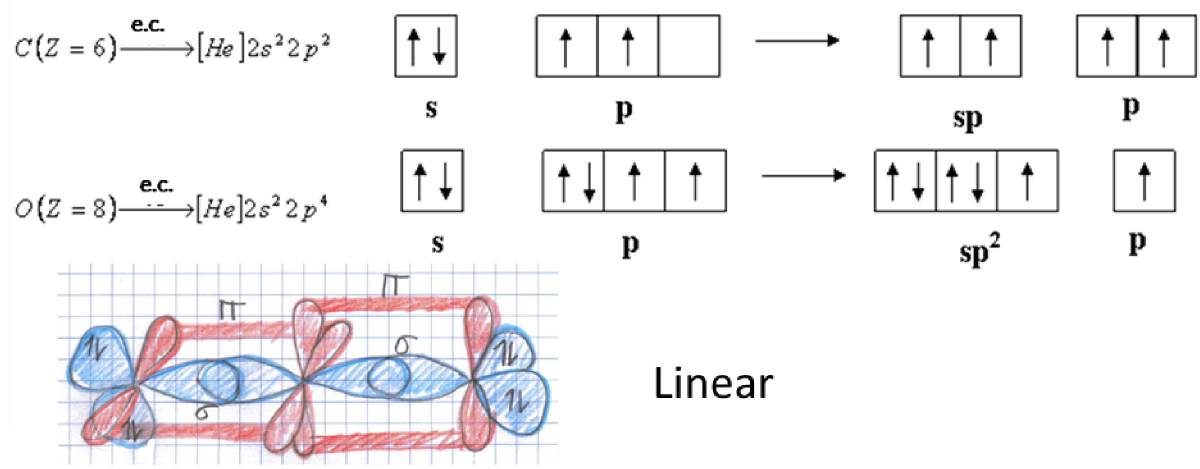
$P(Z=15) \xrightarrow{e.e} [Ne]3s^2 3p^3 3d^0$

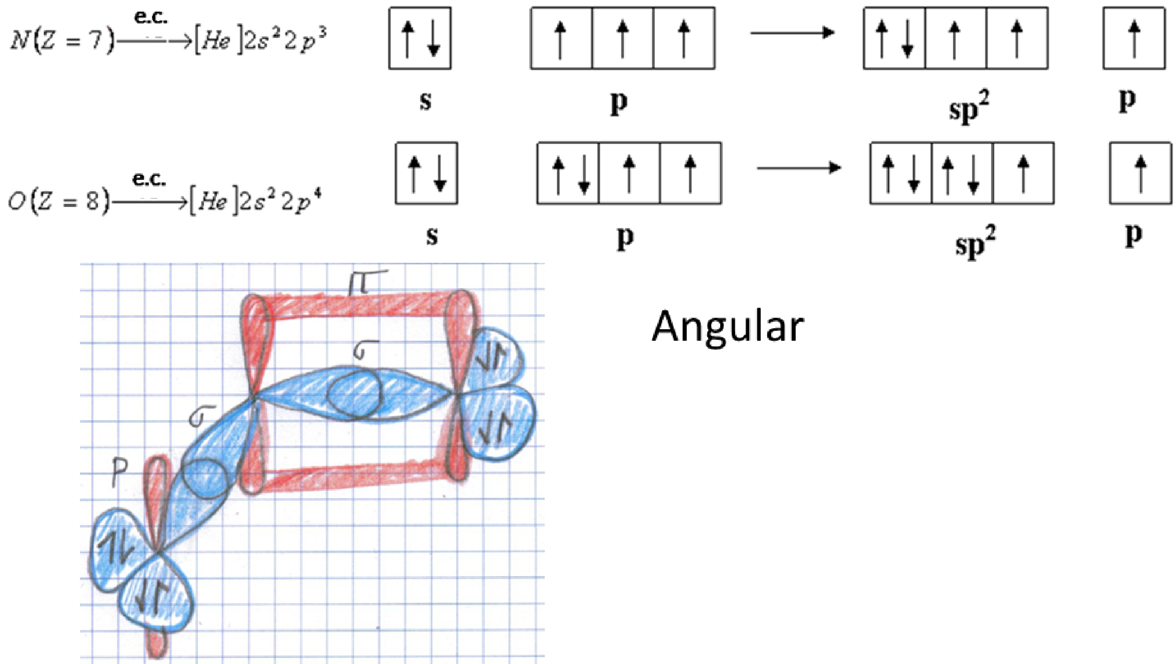




Trigonal bipyramidal

2. Give a detailed explanation of the molecular structure of CO_2 and NO_2. Determine whether they are polar or not and indicate the major interactions of these two molecules in solid state.
Solution:





Chemical bonds are polar both in CO_2 and NO_2 molecules. CO_2 is a non polar molecule because it is linear, whereas NO_2 is a polar molecule. Intermolecular forces: CO_2 → dispersion; NO_2 → dipole-dipole

3. What is the force of attraction between molecules of the following substances? a) PBr_3 b) $FeCl_2$;c) Br_2; d) HF; e) HCl ; f) CH_2O g) H_2SO_4 h) BF_3.

Solution:

a) PBr_3: This is a covalent compound. In the Lewis structure, phosphorus is the central atom. It is bonded to the three bromine atoms. The phosphorus atom also has a lone pair. Therefore the molecular shape is a trigonal pyramid, which makes it a polar compound. It therefore has dipole-dipole forces

b) $FeCl_2$: This is an ionic compound of the metal ion Fe^{2+} and the non-metal Cl^-. Therefore it has ion-ion forces

c) Br_2 : This is a covalent compound. All atoms are the same type, so the bonds are all non-polar and the molecule is non-polar. Therefore this has London (or dispersion) forces

d) HF: This is a covalent compound. Hydrogen must be bound to fluorine. Since fluorine is one of the most electronegative atoms (F, O, N), this compound will form hydrogen bonding

e) HCl: This is a covalent compound with hydrogen bonded to chlorine. This is a linear, polar molecule, so the force of attraction is dipole-dipole

f) CH_2O: This is, formaldehyde, a covalent compound with both hydrogens and the oxygen bonded to the carbon. The carbon-oxygen bond is a double bond. Since the hydrogens are not bonded to the oxygen, this does NOT form hydrogen bonding. It is, however, polar, so the force of attraction is dipole-dipole

g) H_2SO_4: This is a covalent molecule. In fact, it is an oxoacid. Recall that the structure of oxoacids is that hydrogen is bonded to oxygen. Since hydrogen is directly bonded to electronegative oxygen, this compound will form hydrogen bonds.
h) BF_3: This is a covalent compound. Boron is satisfied with a deficient octet. Therefore the structure of this compound is that all three fluorines are bonded to the boron, with no other bonds or lone pairs. The molecular geometry is trigonal planar. Since the molecule is the same on all sides, the molecule is non-polar. Therefore this compound has dispersion (or London) forces of attraction.

4. Which of the following molecules have either zero or permanent dipole moment?

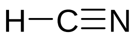
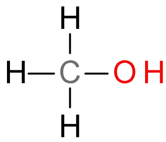
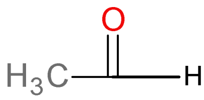
		Dipole moment(= 0; ≠0)
AX_1E_0	HBr	≠0
AX_2E_0	CO_2	=0
AX_2E_1	SO_2	≠0
AX_2E_2	H_2O	≠0
AX_2E_3	XeF_2	=0
AX_3E_0	SO_3	=0
AX_3E_1	PCl_3	≠0
AX_3E_2	BrF_3	≠0
AX_4E_0	CH_4	=0
AX_4E_1	SF_4	≠0
AX_4E_2	XeF_4	=0
AX_5E_0	PCl_5	=0
AX_5E_1	ClF_5	≠0
AX_6E_0	SF_6	=0

5. According to the Molecular Orbital Theory, draw the energy level diagram for the following molecules: H_2^+, H_2, He_2^+, He_2. Order them in increasing order of internuclear distance and of bonding energy.
Solution: $[H_2^+] = \sigma_S^1$; $[H_2] = \sigma_S^2$; $[He_2^+] = \sigma_S^2\ \sigma^*{}_S^1$; $[He_2] = \sigma_S^2\ \sigma^*{}_S^2$; Internuclear distance: $H_2^+ < H_2 < He_2^+ < He_2$; Bond energy $He_2 < He_2^+ < H_2^+ < H_2$

6. In each of the following pairs of molecules, which one has the highest bond energy?
a) Cl_2, Cl_2^+
b) NO, NO^-
c) BN, BO
d) NF, NO
e) Be_2, Be_2^+
Solution:
a) Cl_2 : Bond order = 1, Cl_2^+: Bond order = 3/2; Highest Cl_2^+
b) NO: Bond order = 5/2: NO^-: Bond order = 2; Highest NO
c) BN : Bond order = 2; BO: Bond order = 5/2; Highest BO
d) NF: Bond order = 2; NO: Bond order = 5/2; Highest NO
e) Na_2: Bond order = 0; Na_2^+: Bond order = 0.5; Highest Na_2^+

7. Propose a hybridization scheme to account for bonds formed by the central carbon atom in each of the following molecules: (a) hydrogen cyanide, HCN; (b) methyl alcohol, CH_3OH; (c) acetalehyde, CH_3COH

Solution:

 sp  sp^3  sp^2

8. For each of the following substances describe the importance of dispersion (London) forces, dipole-dipole interactions and hydrogen bonding: a) HCl, b) I_2, c) BrCl; d) HF; e) SiH_4.

Solution:

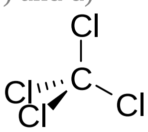
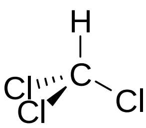
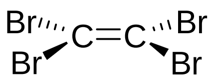
a) HCl: Dipolar; b) I_2: Dispersion; c) BrCl: Dispersion; d) HF: Hydrogen bonding; e) SiH_4: Dispersion

9. For the following molecules (CCl_4, $HCCl_3$, $Br_2C{=}CBr_2$):

a) Determine their molecular geometry
b) Indicate the hybridization of the carbon atoms
c) Order the chemical bonds in terms of increasing polarity
d) Determine whether the molecules are polar or not

Solution:

a), b) and d)

 sp^3, apolar  sp^3, polar  sp^2, apolar

c)μ(C-Cl) > μ(C-Br) > μ(C-H)

10. Arrange the following substances in order of increasing boiling point: CsF, CO_2, CH_3CH_2OH, CH_3Br. Explain your reasoning.

Solution: $CO_2 < CH_3Br < CH_3CH_2OH <$ CsF. CO_2 is linear apolar; CH_3Br and CH_3CH_2OH are polar but the alcohol has hydrogen bonding; CsF is an ionic salt.

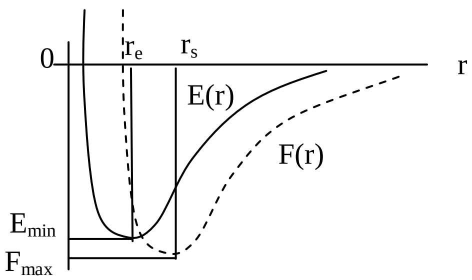
11. The total interaction energy of a pair of atoms is given by the Lennard-Jones potential.

$$E_{LJ} = -A\left(\frac{1}{r}\right)^6 + B\left(\frac{1}{r}\right)^{12}$$

where the values for A and B are known: $A = 10^{-67}\ J\cdot m^6$ and $B = 5.368\cdot 10^{-125}\ J\cdot m^{12}$. Make a sketch of how the interaction energy E_{LJ} and the force F vary with interatomic distance and answer the following questions:

a) Calculate de equilibrium distance r_e, at which energy is minimum (in nm).
b) Calculate the distance r_s at which the adhesion force is maximum (in nm).
c) Calculate de equilibrium bond energy (in J).

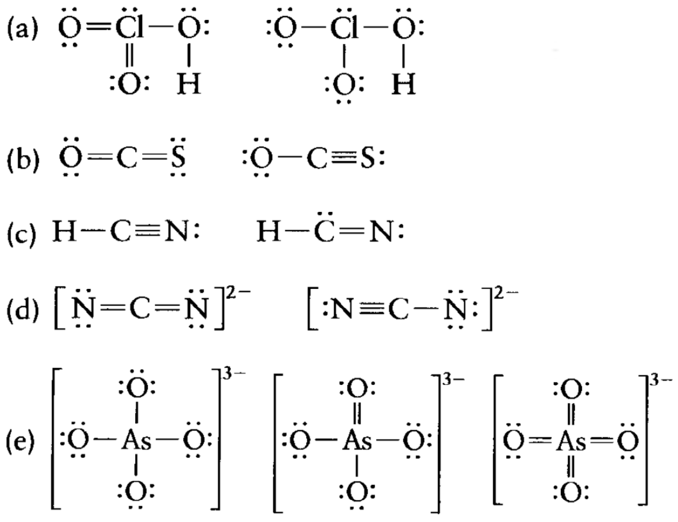
Solution:



a) E(r) reaches a minimum when dE(r)/dr = 0; at this point the equilibrium distance is $r_e = (2B/A)^{1/6} = 3.2\cdot 10^{-10}$ m = 0.32 nm

b) Force is given by F=-dE(r)/dr, and F_{mx} occurs when $d^2E(r)/dr^2 = 0$. So the distance at which the adhesion force is maximum will be $r_s = (26B/7A)^{1/6} = 0.3548$nm.
c) Bond energy is $E(r = r_e) = -4.7\cdot 10^{-11}$ J

12. Determine the formal charge on each atom in the following molecules. Identify the structure of the lower energy in each pair



13. Which of the following species are radicals? (a) NO_2^- (b) CH_3 (c) OH (d) CH_2O (e) ClO_2 (f) BF_4^- (g) BrO.
Solution: CH_3, OH, ClO_2, BrO.

14. Determine the number of electron pairs, both bonding and lone pairs, on the iodine and phosphorus atoms in (a) PCl_6^- (b) PCl_4 (c) ICl_2^+ (d)ICl_3^+
Solution: a) 6 bonding pairs and no lone pairs; b) 4 bonding pairs and no lone pairs; c) 2 bonding pairs and 2 lone pairs; d) 3 bonding pairs and 2 lone pairs

15. Dipole moments of halogen hydrides are HCl (1.05 D) HBr (0.82 D) HI (0.38 D). Calculate the average charge on each atom. (Hint: make use of bond length table)
Solution: $2.758\cdot 10^{-20}$ for HCl, $1.833\cdot 10^{-21}$ for HBr, $7.44\cdot 10^{-22}$ for HI.

16. Water solubility depends on the ionic/covalent character of compounds. Making use of the electronegativity tables, predict which of the following compounds is the more soluble in water (a) $MgCl_2$ or KCl, (b) CaO or BaO, (c) MgS or MgO.
Solution: a)KCl; b)CaO; c)MgO

17. Place the following molecules or ions in order of increasing bond order (a) N-O bond in NO, NO_2, NO_3^- (b) C-C bond in C_2H_2, C_2H_4, C_2H_6 (c) C-O bond in CH_3OH, CH_2O, CH_3OCH_3.
Solution: a) NO > NO_2 > NO_3^-; b) C_2H_2 > C_2H_4 > C_2H_6; c) CH_3OH = CH_3OCH_3 > CH_2O

18. Write the VSEPR formula and molecular shape for each of the following species (a) iodine trichloride (b) PF_4^- (c) I_3^- (d) IO_3^- (e)N_2O (f) IF_4^+.
Solution: a) AX_3E_2, T-shaped; b) AX_4E_2, see-saw; c) AX_2E_3, linear; d) AX_3E, trigonal pyramidal; e) AX_2, linear; f) AX_4E, see-saw.

19. Predict whether each of the following molecules is likely to be polar or non-polar (a) C_5H_5N – pyridine, similar to benzene except that one –CH= group is replaced by a nitrogen atom (b) trichloromethane (c) CH_3OH – methanol (d) CH_3-CO-CH_3 – acetone.
Solution: a) polar; b) polar; c) polar; d) polar.

20. State the hybridization of the underlined atom in each of the following molecules (a) $\underline{Be}Cl_2$ (b) $\underline{B}H_4^-$ (c) $H_2\underline{N}$ – CH(CH_3) –COOH (alanine) (d) $H_2C\underline{C}CH_2$ (e) $HC\underline{C}H$
Solution: a) sp; b) sp^3; c) sp^3; d) sp^2; e) sp

21. Both NH_2^- and NH_2^+ are angular species, but the bond angle in the former is less than in the latter. What is the reason for this difference?
Solution: NH_2^- has a tetrahedral distribution of electron pairs so the angle is 109º. NH_2^+ has a triangular distribution of electron pairs so the angle is 120º.

22. Write the molecular orbital configuration of the valence molecular orbitals for (1) O_2^- ;(2) O_2^+; (3) O_2^{2-} (4) O_2. (a) Give the expected bond order. (b) Which are paramagnetic, if any? (c) Is the highest-energy orbital that contains an electron σ or π in character?
Solution: a) (1) BO= 1.5;(2) BO= 2.5; (3) BO= 1 (4) BO=2; b) O_2^- ,O_2^+ and O_2; c) It is π

23. Based on their electron valence shell electron configurations which of the following species would you expect to have the lowest ionization energy. (a) F_2^+ (b) F_2 (c) F_2^- ?
Solution: F_2^- because the outermost electron is located in an energy level higher than F_2^+ and F_2