Date: 16/10/2021

Q1. Give reason for the following: covalent bonds are directional bonds whie ionic bonds are non-directional.

Q2. Give reason for the following: The bond angle in water is less than that of ammonia.

Q3. Predict the shape of AsF_5 and PH_3 according to VSEPR theory.

Q4. Is there any change in the hybridisation of B and N atom as a result of the reaction?

$$BF_3 + NH_3 \longrightarrow F_3B \cdot NH_3$$

Q5. In NO_3^- ion, calculate the number of bond pairs and lone pairs of electrons on nitrogen atom.

Q6. Draw the shape of PCl_3 and BrF_5.

Q7. Give reason for the following: Be_2 molecule does not exist.

Q8. Calculate the bond order of Li_2, B_2 and C_2. Also predict their paramagnetic behaviour.

Q9. What will be the correct order of vapour pressure of water, acetone and ether at 30°C? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point.

Q10. Explain why HF is less viscous than H_2O?

Q11.(a) On the basis of VSEPR theory, explain the shape of ClF_5.

(b) Write the formula of sulphuric acid and calculate the formal charge on each oxygen atom.

Q12. Consider the following two compounds:

Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding?

Q13. On the basis of VSEPR theory, predict the shapes of the folloiwng:

(a) NH_2^- (b) O_3

Q14. (a) Arrange the following in increasing order of stability:

$$H_2, \quad H_2^+ \quad \text{and} \quad H_2^-.$$

(b) Using VSEPR theory, draw the structure of IF_5.

Q15. (a) Calculate the formal charge on each oxygen atom and P — O bond order in PO_4^{3-} ion.

(b) The electronegativity difference between N and F is greater than N and H yet the dipole moment of NH_3 is larger than that of NF_3. Explain.

Q16. (a) Although, both CO_2 and H_2O are triatomic molecules, the shape of the H_2O molecule is bent while that of CO_2 linear. Explain this on the basis of dipole moment.

(b) Find out the isoelectronic species from the following:

$$CO, \ NO^+, \ N_2, \ MgCl_2, \ NO_2^-$$

Q17. Compare the bond energy and magnetic character of O_2^+ and O_2^- species. (Using molecular orbital theory)

Q18. Draw the structures of $XeOF_2$ and $XeOF_4$.

Q19. (a) What type of hybridisation is whown by NO_3^- and H_2Se?

(b) Why N — F bond length in NF_3 is greater than the sum of the single covalent radii of N and F?

(c) Arrange the folowing bonds in order of increasing ionic character:

$$N-H, \ F-H, \ C-H \ \text{ and } \ O-H.$$

Q20. (a) Why is NF_3 pyramidal but BF_3 triangular planar?

(b) Which d-orbital is involved in sp^3d hybridisation?

(c) Solubility of $MgCl_2$ much greater than MgF_2. Why?

Q21. (a) Write the molecular orbital (MO) electronic distribution of O_2. Specify its bond order and magnetic property.

(b) Draw the molecular structures of XeF_2, XeF_4 and XeO_2F_2, indicating the location of lone pair(s) of electrons.

(c) H_2^+ and H_2^- ions have the same bond order but H_2^+ ions are more stable than H_2^-. Why?

Q22. (a) Draw the structure of IF_5 on the basis of VBT.

(b) Group the following as linear an non-linear molecules:

$$H_2O, \ HOCl, \ BeCl_2, \ Cl_2O.$$

(c) Why are the axial bonds longer as compared to that of equatorial bonds in PCl_5.

Q23. (a) Among the following, which one is polar and has the central atom with sp^2-hybridisation?

$$H_2CO_3, \ SiF_4, \ BF_3 \ \text{ and } \ HClO_4.$$

(b) Why CO_3^{2-} cannot be represented by a single Lewis structure. How can it be best represented?

(c) Molecules *viz*., H_2, Li_2 and B_2 have the same bond order yet they are not equally stable. Explain.

Date: 16/10/2021

S1. A covalent bond is formed by the overlapping of atomic orbitals. The direction of overlapping gives the direction of bond. In ionic bond, the electrostatic field of an ion is non-directional. Each positive ion is surrounded by a number of anions in any direction depending upon its size and *vice-versa*. That's why covalent are directional bonds while ionic bonds are non-directional.

S2. In H_2O molecule, there is *lp-lp* repulsion due to the presence of two lone pairs of electrons on central oxygen atom while in NH_3 molecule, there is only *lp-bp* repulsion. According to VSEPR theory, the *lp-lp* repulsion is stronger than *lp-lp* repulsion causes lesser bond angle. Hence, the bond angle in water is less than that of ammonia.

NH_3
bp = 3, lp = 1

H_2O
bp = 2, lp = 2
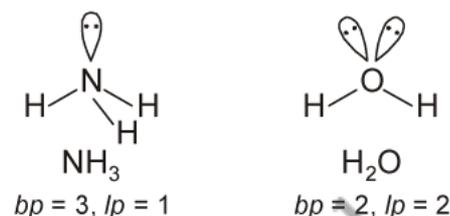
S3. The central atom as has only 5 bond pairs and no lone pair. It is of the type AB_5 and hence, the shape is trigonal bipyramidal.

AsF_5:
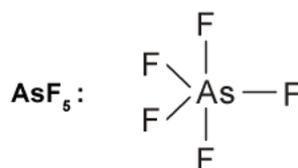
The central atom P has 5 valence electrons. Out of which here are utilised in bonding with H-atoms and one pair remains as lone pair. So, it contains 3 bond pairs and 1 lone pair. It is of the type AB_3E and hence, the shape is pyramidal.

PH_3:
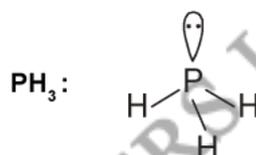
S4. In BF_3, there are 3 bond pairs and 0 lone pair, so boron is sp^2-hybridised and in NH_3, there are 3 bond pairs and 1 lone pair, so nitrogen is sp^3-hybridised. After the reaction, hybridisation of boron changes to sp^3 but hybridisation of nitrogen remains the same because N shapes its lone pair with electron deficient B.

i.e., $BF_3 + NH_3 \longrightarrow F_3B \cdot NH_3.$

S5. The structure of NO_3^- ion is given below:
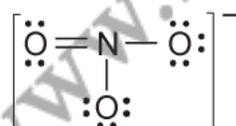
The number of valence electrons of N-atom = 5.

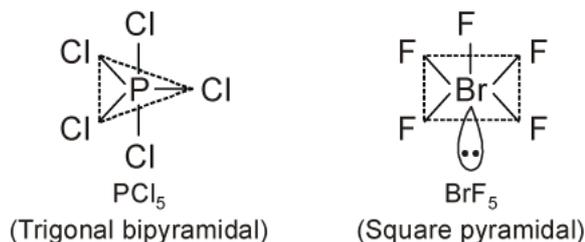Due to the presence of one negative charge, number of valence electrons = 5 + 1 = 6.

One O-atom froms a double bond and each of two other O-atoms form a single bond with N-atom.

Thus, 3 O-atoms shared with 6 electrons onf N-atom.

∴ Number of bond pairs (or shared pairs) = 4.

Number of lone pairs = 0.

S6.

PCl$_5$
(Trigonal bipyramidal)

BrF$_5$
(Square pyramidal)

S7. Electronic configuration of $_4$Be = $1s^2, 2s^2$

Electronic configureation of Be$_2$ molecule (4 + 4 = 8) = $\sigma^1 s^2, \overset{*}{\sigma}^1 s^2, \sigma^2 s^2, \overset{*}{\sigma}^2 s^2$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(4-4) = 0$$

Hence, Be$_2$ does not exist.

S8. (a) Li$_2$(6) = $(\sigma 1s)^2 (\overset{*}{\sigma} 1s)^2 (\sigma 2s)^2$ = Bond order = $\frac{1}{2}(4-2) = \frac{2}{2} = 1$, (paramagnetic)

(b) B$_2$(10) = $(\sigma 1s)^2 (\overset{*}{\sigma} 1s)^2 (\sigma 2s)(\overset{*}{\sigma} 2s)^2 (\pi 2p_x^1 = \pi 2p_y^1)$ = Bond order = $\frac{1}{2}(6-4) = 1$, (paramagnetic)

(c) C$_2$(12) = $(\sigma 1s)^2 (\overset{*}{\sigma} 1s)^2 (\sigma 2s)^2 (\overset{*}{\sigma} 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ = Bond order $\frac{1}{2}(8-4) = 2$, (diamagnetic)

S9. The given compounds are:

Water > Acetone > Ether

(Maximum BP)   (Minimum BP)

Greater the boiling point, lower is the vapour pressure of the solvent. Hence the correct order of vapour pressure will be:

Water < Acetone < Ether.

S10. In H$_2$O, there is a greater intermolecular hydrogen bonding than that of HF. Each H$_2$O molecule forms four H-bonds with other water molecules whereas, HF forms only two H-bonds with other HF molecules. Greater the intermolecular H-bonding, greater is the viscosity. Therefore, HF is less viscous than H$_2$O.

S11. (a) The central atom Cl has seven electrons in the valence shell. Five of these will form bonds with five fluorine atoms and the remaining two electrons are present as one lone pair. Hence, total pairs of electrons are six (5 bond pairs and 1 lone pair). To minimise repulsion between lone pairs and bond pairs, the shape becomes square pyramidal.
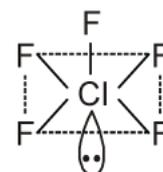
(b) H_2SO_4

Formal charge on an atom = [Total number of valence electrons on atom]

– [Total number of electrons as lone pair]

$-\dfrac{1}{2}$ [Total number of shared electrons]
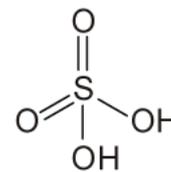
Formal charge on O (1) or O (3) = $6 - 4 - \dfrac{1}{2} \times 4 = 0$

Formal charge on O (2) or O (4) = $6 - 6 - \dfrac{1}{2} \times 2 = -1$

S12. For intramolecular hydrogen bonding, the molecule should contain two groups at successive positions such that one group contains H-atom linked to a highly electronegative atom and the other group should also contain a highly electronegative atom linked to a lesser electronegative atom. As this condition is applicable only on *o*-nitrophenol, hence it will form intramolecular hydrogen bonding which leads to the formation of a six-membered ring including the H-atom. While the other molecule forms intermolecular H-bonding with other molecule.

o-nitrophenol

p-nitrophenol
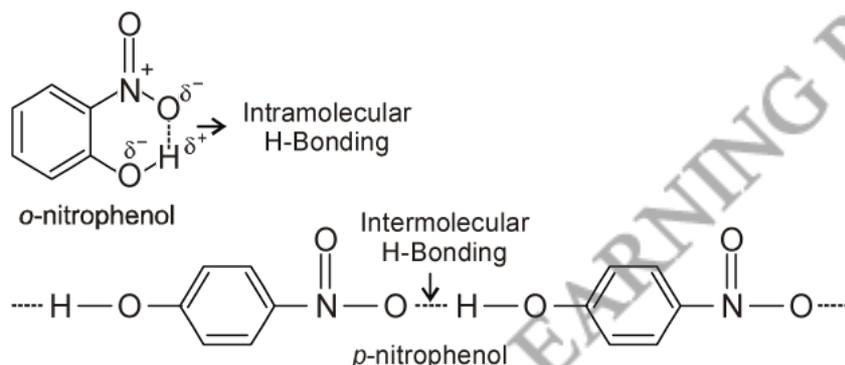
S13. (a) **Shape of NH_2^-**

Number of valence electrons of central N-atom = 5 + 1 = 6 (due to one unit of negative charge)

Number of atoms linked to it = 2

∴ Total number of electron pairs around N = $\dfrac{6+2}{2} = 4$

Number of bond pairs = 2

∴ Number of lone pairs = 4 – 2 = 2

Thus, the ion is of the type AB_2E_2. Hence, it has bent-shape (V-shape)
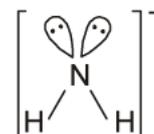
(b) **Shape of O_3 :** For predicting geometry of molecules containing π-bond (double or triple bond) each π-bond is considered as an electron pair. In case of ozone, its two resonating structures are:

$$:\ddot{O} - \ddot{O} = \ddot{O} \longleftrightarrow \ddot{O} = \ddot{O} - \ddot{O}:$$

Thus, the central O-atom is considered to have two bond pairs and one lone pair, *i.e.*, it is of type AB_2E. Hence, it is a bent-shaped molecule.
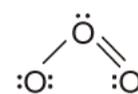
S14. (a)   Stability $\propto$ Bond order

$H_2 = \sigma 1s^2$, $BO = \dfrac{2-0}{2} = 1$

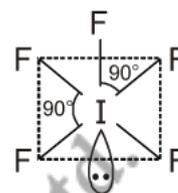$H_2^+ = \sigma 1s^1$, $BO = \dfrac{1-0}{2} = \dfrac{1}{2}$

$H_2^- = \sigma 1s^2, \overset{*}{\sigma} 1s^1$, $BO = \dfrac{2-1}{2} = \dfrac{1}{2}$

Antibonding orbitals destabilise the molecule, so correct stability order will be $H_2^- < H_2^+ < H_2$.

(b)   In IF_5, number of valence electrons of central-atom = 7

Number of atoms linked to it by single bonds = 5

$\therefore$ Total number of electron pairs around $I = \dfrac{7+5}{2} = 6$

Number of bond pairs = 5

$\therefore$ Number of lone pairs = 6 – 5 = 1

Thus, the molecule of the type AB_5L.

Hence, it has square pyramidal shape.

S15. (a)   Average P — O bond order and average formal charge on each O-atom in PO_4^{3-} can be calculated as:

Total number of electrons present in valence shell of (P — O) = 5 + 8 = 13

Total number of electrons involved in bond formation = 13 – 3 = 10

Number of bonds in PO_4^{3-} ion = $\dfrac{10}{2} = 5$

Therefore, average P — O bond order = $\dfrac{5}{4}$ = 1.25 and average formal charge on each O-atom

$= \dfrac{\text{Total charge}}{\text{Total entity of O-atom}} = \dfrac{3}{4} = -0.75$

(b)   Electronegativity of N is greater than that of H, but in NF_3, electronegativity of F is greater than that of N. So, in NH_3, the atomic dipole and bond dipole are in the same direction whereas, in NF_3, these are in opposite directions. Therefore, dipole moment of NF_3 is less than that of NH_3.
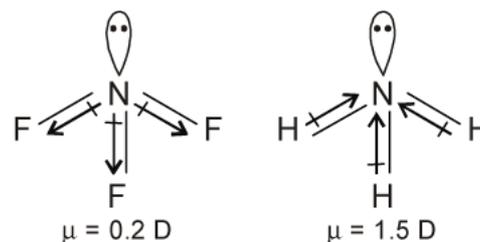
S16. (a)   The net dipole moment of CO_2 is zero. This is because the two equal bond dipole (C — O) points are in opposite directions and cancel the effect of each other. Hence, CO_2 is linear. On the other hand, H_2O molecule is found to have a net dipole moment (1.84 D) which suggests that the two O — H dipoles are not in a straight line and this dipole moment is the resultant of the dipole moments of two O — H bonds. Thus, H_2O molecule has a bent structure in which the two O — H bonds are oriented at an angle of 104.5°.

We have, in case of H_2O: $\mu_{net} = \mu_1 + \mu_2$

But in case of CO_2: $\mu_1 = -\mu_2$ $[\because \mu_{net} = 0]$

(b) Isoelectronic species have same number of electrons

Electrons present in $CO = 6 + 8 = 14$

$NO^+ = 7 + 8 - 1 = 14$

$N_2 = 7 + 7 = 14$

$MgCl_2 = 12 + 17 \times 2 = 12 + 34 = 46$

$NO_2^- = 7 + 16 + 1 = 24$

Hence, CO, NO^+ and N_2 are isoelectronic species.

S17. According to molecular orbital theory, electronic configuration of O_2^+ and O_2^- species are as follows:

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

Bond order of O_2^+ = $\dfrac{10-5}{2} = \dfrac{5}{2} = 2.5$

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

Bond order of O_2^- = $\dfrac{10-7}{2} = \dfrac{3}{2} = 1.5$

Due to higher bond order, O_2^+ is more stable than O_2^-. Both the species have unpaired electrons. So, both are paramagnetic in nature.

S18. In $XeOF_2$,

Number of s-bonds = 3

Number of lone pairs = 2

$\therefore$ Total number of electron pairs = 3 + 2 = 5
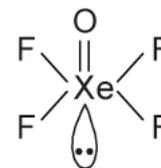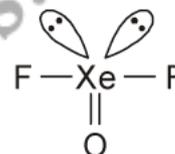
Hybridisation $\rightarrow sp^3d$

Shape $\rightarrow$ T-shaped geometry

The structure of $XeOF_4$ is

Total number of electron pairs = +6

Hybridisation $\rightarrow d^2sp^3$

Shape $\rightarrow$ Square pyramidal.

S19. (a) **Thinking process:**

Number of hybrid orbitals (x) formed by the central atom can be calculated as:

$X = \dfrac{1}{2}$ [(Number of valence electrons of the central atom)

+ (Number of monovalent atom groups surrounding the central atom)
– (Charge on the cation) + (Charge on the anion)]

$$X = \frac{1}{2} [VE + MA - C + a] = 3.$$

Value of X	2	3	4	5	6	7
Types of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

$$NO_3^- [N = 2, 5] = \frac{1}{2} [5 + 0 - 0 + 1]$$
$$X = 3$$

Thus, hybridisation is sp^2, hence shape is triangular planar.
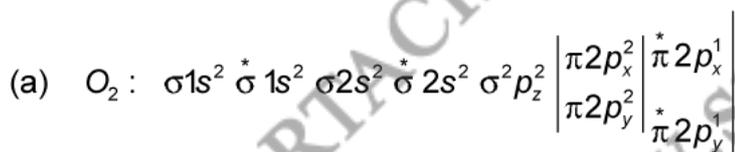H_2Se ($Se = 4s^2 4p^4$),

$$X = \frac{1}{2} [6 + 0 - 0 + 0] = 3.$$

Thus, hybridisation is sp^2 and hence, shape is triangular planar.

(b) Because both N and F have small size and high electron density. So, they repel the bond pairs, therby making N — F bond length larger than the single covalent radii of N and F.

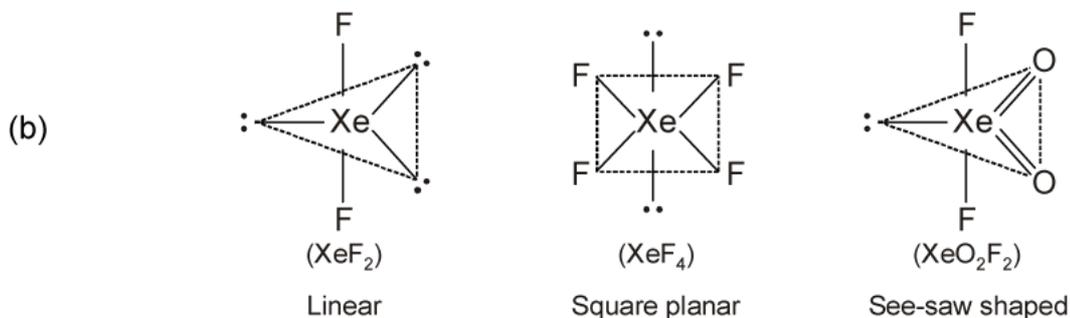(c) As greater is the electronegativity difference betwee the two bonded atoms, greater is the ionic character.

Electronegativity	(2.5 – 2.1)	3.0 – 2.1	3.5 – 2.1	4.0 – 2.1
Difference	= 0.4	= 0.9	= 1.4	= 1.9

S20. (a) In NF_3, N has sp^3 hybridisation with one position occupied by lone pair of electrons while in BF_3. B has sp^2 hybridisation.

(b) It is the d_{z^2} orbital. The three planar triangular hybrid orbitals may be assumed to be formed from one s and two p-orbitals (sp^2) and the remaining p-orbital may combine with d_{z^2} to form two axial hybrid orbitals.

(c) Cl^- ions are much larger in size than that of F^- ions. Therefore, lattice enthalpy of $MgCl_2$ and thus, solubility of $MgCl_2$ is more.

S21.

(a) $O_2 :$ $\sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2 \sigma^2 p_z^2 \begin{vmatrix} \pi 2p_x^2 & \overset{*}{\pi} 2p_x^1 \\ \pi 2p_y^2 & \overset{*}{\pi} 2p_y^1 \end{vmatrix}$

Bond order $= \dfrac{10 - 6}{2} = 2$, paramagnetic (due to the presence of unpaired electrons)

(b)

| (XeF₂)	(XeF₄)	(XeO₂F₂)
Linear	Square planar	See-saw shaped

(c) $H_2^+ = \sigma 1s^1$, bond order $= \dfrac{1-0}{2} = \dfrac{1}{2}$

$H_2^- = \sigma 1s^2, \overset{*}{\sigma} 1s^1$, bond order $= \dfrac{2-1}{2} = \dfrac{1}{2}$

Since, H_2^- has one electron in its antibonding orbiral due to which there is some destabilising effect arises and hence it is less stable than H_2^+.

S22. (a) In IF_5, the ground state and the excited state outer electronic configurations of iodine ($Z = 53$) are represented below:
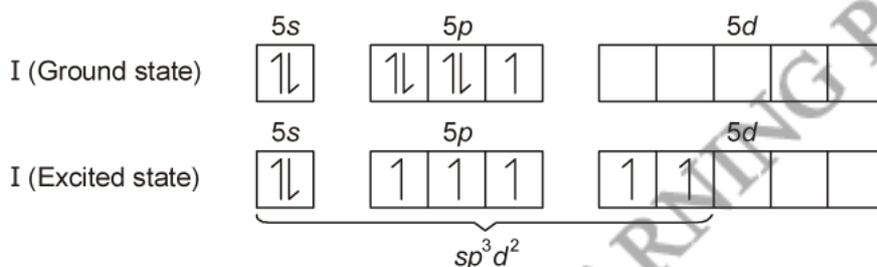
Is sp^3d^2-hybrideised, therefore shape of IF_5 is square pyramidal.

(b) The structures of the given molecules are:

Therefore, only $BeCl_2$ is linear and rest of the molecules are non-linear.

(c) In PCl_5, three Cl-atoms lie in same plane as P-atom and are called equatorial Cl-atoms and bonds formed are called equatorial bonds. The outer two Cl-atoms lie perpendicular to the plane of equatorial bonds and are called axial Cl-atoms and bonds formed by them are called axial bonds. Axial bonds are longer than equatotial bonds due to the greater repulsion on the axial bond pairs by equatorial bond pairs of electrons.

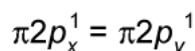**S23.** (a) SiF_4 and $HClO_4$ have sp^3-hybridisation while H_2CO_3 and BF_3 have sp^2-hybridisation.
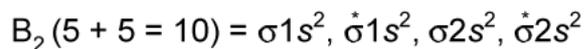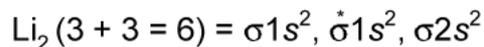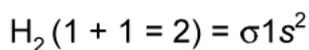
The resultant dipole moment of two B — F bonds is equal and opposite to the dipole moment of third B — F bond. Hence, BF_3 is a non-polar molecule. In contrast, the dipole moment of two — OH bonds is not equal to that of C = O bond and hence, H_2CO_3 has a resultant dipole moment and thus, it is a polar molecule.

$\mu_1 + \mu_2 = -\mu_3$

$\mu_{net} = 0$
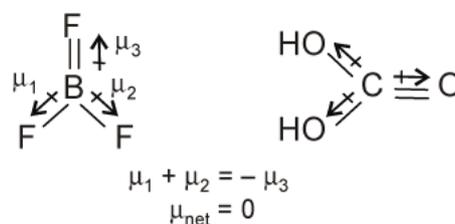
(b) A single Lewis structure of CO_3^{2-} cannot explain all the properties of this ion *e.g.*, bond length and bond strength. It can be represented as a resonance hybrid of the following structures:
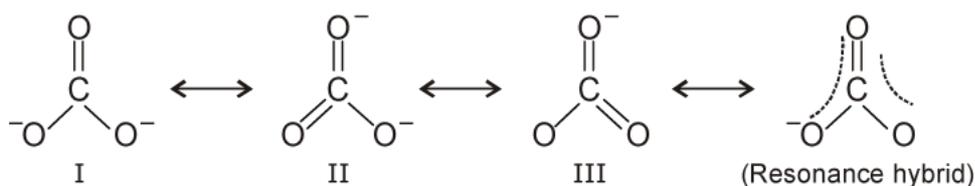
(c) The MO configuration of the given species can be written as

$$H_2 \, (1 + 1 = 2) = \sigma 1s^2$$

$$Li_2 \, (3 + 3 = 6) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2$$

$$B_2 \, (5 + 5 = 10) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2$$

$$\pi 2p_x^1 = \pi 2p_y^1$$

As the number of antibonding electrons ($\overset{*}{\sigma}$ or $\overset{*}{\pi}$) increases, energy increases and stability decreases. Thus, the correct order of stability is

$$H_2 \, < \, Li_2 \, < \, B_2.$$