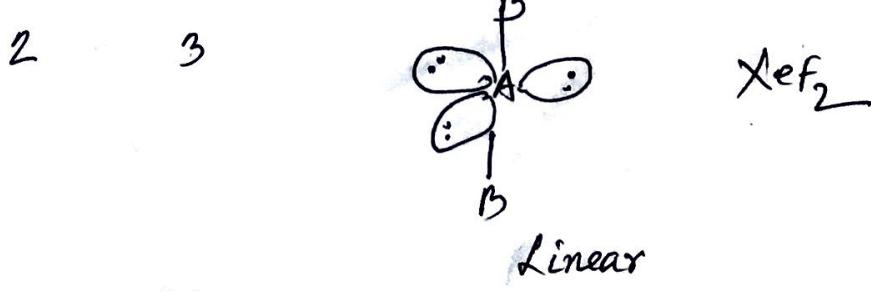
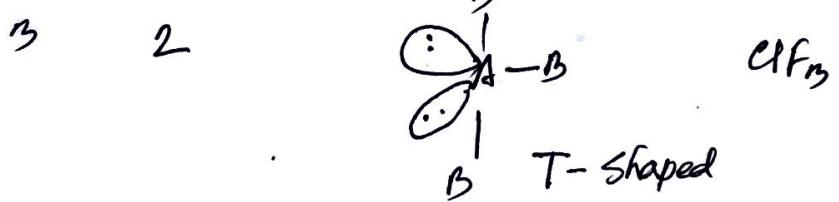
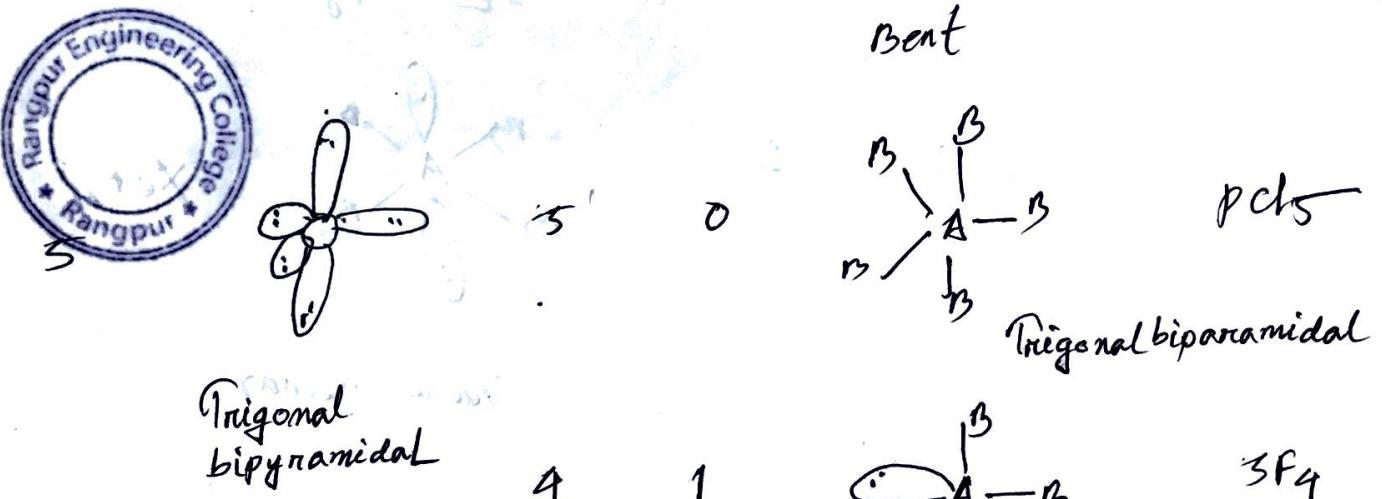
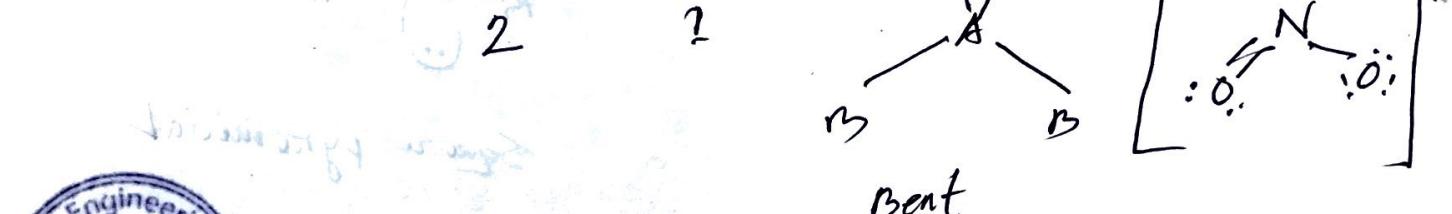
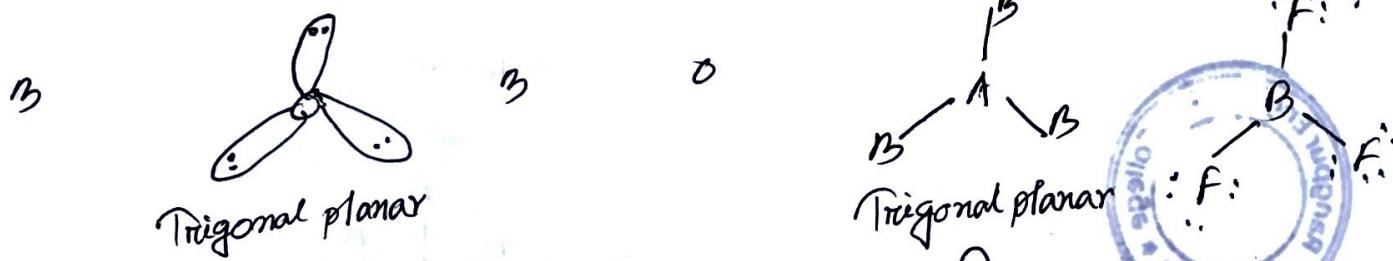


Some common rules

things geometry atoms lone pairs shape example

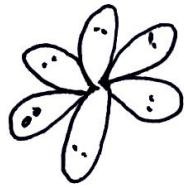


Linear

tthings

Geometry

6



atoms

lone pair

6

0

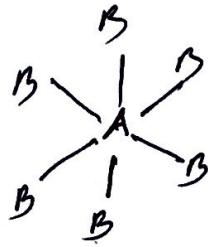
Octahedral



5

1

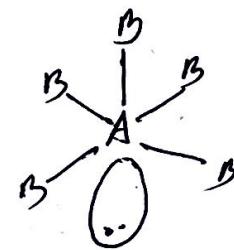
Shape



example

SF₆

Octahedral

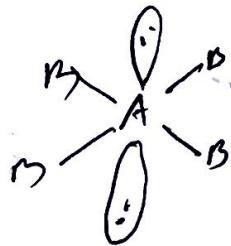


BrF₅

4

2

Square pyramidal

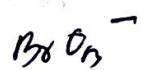
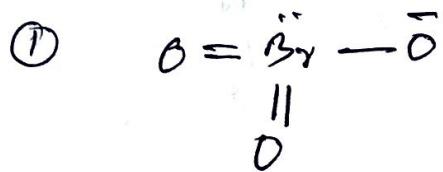


Square planar ..

Q12. We are given some molecules/ ions that have been grouped into four pairs :

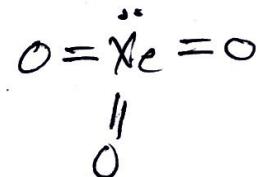
- (i) BrO_3^- , XeO_3 (ii) SF_4 , XeF_4 (iii) SO_3^{2-} , NO_3^-
 (iv) BF_3 , NF_3 . out of these pairs which pair is isostuctural

Ans. The Structure of the given pairs are given below :



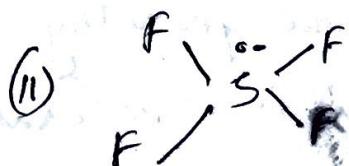
$$\sigma \text{bonds} + \text{lpn} = 3 + 1 = 4$$

(Trigonal
pyramidal)



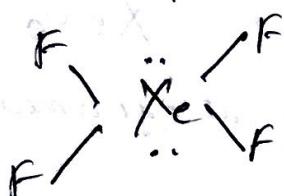
$$\sigma \text{bonds} + \text{lpn} = 3 + 1 = 4$$

(Trigonal pyramidal)



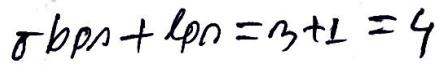
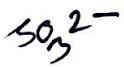
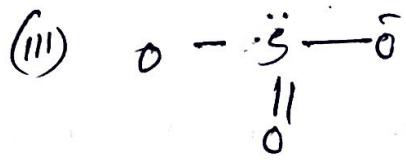
$$\sigma \text{bonds} + \text{lpn} = 4 + 1 = 5$$

(see-saw geometry)

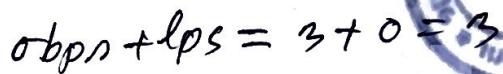
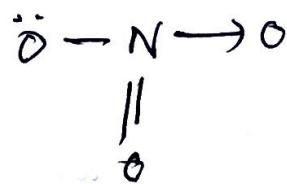


$$\sigma \text{bonds} + \text{lpn} = 4 + 2 = 6$$

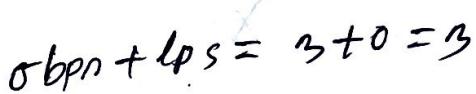
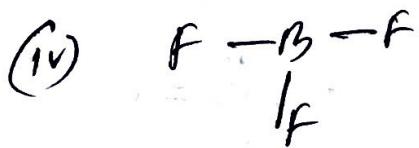
(square planar)



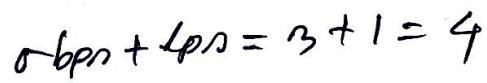
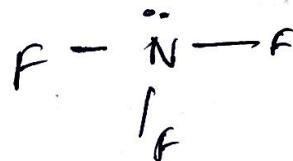
(Trigonal pyramidal)



(Trigonal planar)



(Trigonal planar)



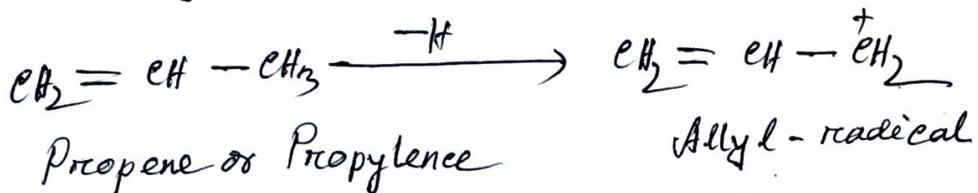
(Trigonal pyramidal)

Since BrO_3^- , XeO_3 pair has the same geometry (Trigonal pyramidal) this pair is isostructural.

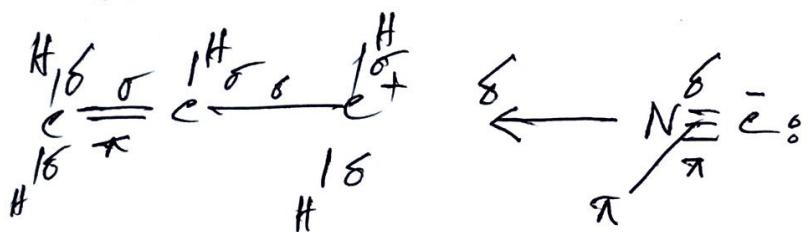
Q2Q. How many Sigma (σ) and pi (π) bonds are there in allyl-isocyanide?



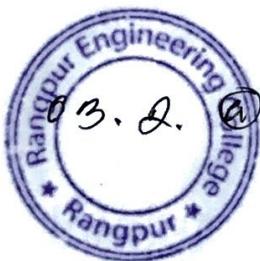
Ans. The radical obtained by removing H-atom from propene ((also) called propylidene), $\text{CH}_2=\text{CH}-\text{CH}_3$ is called allyl radical. This radical has positive charge



Obviously the structure of allyl isocyanide molecule can be written as :



obviously allyl isocyanide has 9 σ and 3 π bonds



Calculate bond-order (B.O) in NO_2^+ , NO_2^- , NO_3^-
 CO_3^{2-} and N_3^- ions

(b) Compare the Nitrogen - oxygen bond lengths in NO_2^+ , NO_2^- and NO_3^- ions.

Ans. @ We know that, B.O of a given species showing resonance

Total number of bonds between two specific

$$= \frac{\text{atoms in all the resonating structures}}{\text{Total number of resonating structures.}}$$

(i) NO_2^+ ion. This ion shows resonance. It is a resonance hybrid of the following two resonating structures.



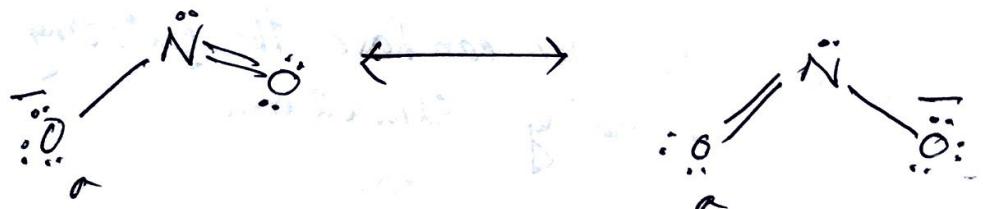
\therefore Bond order of NO_2^+ ion

Total number of bonds between N and O_2 atoms in the two resonating structures shown above

$$= \frac{\text{Total number of resonating structures}}{2}$$

$$= \frac{2+2}{2} = \frac{4}{2} = 2 \text{ (Ans.)}$$

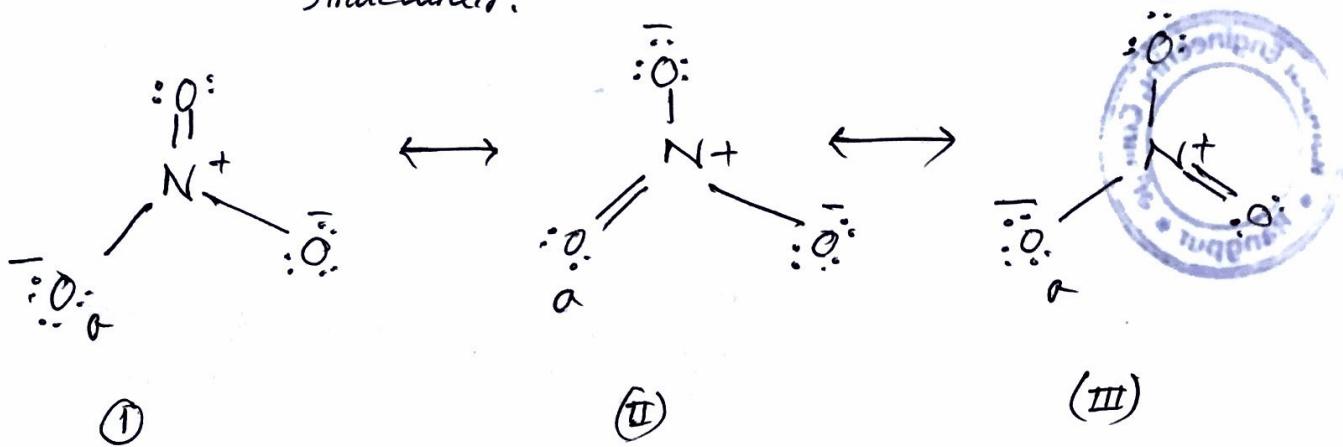
(ii) NO_2^- ion. This ion is a resonance hybrid of the following two resonating structures



$$\therefore \text{B.O of } \text{NO}_2^- \text{ ion} = \frac{\text{Total number of bonds between N and O atoms in the two resonating structures}}{\text{Total Number of resonating Structures}}$$

$$= \frac{1+2}{2} = \frac{3}{2} = 1.5 \text{ (Ans)}$$

(iii) NO_3^- ion: This ion has the following three resonating structures.

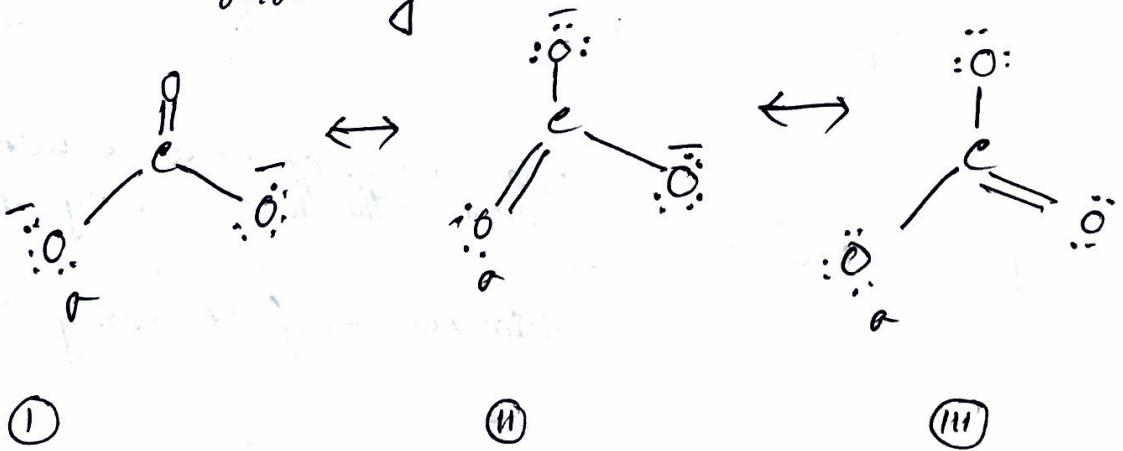


Total number of bonds between N+ and O⁻ atoms in all the three resonating structures

$$\therefore \text{B.O. of } \text{NO}_3^- \text{ ion} = \frac{\text{Total number of bonds between N+ and O}^- \text{ atoms in all the three resonating structures}}{\text{Total number of resonating structures}}$$

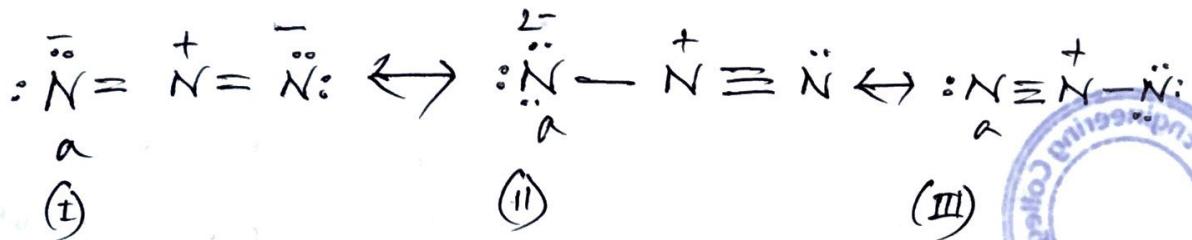
$$= \frac{1+2+1}{3} = \frac{4}{3} = 1.33 \text{ (Ans)}$$

(iv) CO_3^{2-} ion: CO_3^{2-} ion can have the following three resonating structures



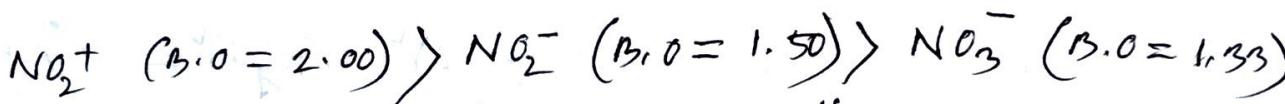
$$\therefore \text{B.O. of } \text{CO}_3^{2-} \text{ ion} = \frac{1+2+1}{3} = \frac{4}{3} = 1.33 \text{ (Ans)}$$

(v) N_3^- ion (Azide). We know that this ion is a resonance hybrid of the following three structures



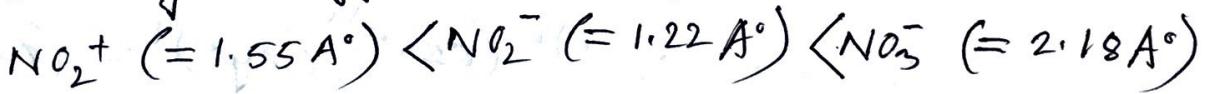
$$\text{B.O of } \text{N}_3^- \text{ ion} = \frac{2+1+3}{3} = \frac{6}{3} = 2 \text{ (Ans)}$$

(b) Since B.O. of NO_2^+ , NO_2^- and NO_3^- ions is in the order :



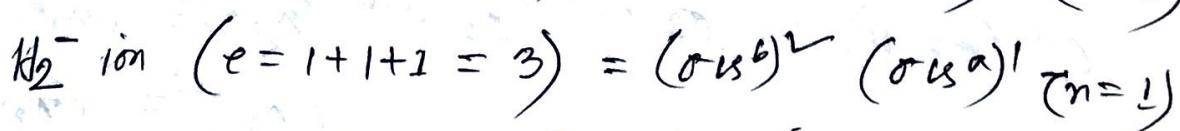
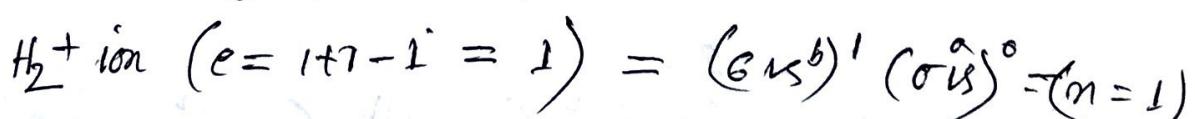
Nitrogen - oxygen bond lengths are in the reverse order,

i.e. nitrogen - oxygen bond - lengths are in the order :



Explain H_2^+ and H_2^- ions have the same bond order (0.5) yet H_2^- ion is slightly less stable than H_2^+ ion

Ans: MOEC of H_2^+ and H_2^- ions are as :



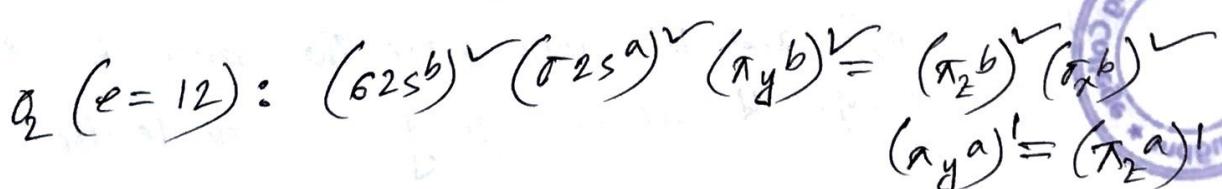
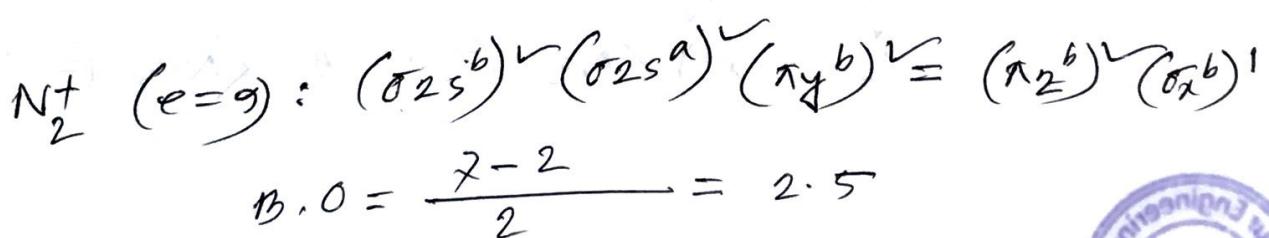
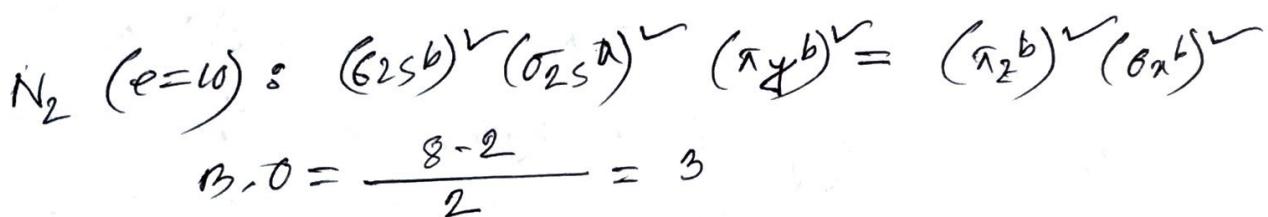
These configuration show that, H_2^- ion contains one unpaired electrons in anti-bonding MO (σ_{1s}^a) which

Producers destabilising effect and hence decreases the stability of H_2^- ion. On the other hand H_2^+ ion does not contain any electron in antibonding MO



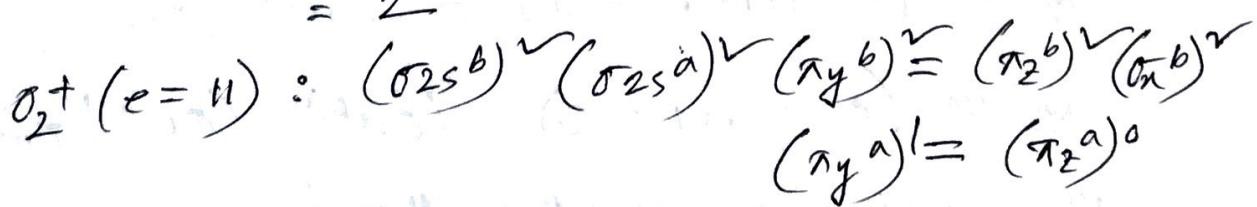
OB D. N_2^- has greater bond dissociation energy than N_2^+ whereas O_2^+ has greater bond dissociation energy than O_2

Ans. MOEC and B.O's of the given species are given below



$$B.O = \frac{8-4}{2}$$

$$= 2$$



$$B.O = \frac{8-3}{2} = 2.5$$

Since $(B.O)_{N_2} (= 3.0) > (B.O)_{N_2^+} (= 2.5)$, N_2 has greater bond dissociation energy. On the other hand since $(B.O)_{O_2^+} (= 2.5) > (B.O)_{O_2} (= 2.0)$, O_2^+ has greater bond dissociation energy.



Q8 Q Explain Bond in H_2^+ is larger than that in H_2

Ans. MOEC and B.O's of H_2^+ and H_2 are

$$H_2^+ (e=2-1=1) = (6s^b)^1, B.O = \frac{1}{2} = 0.5$$

$$H_2 (e=2) = (6s^b)^2; B.O = \frac{2}{2} = 1$$

Now since $(B.O)_{H_2^+} (= 0.5) < (B.O)_{H_2} (= 1.0)$, bond in H_2^+ is larger than that in H_2 .



Q9 Q Explain Superoxide ion (O_2^-) is paramagnetic but peroxide ion (O_2^{2-}) is not.

Ans. MOECs of O_2^- and O_2^{2-} ion are given below:

$$O_2^- (e=6\times 2 + 1 = 13) = (6s^b)^2 (6s^a)^2 (\pi_y^b)^2 = (\pi_z^b)^2 \\ (\pi_x^b)^2$$

$$(\pi_y^a)^2 = (\pi_z^a)^1 (n=1)$$

$$O_2^{2-} (e=6\times 2 + 2 = 14) \\ = (6s^b)^2 (6s^a)^2 (\pi_y^b)^2 = (\pi_z^b)^2 (6s^b)^2 (\pi_y^a)^2 \\ = (\pi_z^a)^2 (n=0)$$

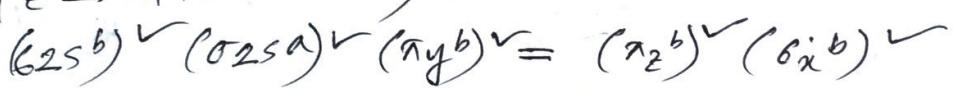
Now since O_2^- ion has one unpaired electron ($\lambda=1$)
then ion is paramagnetic.

On the other hand, since O_2^{2-} ion does not have any paired electron, then ion not paramagnetic. Rather
 O_2^{2-} ion is diamagnetic

10 Q. Bond-order of CO^+ ion is higher than that of CO molecule. Explain

Carbon—oxygen bond length in CO^+ ion is lower than that in CO molecule. Explain.

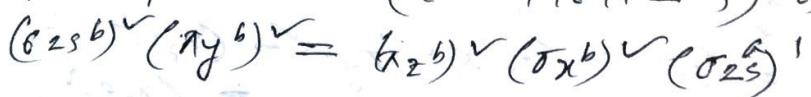
Ans. We know that the MOEC of CO molecule ($e = 4 + 6 - 10 = 0$) is :



$$B.O \text{ of } CO = \frac{N_B - N_A}{2}$$

$$= \frac{8-2}{2} = 3.00$$

In case of CO^+ ion, it has been suggested that $2s$ orbital of C -atom has higher energy than $2s$ orbital of O atom. When these $2s$ orbitals mix together to form σ_{2s}^b and σ_{2s}^a MOs, σ_{2s}^a MO has so high energy that it occupies a position in the energy level diagram above π_y^2 , π_2^b and σ_x^b MOs. Then MOEC of CO^+ ion ($e = 4 + 6 + 1 = 9$) is :



$$B.O \text{ of } \text{CO}^+ = \frac{N_b - N_a}{2}$$

$$= \frac{8-1}{2} = 3.5$$

obviously $B.O$ of CO^+ ion (3.5) is higher than that of CO molecule ($= 3$). It is because of higher $B.O$ of CO^+ ion that the carbon-oxygen bond length in CO^+ ion ($= 1.115 \text{ \AA}$) is lower than carbon-oxygen bond length in CO molecule ($= 1.128 \text{ \AA}$).

11.Q. What is Valence Bond Theory (VBT) of covalent Bond?

Ans. In-order to explain how a covalent bond is formed Heitler and London in 1927 put forward a theory which is called Valence Bond Theory (VBT)

Postulates of VBT. According to this theory:

01. An atomic orbital of the outermost shell of an atom containing one electron has a tendency to overlap with another atomic-orbital of another atom containing one electron of opposite-Spin. This type of overlap gives to the formation of bond which is called covalent bond.
02. The overlap of two atomic orbitals gives rise to a single bond orbital which is a localised orbital and occupied by both the electrons.
03. The two electrons that occupy the bond orbital have opposite Spins.

04. Each electrons occupies the entire bond orbital and hence may be considered to belong to both the atomic orbitals, i.e the electron pair present in the bond orbital now belongs to each of the atomic orbitals.
05. As a result of overlapping there is maximum electron density somewhere between the two atoms.
 A large part of the bonding force of covalent bond results from the electrostatic attraction between the nuclei and the accumulated electron clouds between them.



12.Q. Discuss about VBT and MOT (Molecular-orbital Theory)

(A)

Similarities:

01. Both the theories are the interpretation of covalent bond
02. According to both the theories the A.O's of the two atoms must overlap to form a covalent bond. The A.O's overlapping each other must have the same symmetry and must be of the same energy.
03. According to both, the electronic charge resides in the region between the atomic nuclei
04. Both the theories postulate that a covalent bond possesses directional properties.

(B) Differences:



MOT

(i) MOs are formed by LCAO approximation method. The AOs involved in the formation of these MOs are from valence shell of two atoms.

(ii) AOs of the resulting molecule lose their individual identity

(iii) MOT starts with the nuclei of the constituent atoms

(iv) MOT offers a satisfactory explanation of the paramagnetic character of O_2 molecule.

(v) Resonance plays no role in MOT

VBT

(i) Two AOs give an interatomic orbital obtained by the combination of the space functions of two unpaired electrons; one being in each of the two AOs

(ii) The resulting molecule consists of atoms which, although, interacting, retain a large measure of their individual character.

(iii) VBT starts with the individual atoms and considers the interaction between them.

(iv) VBT fails to account for the paramagnetic character of O_2 molecule.

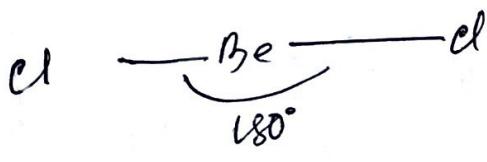
(v) Resonance plays an important role in VBT.



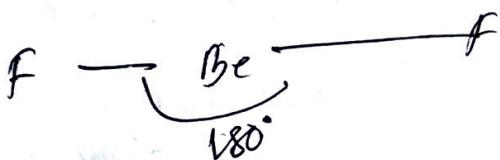
Q. Draw the shape of the following molecule or ion
 $\text{BeCl}_2, \text{BeF}_2$

Ans. Here $bps = 2$
 $lp = 0$

So these have σ -bonding electron pairs and no lone pair ($bps = 2; lp = 0$). These have linear shape.



And



* Shape of Molecules / Ions on the basis of VSEPR Theory :

01 Shape of molecules / ions where central atom / ion has two electron pairs.

Such molecules may be of AB_2 (BeF_2) type. These have two σ -bonding electron pairs and no lone pair ($bps = 2; lp = 0$). These have linear shape.

Hence, A is the central atom / ion and B are the atoms bonded to atom A by σ -bonds only π -bonds are not present.

02. Shape of molecules / ion whose central atom / ion has 3 electron pairs. Such species may be of AB_3 ($bps = 3, lp = 0$) and AB_2 (lp) ($bps = 2, lp = 1$) type. The species of AB_3 (e.g. BF_3 , $GaCl_3$) and AB_2 (lp) e.g. $SnCl_2$ (gaseous) $PbCl_2$] type have trigonal planar and angular or V- shape respectively.



03. Shape of molecules / ions whose central atom / ion has four electron pairs.

such species may be of AB_4 ($bps = 4, lp = 0$) AB_3 (lp) ($bps = 3, lp = 1$), AB_2 (lp)₂ ($bps = 2, lp = 2$) and AB (lp)₃ ($lp = 1, bps = 3$) type.

The species of AB_4 (e.g. CH_4), PCl_4^+ , $SiCl_4$, BH_4^- , NH_4^+ have regular tetrahedral in shape.

The Species AB_3 (lp) for example : NH_3 : PA_3 have trigonal pyramidal in shape.

AB_2 (lp)₂ for example, H_2O , ICl_2^+ , SCl_2 have angular or V- shape

AB (lp)₃ for example, ICl have linear shape.

04. Shape of molecules / ions whose central atom / ion has five electron pairs:

such species may be of AB_5 ($bps = 5, lp = 0$)
 AB_4 (lp) ($bps = 4, lp = 1$)
 AB_3 (lp)₂ ($bps = 3, lp = 2$)
 AB_2 (lp)₃ ($bps = 2, lp = 3$) type.

The Species of AB_5 . For example, PF_5 , PCl_5 have trigonal bipyramidal in shape.

The Species $AB_4 (lp)$

for example SF_4 , IF_5^+
have distorted trigonal bipyramidal in shape

The Species $AB_3 (lp)_2$

for example ClF_3 , BrF_3 have T- shape

The Species $AB_2 (lp)_3$

for example, XeF_2 , I_3^- , ICl_2^-
have linear in shape.

05. Shape of molecules / ions where central atom / ion has six electron pairs:

Such species may be of AB_6 ($bps = 6$, $lp = 0$)

$AB_5 (lp)$ ($bps = 5$, $lp = 1$)

$AB_4 (lp)_2$ ($bps = 4$, $lp = 2$) type.

The Species of AB_6 for example SF_6 , PCl_6^-
have regular octahedral in shape.

The Species of $AB_5 (lp)$ for example SbX_5^{2-} , BrF_5 , IF_5
have square pyramidal in shape.

The Species $AB_4 (lp)_2$ for example XeF_4 , ICl_4^-
have square planar in shape

Q6. Shape of molecules / ions whose central atom / ion has seven electron pairs.

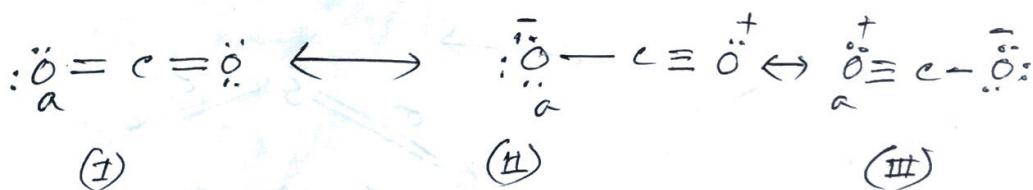
- Such species may be of AB_7 ($bps = 7, lp = 0$)
and AB_6 (lp) ($bps = 6, lp = 1$)

The Species of AB_7 for example IF_7 has trigonal bipyramidal [and distorted octa-hedral shapes].

The Species of AB_6 (lp) For example XeF_6 has

Q. Calculate the Bond - order of CO_2 molecule :

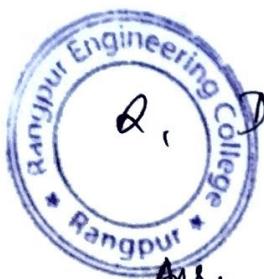
Ans. CO_2 shows resonance and it has three resonating structures given below —



$$B.O \text{ of } CO_2 = \frac{\text{Total number of bonds between C and O atoms in all the three resonating structures}}{\text{Total number of resonating structures}}$$

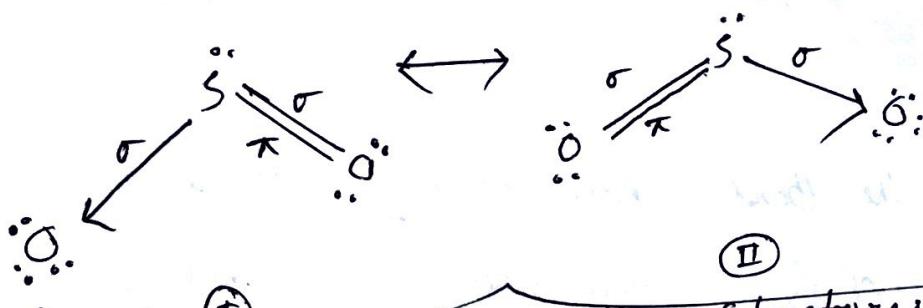
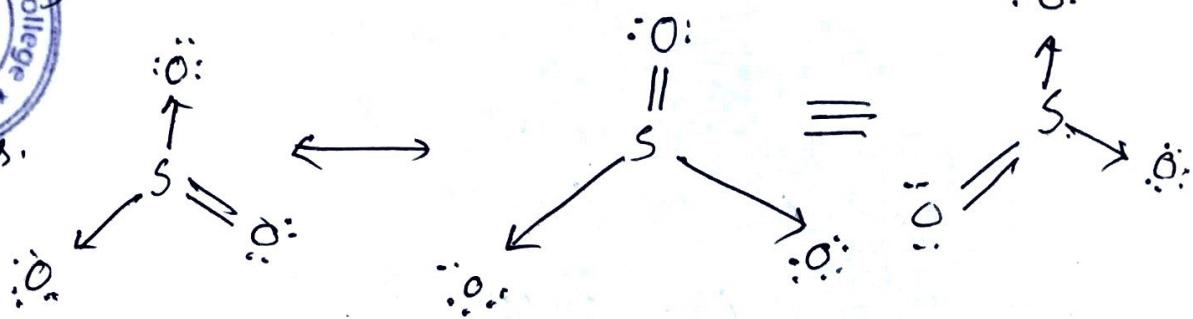
$$= \frac{2 + 1 + 3}{3} = \frac{6}{3} = 2$$

So the Bond order of CO_2 is 2

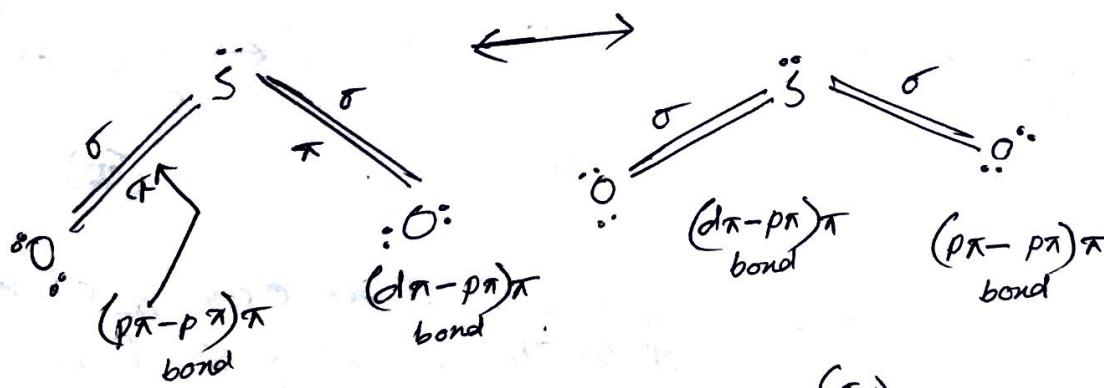


Q. Deduce the Resonance of SO_3 , SO_2

Ans.



Resonating Structures

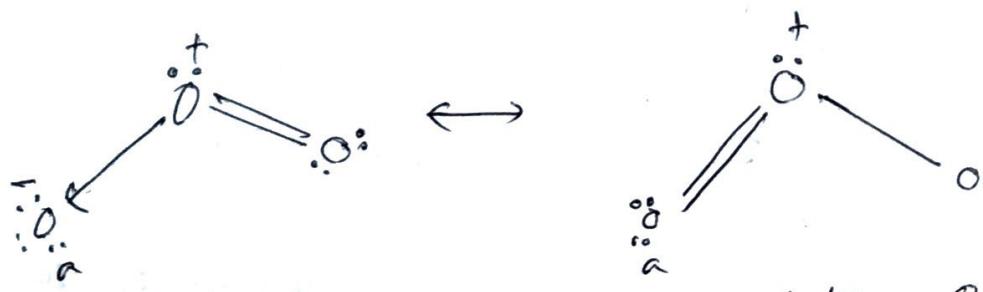


(III)

(IV)

Resonating Structures

B.O of O_3



Total Number of bonds between O_a and central O atom
in the two resonating Structures

$$B.O \text{ of } O_3 = \frac{\text{Total Number of bonds between O}_a \text{ and central O atom}}{\text{Total Number of resonating Structures.}}$$

$$= \frac{1+2}{2} = \frac{3}{2} = 1.5$$

Q. Describe about VSEPR theory.

Ans. VSEPR means Valence shell Electron pairs Repulsion theories.

According to this theory, the geometry of a molecule depends on the bonding and the Number of the anti-bonding electron pairs in the central atom which arrange themselves in such a way that there is maximum repulsion between them so that the molecule has minimum energy.

The following rules have been proposed by Gillespie to explain the shape of some covalent molecules.

Rule 01: If the central atom of a molecule is surrounded only by bonding electron pairs (BPS) and not non bonding electron pairs called lone pairs (LP) the geometry of the molecule will be regular.

For example. it will be linear, triangular planar, regular tetrahedral, trigonal bipyramidal

and regular octahedral for, 2, 3, 4, 5, 6 bonding electrons.



Rule-02: When the central atom in a molecule is surrounded by both bps and lp's the molecule does not have a regular shape

The repulsion is given below—

if the adjacent electron pair is a lp then

$$(lp - lp) > (lp - bp) \longrightarrow \textcircled{1}$$

Again, if the adjacent electron pair is a bp, then

$$(lp - bp) > (bp - bp) \longrightarrow \textcircled{11}$$

So the combination of relation ① and ⑪ we get,

$$(lp - lp) > (lp - bp) > (bp - bp)$$

Rule-03: B-A-B bond angle decreases with the increase in the electronegativity of atom B in AB₃ molecule where A is the central atom

for example:

$$\textcircled{1} \text{ } \text{PF}_3 \text{ (102}^\circ\text{)} > \text{PBr}_3 \text{ (101.5}^\circ\text{)} > \text{PCl}_3 \text{ (100}^\circ\text{)}$$

$$\textcircled{11} \text{ } \text{AsI}_3 \text{ (101}^\circ\text{)} > \text{AsBr}_3 \text{ (100.5}^\circ\text{)} > \text{AsCl}_3 \text{ (98.4}^\circ\text{)}$$

Rule-04: Bond angles involving multiple bonds are generally larger than those of involving only single bonds. However, the multiple bonds do not affect the geometry of a molecule.

Rule-05 : Repulsion between electron pairs in filled shells are larger than the repulsion between electron pairs, in incompletely filled shells

For examples : $\text{H}-\text{O}-\text{H}$ and $\text{H}-\text{S}-\text{H}$
(105.5°) (92.2°)

Limitations of VSEPR Theory :

- (i) VSEPR theory cannot explain the shapes of the molecules which have very polar bond angles.
For example Li_2O should have the same structure as H_2O but in fact it is linear.
- (ii) This theory is unable to explain the shapes of molecules having extensive delocalised electron system.
- (iii) This theory cannot explain the shapes of certain molecule which have an inert-pair of electrons.
- (iv) This theory is not able to predict the shapes of certain transition metal complexes.





Important - Question

Explain why the bond energy of He_2^+ is 57 kcal/mol
but in H_2 is 103 kcal/mol

02. Explain N_2 molecule is diamagnetic but O_2 is paramagnetic in Nature.
03. Explain, why there is not existence of Be_2 .
04. Show that, the Bond-order and Bond energy of N_2 is greater than N_2^+ .
05. Explain the magnetic properties, B.O and Bond length of the following
 $\text{O}_2^+, \text{O}_2, \text{O}_2^{2-}, \text{O}_2^-$
06. Determine the B.O (Bond-order) Magnetic Properties of the following
 $\text{B}_2, \text{C}_2, \text{N}_2, \text{NO}, \text{NO}^+, \text{NO}^-, \text{CO}$
7. What is HOMO (HOMO) and LUMO

Ans. Highest occupied molecular orbital is known as HOMO and Lowest unoccupied molecular orbital is known as LUMO.

8. Explain why H_2O is liquid but H_2S , H_2Se and H_2Te is gaseous.