Dedication!	Determination!!	Distinction!!!

(ACTC) ADVANCED CHEMISTRY TUITION CENTRE, 41/1 PWD ROAD, NAGERCOIL, KANYAKUMARI DIST. **9952340892**

Unit : 10 Chemical Bonding

31. Define the following i) Bond order   ii) Hybridisation iii) σ- bond

i) Bond order: The number of bonds formed between the two bonded atoms in a molecule is called the bond order

ii) Hybridisation: Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy.
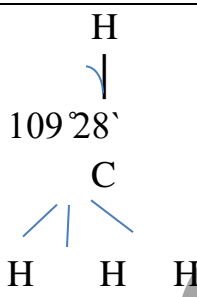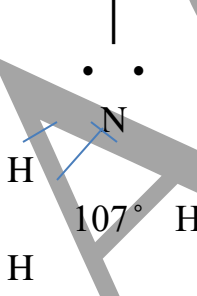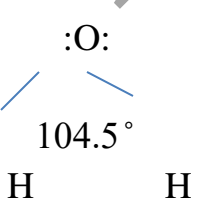
iii) σ- bond: When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (**σ)** bond

32. What is a pi bond?

When two atomic orbitals overlaps sideways, the resultant covalent bond is called a pi (π) bond

33. In CH_4, NH_3 and H_2O, the central atom undergoes sp^3 hybridisation - yet their bond angles are different. why?

Bond angles are different due to the presence of lone pair of electrons.

Molecule	Structure	Atomic arrangement	Bond angle	Reason for reduction in bond angle
CH_4	H | 109˚28` C H H H	The central carbon atom has four valence electrons and each hydrogen atom gives and electrons Minimum repulsions between the bond pairs	109˚28`	The minimum repulsion between the bond pairs leads to a regular tetrahedron with an angle of 109˚28`
NH_3	| • • N H 107˚ H H	The central N – atom is surrounded by three bone pairs and one bone pair Lp – lp repulsions > lp – lp repulsion	107˚	The Repulsion between these electron pairs will be minimum if the shape of NH_3 is pyramidal. Hence the bond angle gets reduced from 109˚28` to 107˚
H_2O	:O: 104.5˚ H H	The central O – atom has 2 lone pairs & 2 bond pairs. The lp – lp repulsions > lp – lp repulsion.	104˚ 5'	Due to greater lp – lp repulsion the bond angle gets reduced to 104˚5'

E.MUTHUSAMY MSc.₍Che₎, MSc.₍Psy₎, MEd., MPhil., MA(T).,MA(En)., MA(Soc)., MA(P.Ad).,BLISc.,DMLT, PGDCA
 LESSON 10 BOOK BACK ANSWER   **Whatsapp: 9940847892**   email: **e.muthusamy@gmail.com**
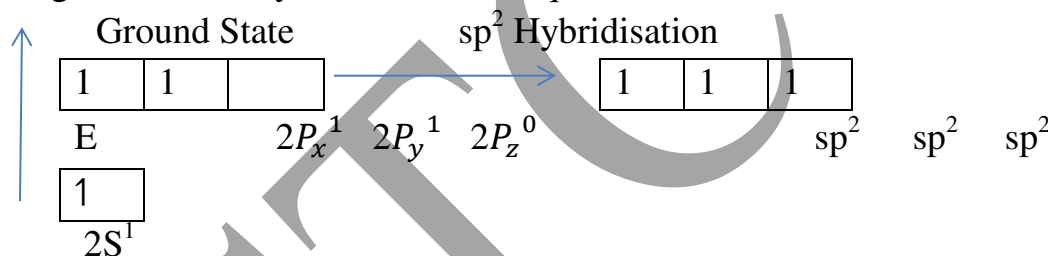
34. Explain Sp^2 hybridisation in BF_3

Sp^2 Hybridisation :Consider boron trifluoride molecule. The valence shell electronic configuration of boron atom is [He] $2s^2\ 2p^1$

Ground State

E

| 1 | | |

$\qquad 2P_x^{\ 1}\quad 2P_y^{\ 0}\quad 2P_z^{\ 0}$

| 1↓ |

$2S^2$
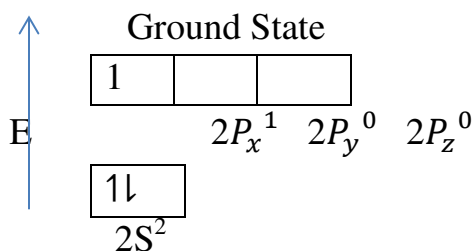
In the ground state boron has only one unpaired electron in the valence shell. In order to form three covalent bonds with fluorine atoms, three unpaired electrons are required. To achieve this, one of the paired electrons in the 2s orbital is promoted to the $2p_y$ orbital in the excite state.

In boron, the s orbital and two p orbitals (p_x and p_y) in the valence shell hybridses, to generate three equivalent sp^2 orbitals as shown in the Figure. These three orbitals lie in the same xy plane and the angle between any two orbitals is equal to 120^0

Ground State sp^2 Hybridisation

| 1 | 1 | | $\longrightarrow$ | 1 | 1 | 1 |

$E \qquad\qquad 2P_x^{\ 1}\quad 2P_y^{\ 1}\quad 2P_z^{\ 0} \qquad\qquad\qquad sp^2 \quad sp^2 \quad sp^2$

| 1 |

$2S^1$

Overlap with 2pz orbitals of fluorine:

The three sp^2 hybridised orbitals of boron now overlap with the 2pz orbitals of fluorine (3 atoms). This overlap takes place along the axis as shown below.

35. Draw the M.O diagram for oxygen molecule calculate its bond order and show that O_2 is paramagnetic.

Molecular orbital diagram of oxygen molecule (O_2)

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

Electronic configuration of O2 molecule

$\sigma 1s^2, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}2s , \sigma^2_{2px}, \pi^2_{2py} , \pi^2_{2pz}, \pi^{*1}_{2py} , \pi^{*1}_{2pz},$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-6}{2} = 2$

Molecule has two unpaired electrons hence it is paramagnetic.

36. Draw MO diagram of CO and calculate its bond order.

Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom $1s^2\ 2s^2\ 2p^2$

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

Electronic configuration of CO molecule

$\sigma^2 1s$, $\sigma^{*2} 1s$, $\sigma^2 2s$, $\sigma^{*2} 2s$, $\pi^2 2py$, $\pi^2 2pz$, $\sigma^2 2px$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

37. What do you understand by Linear combination of atomic orbitals in MO theory.

i) The wave functions for the molecular orbitals can be obtained by solving Schrodinger wave equation for the molecule. Since solving the Schrodinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

ii) Atomic orbitals are represented by the wave function Ψ. Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals.

iii) One is bonding molecular orbital($\psi_{bonding}$) and the other is antibonding molecular orbital($\psi_{antibonding}$).

iv) The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$\psi_{bonding} = \psi_A + \psi_B$

$\psi_{antibonding} = \psi_A - \psi_B$

v) The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals.

vi) The formation of the two molecular orbitals from two 1s orbitals is shown below.

38. Discuss the formation of N_2 molecule using MO Theory

Molecular orbital diagram of nitrogen molecule (N_2)

Electronic configuration of N atom $1s^2\ 2s^2\ 2p^3$

Electronic configuration of N_2 molecule

$\sigma^2 1s$, $\sigma^{*2} 1s$, $\sigma^2 2s$, $\sigma^{*2} 2s$, $\pi^2 2py$, $\pi^2 2pz$,$\sigma^2 2px$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

39. What is dipole moment?

i)The polarity of a covalent bond can be measured in terms of dipole moment which is defined as **$\mu = q\ x2d$**

Where, μ - dipole moment,

q - the charge and
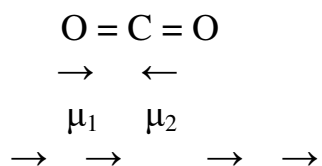
2d - distance between the two charges.

ii) The dipole moment is a vector quantity and the direction of the dipole moment points from the negative charge to positive charge.

iii) The unit of dipole moment is coulomb metre(C m) (Debye= 3.336×10^{-30} C m).

40. Linear form of carbondioxide molecule has two polar bonds. yet the molecule has Zero dipolement why?

In CO_2, the dipole moments of two polar bonds (C=O) are equal in magnitude but have opposite direction. Hence, the net dipole moment of the CO_2 is, $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

$$O = C = O$$
$$\rightarrow \quad \leftarrow$$
$$\mu_1 \quad \mu_2$$
$$\rightarrow \quad \rightarrow \qquad \rightarrow \quad \rightarrow$$

In this case $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

41. Draw the Lewis structures for the following species.

i) NO_3^- ii) SO_4^{2-} iii) HNO_3 iv) O_3

42. Explain the bond formation in $BeCl_2$ and $MgCl_2$.

Bond formation in $MgCl_2$:

Mg is a metal with 2 valence electrons. Cl is a non-metal with 7 valence electrons and hence it needs one electron to complete the octet. Thus Mg donates one electron to each Cl and becomes positively charged. Each Cl accepts one electron and becomes negatively charged.

Bond formation in $BeCl_2$:

In AB_2 type the central atom A has two bond pairs only the two bond pairs orient themselves at $180°$ to have minimum repulsion among themselves.

$BeCl_2$ is linear and forms a pair of covalent bonds instead for forming ionic bonds. Be uses its two hybrid orbitals to form two Be – Cl bonds. The bond angle is $180°$

43. Which bond is stronger σ or π? Why?

*   Sigma(σ) bonds are strong than pi (π) bonds.
*   Sigma bonds are formed by head on overlap of atomic orbitals so extent of overlapping is maximum.(axial overlapping)
*   Pi bonds are weaker, since according to quantum mechanics, the orbital path are parallel to there is much less overlap between the p orbitals. (lateral overlapping)

44. Define bond energy.

The bond enthalpy (bond energy) is defined as **the minimum amount of energy required to break one mole of a particular bond in molecules in their gaseous state.**

The unit of bond energy is **kJmol^{-1}.**

45. Hydrogen gas is diatomic where as inert gases are monoatomic – explain on the basis of MO theory.

- Hydrogen gas is diatomic where as inert gases are monoatomic because noble gases are having its valence shell filled with octet electrons.
- So there is no necessity for the noble gases to involve in the formation of covalent bonds.
- This could be further explained by MO diagram of H_2 and He_2
- **Molecular orbital diagram of hydrogen molecule (H_2):**
  Electronic configuration of H atom $1s^1$
  Electronic configuration of H_2 molecule $\sigma^2{}_{1s}$
  Bond order $= \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$

Molecule has no unpaired electrons hence it is diamagnetic.

- The electronic configuration of He (Z = 2) in the ground state is $1s^1$
- As each helium atom contains two electrons, there will be four electrons in He_2 molecule. Keeping in view the Aufbau principle and pauli's exclusion principle its electronic configuration would be as follows.
- $He_2 : (\sigma_{1s})^2 (\sigma^*_{1s})^2$
  $N_b = 2$ and $N_a = 2$ Bond order $= \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$
- As the bond order of He_2 come out to be zero, this molecule does not exist.

46. What is Polar Covalent bond? Explain with example.

Polar covalent bond is formed between atoms having different electronegativities, the atom with higher electronegativity will have greater tendency to attract the shared pair of electrons towards itself than other atom.

Example: HF

consider the covalent bond between hydrogen and fluorine in hydrogen fluoride. The electronegativities of hydrogen and fluorine on Pauling's scale are 2.1 and 4 respectively. It mean that fluorine attracts the shared pair of electrons approximately twice as much as the hydrogen which leads to partial negative charge on fluorine and partial positive charge on hydrogen. Hence , the H-F bond is said to be polar covalent bond.

47. Considering x- axis as molecular axis, which out of the following will form a sigma bond.

i) 1s and $2p_y$ ii) $2P_x$ and $2P_x$ iii) $2P_x$ and $2P_z$ iv) 1s and $2P_z$

i) 1s and $2p_y$ – No sigma bond

ii) $2P_x$ and $2P_x$ – sigma bond

iii) $2P_x$ and $2P_z$ – No sigma bond

iv) 1s and $2P_z$ – No sigma bond

When we consider x- axis as molecular axis , the $p_x - p_x$ overlap will result in σ- bond

48. Explain resonance with reference to carbonate ion?

The skeletal structure of carbonate ion (The oxygen atoms are denoted as O_A, O_B & O_C)

Total number of valence electrons = [1 x 4(carbon)] + [3 x 6 (oxygen)] + [2 (charge)] = 24 electrons.

Distribution of these valence electrons gives us the following structure.

Complete the octet for carbon by moving a lone pair from one of the oxygens (OA) and write the charge of the ion (2-) on the upper right side as shown in the figure.

In this case, we can draw two additional Lewis structures by moving the lone pairs from the other two oxygens (OB and OC) thus creating three similar structures as shown below in which the relative position of the atoms are same. They only diff er in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance.

It is evident from the experimental results that all carbon-oxygen bonds in carbonate ion are equivalent. Th e actual structure of the molecules is said to be the resonance hybrid, an average of these three resonance forms. It is important to note that carbonate ion does not change from one structure to another and vice versa. It is not possible to picturise the resonance hybrid by drawing a single Lewis structure. However, the following structure gives a qualitative idea about the correct structure.

It is found that the energy of the resonance hybrid (structure 4) is lower than that of all possible canonical structures (Structure 1, 2 & 3). Th e diff erence in energy between structure 1 or 2 or 3, (most stable canonical structure) and structure 4 (resonance hybrid) is called resonance energy

49. Explain the bond formation in ethylene and acetylene.

Th e bonding in ethylene can be explained using hybridisation concept. The molecular formula of ethylene is C2H4. The valency of carbon is 4. Th e electronic
configuration of valence shell of carbon in ground state is $[He]2s^2 2p_x^1 2p_y^1 2p_z^0$. To satisfy
the valency of carbon promote an electron from 2s orbital to 2pz orbital in the excited state.

Ground State
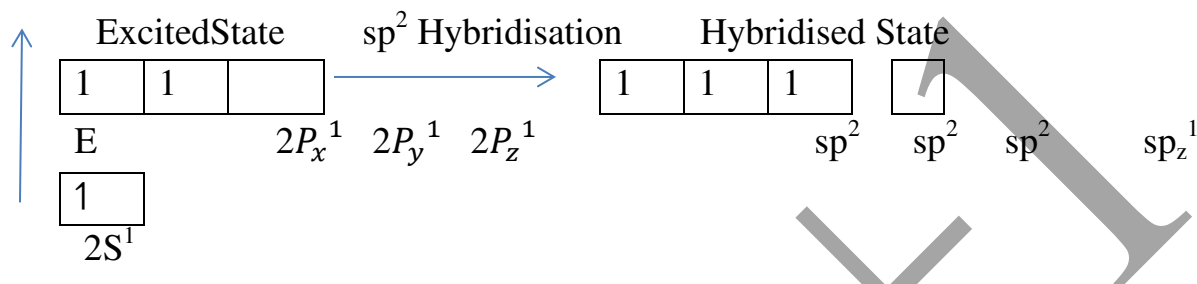
$2P_x^1 \quad 2P_y^1 \quad 2P_z^0$

$2S^2$
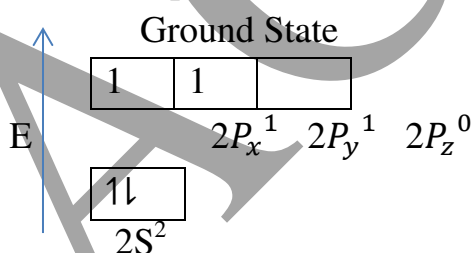
In ethylene both the carbon atoms undergoes sp2 hybridisation involving 2s, 2px and 2py orbitals, resulting in three equivalent sp^2 hybridised orbitals lying in the xy plane
at an angle of 120^0 to each other. The unhybridised $2p_z$ orbital lies perpendicular
to the xy plane.

Formation of sigma bond:

One of the sp_2 hybridised orbitals of each carbon lying on the molecular axis (x-axis) linearly overlaps with each other resulting in the formation a C-C sigma bond. Other two sp^2 hybridised orbitals of both carbons linearly overlap with the four 1s orbitals of four hydrogen atoms leading to the formation of two C-H sigma bonds on each carbon.

ExcitedState sp^2 Hybridisation   Hybridised State

| 1 | 1 | | → | 1 | 1 | 1 | | |

E $2P_x{}^1$ $2P_y{}^1$ $2P_z{}^1$ sp^2 sp^2 sp^2 $sp_z{}^1$

| 1 |

$2S^1$

Formation of pi bond:

Th e unhybridised 2pz orbital of both carbon atoms can overlap only sideways as they are not in the molecular axis. Th is lateral overlap results in the formation a pi bond between the two carbon atoms as shown in the figure.

Bonding in acetylene:

Similar to ethylene, the bonding in acetylene can also be explained using hybridization concept. The molecular formula of acetylene is C_2H_2. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2 \, 2p_x{}^1 \, 2p_y{}^1 \, 2p_z{}^0$. To satisfy the valency of carbon promote an electron from 2s orbital to 2pz orbital in the excited state.

In acetylene molecule, both the carbon atoms are in sp hybridised state. The 2s and $2p_x$ orbitals, resulting in two equivalent sp hybridised orbitals lying in a straight line along the molecular axis (x-axis). The unhybridised $2p_y$ and 2pz orbitals lie perpendicular to the molecular axis.

Formation of sigma bond:

One of the two sp hybridised orbitals of each carbon linearly overlaps with each other resulting in the formation a C-C sigma bond. The other sp hybridised orbital of both carbons linearly overlap with the two 1s orbitals of two hydrogen atoms leading to the formation of one C-H sigma bonds on each carbon.

Formation of pi bond:

The unhybridised $2p_y$ and 2pz orbitals of each carbon overlap sideways. This lateral overlap results in the formation of two pi bonds (py-py and pz-pz) between the two carbon atoms as shown in the figure.

50. What type of hybridisations are possible in the following geometeries? a) octahedral b) tetrahedral c) square planer.

Molecular Geometry	Hybridisation	Example

Octahedral	Sp^3d^2	SF_6
Tetrahedral	Sp^3	CH_4
Square planner	dsp^2	$[Ni(CN)_4$

51. Explain VSEPR theory. Applying this theory to predict the shapes of IF_7, and SF_6

1. The shape of the molecules depends on the number of valence shell electron pair around the central atom.
2. There are two types of electron pairs namely bond pairs and lone pairs.
3. The bond pair of electrons are those shared between two atoms, while the lone pairs are the valence electron pairs that are not involved in bonding.
4. Each pair of valence electrons around the central atom repels each other and hence, they are located as far away as possible in three dimensional space to minimize the repulsion between them.
5. The repulsive interaction between the different types of electron pairs is in the following order.

    lp - lp > lp - bp > bp-bp   lp- lone pair ; bp- bond pair

52. CO_2 and H_2O both are triatomic molecule but their dipole moment values are different. Why?

$\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

$$O== C == O$$

$$\rightarrow \quad \leftarrow$$

$$\mu_1 \quad \mu_2$$

$$\rightarrow \quad \rightarrow$$

In this case $\mu = \mu_1 + \mu_2$

$= \mu_1 + (-\mu_1) = 0$

In case of water net dipole moment is the vector sum of $\mu_1 + \mu_2$ as shown.

53. Which one of the following has highest bond order? N_2, N_2^+ or N_2^-

Bond order $= \frac{N_b - N_a}{2}$

Where N_b = Number of electrons in bonding molecular orbitals

N_a = Number of electrons in anti bonding molecular orbitals.

Bond Order of N_2:

Total no. of electrons = 14

Electronic configuration $= \sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2py}, \pi^2_{2pz}, \sigma^2_{2px}$

Bond order $= \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$

Bond Order of N_2^+ :

Total no. of electrons = 13

Electronic configuration = $\sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2py} = \pi^2_{2pz}, \sigma^2_{px}{}^1$

　　Bond order = $\frac{N_b - N_a}{2} = \frac{9-4}{2} = 2.5$

Bond Order of N_2^- :

Total no. of electrons = 15

Electronic configuration = $\sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2py} = \pi^2_{2pz}, \sigma^2_{2px}\,\sigma^2_{py}{}^1$

　　Bond order = $\frac{N_b - N_a}{2} = \frac{10-5}{2} = 2.5$

Stability of the molecule is directly proportional to bond order.

　　Hence, $N_2 > N_2^+ = N_2^-$

54. Explain the covalent character in ionic bond.

　　The partial covalent character in ionic compounds can be explained on the basis of a phenomenon called polarisation. We know that in an ionic compound, there is an electrostatic attractive force between the cation and anion. The positively charged cation attracts the valence electrons of anion while repelling the nucleus. This causes a distortion in the electron cloud of the anion and its electron density drift s towards the cation, which results in some sharing of the valence electrons between these ions. Thus, a partial covalent character is developed between them. This phenomenon is called polarisation.

55. Describe fajan's rule.

　　The ability of a cation to polarize an anion is called its polarising ability and the tendency of an anion to get polarized is called its polarisability. The extent of polarisation in an ionic compound is given by the Fajans rules

Fajans Rules:

　　i.　To show greater covalent character, both the cation and anion should have high charge on them. Higher the positive charge on the cation, greater will be the attraction on the electron cloud of the anion. Similarly higher the magnitude of negative charge on the anion, greater is its polarisability. (Hence, the increase in charge on cation or in anion increases the covalent character Let us consider three ionic compounds aluminum chloride, magnesium chloride and sodium chloride.) Since the charge of the cation increase in the order $Na^+ < Mg^{2+} < Al^{3+}$, the covalent character also follows the same order $NaCl < MgCl_2 < AlCl_3$.

　　ii.　The smaller cation and larger anion show greater covalent character due to the greater extent of polarisation. Lithium chloride is more covalent than sodium chloride. (The size of Li^+ is smaller than Na^+ and hence the polarising power of Li+ is more. Lithium iodide is more covalent than lithium chloride as the size of I^- is larger than the Cl^-). Hence I^- will be more polarized than Cl^- by the cation, Li^+ .

iii. Cations having $ns^2 np^6 nd^{10}$ configuration show greater polarizing power than the cations with $ns^2 np^6$ configuration. Hence, they show greater covalent character. CuCl is more covalent than NaCl. Compared to Na^+ (1.13 Å) . Cu^+ (0.6 Å) is small and have $3s^2 3p^6 3d^{10}$ configuration.

Electronic configuration of Cu^+

[Ar] $3s^2$, $3p^6$, $3d^{10}$

Electronic Configuration of Na^+

[He] $2s^2$, $2p^6$