

Group A: Unit-1 Atomic structure

Schrodinger's Wave equation:

In 1926, Erwin Schrodinger proposed that since an electron behaves as a wave, it should obey the same equation of motion which all other known types of waves obey. On the basis of this simple idea, he derived an equation which describes the wave motion of an electron-wave propagating in three dimensions (x, y & z) in space. This wave equation is called Schrodinger's wave equation. This is written in different forms:

(A) Cartesian Coordinates form:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (1)}$$

[Where ψ = wavefunction & represent the amplitude of wave. From the wave function almost all physically observable property of a dynamic particle can be described. Its square (ψ^2) has a physical meaning related to probability, m = Mass of particle (electron), E = Total energy of the particle describing wave motion, V = Potential energy of particle due to position, h = Planck's constant ($6.6 \times 10^{-34} \text{ J}$), π = a constant (3.141)]

(B) In term of Laplacian Operator:

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (2)}$$

(Where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, called Laplacian mathematical operator)

$\nabla^2 \psi$ should not mean that ∇^2 is multiplied by ψ . x, y & z are the three space coordinates of the electron with respect to nucleus (0,0,0). Here $\frac{\partial^2 \psi}{\partial x^2}$ is double differential of $\psi(x, y, z)$ with respect to x only keeping y & z constant.

(C) In term of Hamiltonian Operator:

We have, $\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$ or, $\nabla^2 \psi h^2 + 8\pi^2 m E \psi - 8\pi^2 m V \psi = 0$

or, $\frac{\nabla^2 \psi h^2}{8\pi^2 m} + E \psi - V \psi = 0$ or, $(-\frac{h^2 \nabla^2}{8\pi^2 m} + V) \psi = E \psi \quad \text{--- (3)}$

The expression $(-\frac{h^2 \nabla^2}{8\pi^2 m} + V)$ in equation (3) is called Hamiltonian operator, denoted by symbol \hat{H} . Thus, equation (3) can also be written as $\hat{H} \psi = E \psi \quad \text{--- (4)}$

The Hamiltonian operator (\hat{H}) consists of two parts, viz, the kinetic energy part $(-\frac{h^2 \nabla^2}{8\pi^2 m})$ & the potential energy part (V).

(d) Polar coordinate form:

$$\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + \frac{8\pi^2 m r^2}{h^2} (E - V) \psi = 0 \quad \text{--- (5)}$$

Where r, θ & ϕ are polar coordinates.

\Rightarrow Derivation of Schrodinger's wave equation:

Schrodinger assumed that the electronic waves are similar to stationary waves. He considered an electron wave of amplitude ψ . If x is the displacement of the wave in x direction and λ is its wave length, then ψ is given by

$$\psi = A \sin \frac{2\pi x}{\lambda} \quad \text{--- (1)} \quad (\text{where } A = \text{a constant})$$

On differentiating equation (1), we get $\frac{\partial \psi}{\partial x} = (A \cos \frac{2\pi x}{\lambda}) \cdot \frac{2\pi}{\lambda} = \frac{2\pi A}{\lambda} \cos \frac{2\pi x}{\lambda} \quad \text{--- (2)}$

On differentiating equation (2), we get $\frac{\partial^2 \psi}{\partial x^2} = \frac{2\pi A}{\lambda} (-\sin \frac{2\pi x}{\lambda}) \cdot \frac{2\pi}{\lambda} = -\frac{4\pi^2 A}{\lambda^2} \sin \frac{2\pi x}{\lambda}$

or, $\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi$ [$\because \psi = A \sin \frac{2\pi x}{\lambda}$] --- (3)

(2)

This is the wave equation for unidimensional stationary wave vibrating along x-axis
Only when equation (3) is extended to three dimensions, we replace $\frac{\partial^2 \psi}{\partial x^2}$ by $(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2})$
and hence equation (3) becomes: $\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -4\pi^2 \psi \times \frac{1}{\lambda^2}$

or, $\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -4\pi^2 \psi \times \frac{m^2 v^2}{h^2}$ — (4) [from de-Broglie's equation, $\lambda = \frac{h}{mv}$]

Equation (4) is a wave equation which describes the motion of an electron in three dimensions (x, y & z). Now, the total energy (E) of the electron is the sum of its kinetic energy ($\frac{1}{2}mv^2$) and potential energy (V). Thus,

$E = \frac{1}{2}mv^2 + V$ or, $\frac{1}{2}mv^2 = (E - V)$ or, $v^2 = \frac{2(E - V)}{m}$

Substituting the value of v^2 in equation (4), we get

$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 \psi m^2}{h^2} \times \frac{2(E - V)}{m} = \frac{8\pi^2 m}{h^2} (E - V) \psi$

$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$ — (5)

or, $\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$ — (6) [where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, Laplacian operator]

Equations (5) & (6) are forms of Schrodinger's wave equation.

⇒ Physical Significance or Meaning of ψ & ψ^2 :

ψ is wave function and represents the amplitude of wave. From it, almost all physically observable property of a dynamic particle, can be described. It has no significance, since it cannot represent the probability of finding an electron in a small volume around the nucleus. This is because of the fact that the wave function (ψ) can have positive as well as negative value, whereas the probability of finding the electron can be zero or positive but can never be negative.

ψ^2 (square of psi) represents or measures the probability of finding the electron around the nucleus. Its value is always positive. The probability or chance of finding an electron in space/three dimensions around the nucleus is called electron probability function (D). The value of D for an extremely small spherical shell of radius (r) and thickness (dr) around the nucleus is given by

$D = \psi^2 \times \text{volume of spherical shell} = 4\pi r^2 dr \cdot \psi^2$

Thus, the electron probability between $r=0$ & $r=r$ would be equal to $\int_0^r \psi^2 4\pi r^2 dr$.

⇒ Eigen-function & eigen value:

Schrodinger wave equation, being a differential equation of second order, has many solutions. Some of these values are imaginary (non-acceptable) while others are real values. Only those values of ψ which give definite and acceptable value of the total energy (E) of the electron. These acceptable values of the wave function (ψ) are called eigen (acceptable) wave functions.

The value of total energy (E) given by a particular eigen wave function is called eigen value. The acceptable wave functions fulfill following conditions:

- (i) ψ must be single valued solution, i.e., if one of variable is θ , then $\psi(\theta) = \psi(\theta + 2\pi)$.
- (ii) ψ must finish at infinity for bound system, and must satisfy the relation $\int |\psi|^2 dx = 1$.
- (iii) ψ & its first derivative with respect to its variables are finite & continuous.

Unit 2. Molecular Orbital Theory (MOT)

In 1932, Hund & Mulliken developed a theory to explain the formation of covalent bond in molecules or ions, known as molecular orbital theory (MOT) or Hund-Mulliken theory. This theory is based on the ~~formation~~ 'Linear Combination of Atomic Orbitals' (LCAOs) of atoms constituting molecule or ion, and so called LCAO-MO theory

⇒ Salient features of MOT: The MOT has following features:

1. When two isolated atomic orbitals (or their wave functions) residing on two atoms and having similar energy and same symmetry combine linearly with each other by LCAO method, two molecular orbitals are obtained. Two atomic orbitals involve in LCAO may be of the same atoms/elements (Homonuclear diatomic molecules) or ions, e.g. $H_2, N_2, O_2, He_2^+, O_2^-$ etc.) or different atoms/elements (Heteronuclear diatomic molecules or ions, e.g. CO, NO, CN, NO^+ etc.). When three atomic orbitals of similar energy & symmetry combine with one another, three molecular orbitals are obtained. Thus, the number of molecular orbitals obtained is always equal to the number of atomic orbitals combining together.
2. Two different ways of LCAOs (or their wave functions) and formation of bonding and antibonding molecular orbitals. LCAO can be brought about either by adding or subtracting the atomic orbitals wave functions.

If ψ_A & ψ_B be wave functions of two atomic orbitals A & B respectively, then

$$\psi^b(\text{Bonding m.o.}) = \psi_A + \psi_B \dots\dots (1) \quad (\text{Additive or } ++ \text{ overlap})$$

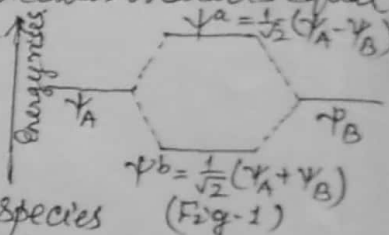
$$\psi^a(\text{Antibonding m.o.}) = \psi_A - \psi_B \dots\dots (2) \quad (\text{Subtractive or } +- \text{ overlap})$$

When we show contributions made by ψ_A & ψ_B in ψ^b & ψ^a molecular orbitals, equation (1) & (2) are written as -

$$\psi^b = \frac{1}{\sqrt{2}}(\psi_A + \psi_B) \dots\dots (3)$$

$$\psi^a = \frac{1}{\sqrt{2}}(\psi_A - \psi_B) \dots\dots (4)$$

Obviously the sum of the squares of the coefficients of atomic orbitals wave functions ψ_A & ψ_B appearing in bonding molecular orbital/antibonding molecular orbital is equal to unity $[(\frac{1}{\sqrt{2}})^2 + (\frac{1}{\sqrt{2}})^2 = 1]$. The relative order of the energy of ψ_A, ψ_B, ψ^b & ψ^a can be shown as in fig. 1.



Bonding m.o. wave function has lower energy than anti-bonding m.o. wave function (ψ^a).

3. Formation of molecular orbitals in homonuclear diatomic species (A_2 type, e.g. $Li_2, Be_2, N_2, O_2, F_2, Ne_2$ etc.) in which both atoms (A) belong to 2nd period of the PT. Ten molecular orbitals are obtained from five atomic orbitals ($1s, 2s, 2p_x, 2p_y, 2p_z$). These molecular orbitals are $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2p_x}, \pi_{2p_y}, \pi_{2p_z}, \pi_{2p_y}^*, \pi_{2p_z}^*, \sigma_{2p_x}^*$. Here σ_{1s} stands for bonding (additive or ++ overlap) m.o., σ_{1s}^* stands for antibonding (Subtractive or +- overlap) m.o. Spectroscopic studies have shown that their relative order of the energy for $Li_2, Be_2, B_2, C_2, N_2$ (i.e. upto 14 electrons system) is as:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi_{2p_y}^* = \pi_{2p_z}^* < \sigma_{2p_x}^* \quad (\text{Case-I})$$

while the relative order of energy of these orbitals (m.o) for O_2, F_2, Ne_2 & their ions (i.e. above 14e systems) is as:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi_{2p_y}^* = \pi_{2p_z}^* < \sigma_{2p_x}^* \quad (\text{Case-II})$$

* [Note: (i) π_{2p_y}, π_{2p_z} & $\pi_{2p_y}^*, \pi_{2p_z}^*$ orbitals (m.o) in both cases have the same energy and hence they are called degenerate molecular orbitals.

(ii) In molecules/ions from Li_2 to N_2 ($\leq 14e$), σ_{2p_x} m.o. has greater energy than π_{2p_y} & π_{2p_z} m.o.s while in case of the molecules viz O_2, F_2 & Ne_2 ($\geq 15e$), σ_{2p_x} m.o. has lower energy than

π_{2p_y} & π_{2p_z} m.o.s. This is because in case of B_2, N_2, C_2 etc. $2s$ & $2p_z$ orbitals have very small difference in their energies and hence they mix together/overlap. On the other hand, the energy difference between $2s$ & $2p_z$ orbitals in O_2, F_2, Ne_2 etc. is very large and hence their mixing together/overlap is not possible. It may be noted that out of the three $2p$ -orbitals, only $2p_z$ orbital can mix with $2s$ -orbital, since these orbitals have the same symmetry.

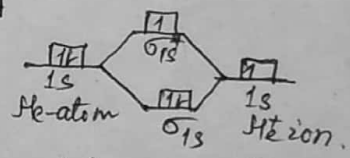
4. Various molecular orbitals (m.o) are filled up with electrons in the increasing order of their energy, i.e., the m.o. having the lowest energy is filled up first while that having the highest energy is filled up in the last (Aufbau principle). In m.o.s having the same energy (degenerate orbitals), the pairing of electrons takes place when each of the m.o.s has at least one electron (Hund's rule).
5. The maximum number of electrons that a m.o. can accommodate in it is two. These two electrons must have opposite spins (Pauli exclusion principle).
6. Since O_2 molecule has the maximum number (2) of unpaired electrons, it has the paramagnetic character, which was not explain by valence bond theory (VBT).

→ Distinguish or Comparison between bonding & antibonding molecular orbitals:

Bonding m.o.	Antibonding m.o.
1. Molecular orbitals (m.o) formed by adding or ++ overlap of wave functions of the two atomic orbitals are called bonding m.o. ψ^b or $\psi_s = \psi_A + \psi_B$ (where ψ_A & ψ_B are wave functions of atomic orbitals A & B respectively) ψ^b or ψ_s is bonding or symmetric molecular wave function.	1. Molecular orbital formed by subtracting or +- overlap of wave functions of the two atomic orbitals are called antibonding molecular orbital. ψ^a or $\psi^* = \psi_A - \psi_B$ (where ψ^a or ψ^* is antibonding or asymmetric molecular wave function)
2. Since repulsion between nuclei in bonding m.o. is minimum, the energy of bonding m.o. is less than that of combining atomic orbitals, hence stable.	2. Since therepulsion between the nuclei in antibonding m.o. is maximum, the energy of antibonding m.o. is more than that of combining atomic orbitals, hence unstable.
3. The difference in energy between m.o. & combining atomic orbitals is called stabilisation energy.	3. The difference in energy between the antibonding m.o. and the combining atomic orbitals is called de-stabilisation energy.
4. Each electron in a bonding m.o. contributes to attraction between the two combining atoms.	4. Each electron in an antibonding m.o. contributes to repulsion between the combining atoms.

→ Bond order: It is defined as half the difference between ^{no. of} electrons in bonding m.o.s (ψ^b) and antibonding m.o.s (ψ^a). i.e., Bond order (B.O) = $\frac{n_b - n_a}{2}$ [where n_b = No. of electrons in bonding m.o.s (ψ^b), n_a = No. of electrons in antibonding m.o. (ψ^a)]

e.g., In He_2^+ ion, bond order = $\frac{2-1}{2} = 0.5$
i.e., one electron σ -bond between He & He⁺ ion in He_2^+ ion.



* Bond order related to Bond length, Bond energy, Stability & Reactivity.

Bond order & Bond length: Bond length (internuclear/atomic distance) decreases with the increase of bond order, i.e.; Bond length $\propto \frac{1}{\text{Bond order}}$ (e.g., Order of bond length: $He_2^+ < He_2^+ < He_2$ (B.O: 1.0 0.5 0.0))

Bond order & Bond energy/strength: Bond energy increases with the increase of bond order, i.e., Bond strength \propto B.O. e.g., order of bond strength: $H-H < O=O < N \equiv N$ (B.O. 1.0, 2.0 & 3.0 respectively)

Bond order & stability/Reactivity: Stability of bond/molecule/ion increases with the increase of bond order, but reactivity decreases with the increase of bond order, i.e.,

Stability \propto B.O.; Reactivity $\propto \frac{1}{\text{B.O.}}$: e.g., N_2 (B.O = 3) is more stable & hence less reactive than O_2 (B.O = 2).

Molecular Orbital theory (MOT) of homonuclear diatomic molecules.

1. He_2^+ ion: He_2^+ ion is formed by combination of He atom & He^+ ion.

Electronic conf. of He: $1s^2$; No. of electrons in He atom = 2

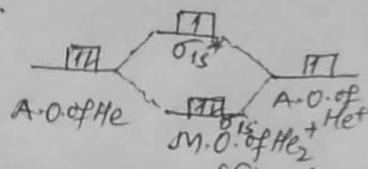
Electronic conf. of He^+ : $1s^1$; No. of electron in He^+ ion = 1

Total no. of electrons in He_2^+ = 2+1 = 3. Two molecular orbitals

(σ_{1s} & σ_{1s}^*) are formed from $1s$ orbitals of two combining species (He & He^+). (Fig. 1)

The ele. conf. of He_2^+ ion is $\sigma_{1s}^2, \sigma_{1s}^*^1$. Molecular orbital diagram is shown in fig. 1.

Bond order $\lambda = \frac{n_b - n_a}{2} = \frac{2-1}{2} = \frac{1}{2} = 0.5$; one electron σ -bond in He_2^+ . He-He.



2. C_2 molecule: C_2 molecule is formed by combination of two C atoms

Electronic conf. of C: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$; No. of electrons in C atom = 6

Total no. of electrons in C_2 = 12. According to MOT, 10 molecular

orbitals ($\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2p_x}, \sigma_{2p_x}^*, \pi_{2p_y}, \pi_{2p_z}, \pi_{2p_y}^*, \pi_{2p_z}^*$) obtained

from 5 atomic orbitals of C-atoms ($1s, 2s, 2p_x, 2p_y, 2p_z$). The elect-

ronic conf. (i.e., distribution of 12 electrons in m.o.s) of C_2 :

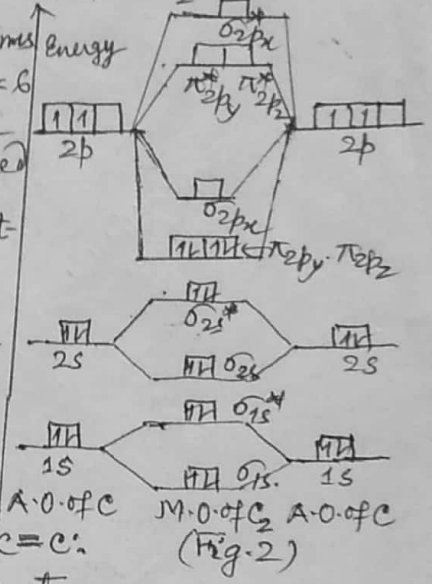
$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2, \sigma_{2p_x}^0, \pi_{2p_y}^{*0}, \pi_{2p_z}^{*0}, \sigma_{2p_x}^{*0}$. The

molecular orbital diagram is shown in fig. 2.

The inner shell ($1s$) is non-bonding, the bonding & anti-

bonding $2s$ orbitals cancel, leaving two π -m.o.s/bonds.

Bond order = $\frac{n_b - n_a}{2} = \frac{4-0}{2} = 2$. Thus, structure of C_2 is: $C=C$.



3. O_2 molecule: O_2 molecule is formed by combination of two O-atoms.

Electronic configuration of O: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

No. of electrons in O-atom = 8

Total no. of electrons in O_2 = 8+8 = 16

According to MOT, 10 molecular orbitals ($\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s},$

$\sigma_{2s}^*, \sigma_{2p_x}, \pi_{2p_y}, \pi_{2p_z}, \pi_{2p_y}^*, \pi_{2p_z}^*, \sigma_{2p_x}^*$) obtained from 5 orbitals

of O-atoms ($1s, 2s, 2p_x, 2p_y, 2p_z$). The electronic conf. (i.e. dist-

ribution of 16 electrons) of O_2 :

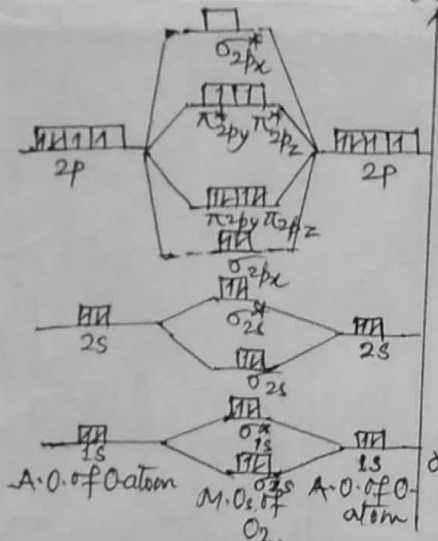
$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*1}, \pi_{2p_z}^{*1}, \sigma_{2p_x}^{*0}$

The m.o. diagram of O_2 is shown in fig. 3. The inner

shell ($1s$) is non-bonding, the bonding & antibonding m.o.s.

of $2s$ cancel, leaving one σ and one π m.o.s/bonds.

Bond order = $\frac{n_b - n_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$. Thus, structure of O_2 is: $\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{O}$



(Fig. 3)

O_2 molecule is paramagnetic since it contains two unpaired electrons

in anti bonding ($\pi_{2p_y}^*, \pi_{2p_z}^*$) m.o.s as shown in m.o. diagram of O_2 . Mag. moment (μ_B) = $\sqrt{2(2+2)} = 2\sqrt{2}$

Q. Arrange the following species in order of bond order/bond length and magnetic property.

$O_2, O_2^+, O_2^-, O_2^{2+}, O_2^{2-}$

Ans: According to MOT, Ele. conf. of O_2 : $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*1}, \pi_{2p_z}^{*1}, \sigma_{2p_x}^{*0}$; B.O. = $\frac{10-6}{2} = 2.0$

Ele. conf. of O_2^+ (15e): $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*1}, \pi_{2p_z}^{*0}, \sigma_{2p_x}^{*0}$; B.O. = $\frac{10-5}{2} = 2.5$

Ele. conf. of O_2^{2+} (14e): $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*0}, \pi_{2p_z}^{*0}, \sigma_{2p_x}^{*0}$; B.O. = $\frac{10-4}{2} = 3.0$

Ele. conf. of O_2^- (17e): $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*2}, \pi_{2p_z}^{*0}, \sigma_{2p_x}^{*0}$; B.O. = $\frac{10-7}{2} = 1.5$

Ele. conf. of O_2^{2-} (18e): $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*2}, \pi_{2p_z}^{*2}, \sigma_{2p_x}^{*0}$; B.O. = $\frac{10-8}{2} = 1.0$

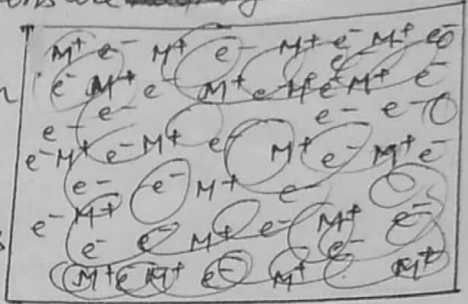
* Increasing sequence of bond orders (B.O.): $O_2^{2+} < O_2^+ < O_2 < O_2^- < O_2^{2-}$ (Bond order increases with rise of + charge & decreases with -ve charge).

* Increasing order of bond length: $O_2^{2+} < O_2^+ < O_2 < O_2^- < O_2^{2-}$ (Bond length $\propto 1/\text{Bond order}$)

* Diamagnetic species: O_2^{2+}, O_2^-, O_2 ; Paramagnetic species: O_2, O_2^+, O_2^{2-} (since they have unpaired electrons)

(b) Metallic bond?

In metallic crystals, metal cations are surrounded by a sea of mobile electrons. The metal cations are in their positions and mobile electrons are ~~held together~~ in the interstices between them. The metal cations and mobile electrons are held together by electrostatic force of attraction known as metallic bond.



Thus, metallic bond can be defined as "the force of attraction between the metal cations and the mobile electrons and this force holds the metal atoms finally together in the metallic crystal/lattice". Most of metals, e.g. Hg, W, alkali metals, Cs, Cu, Bi, Fe, Au etc. and alloys have metallic bond.

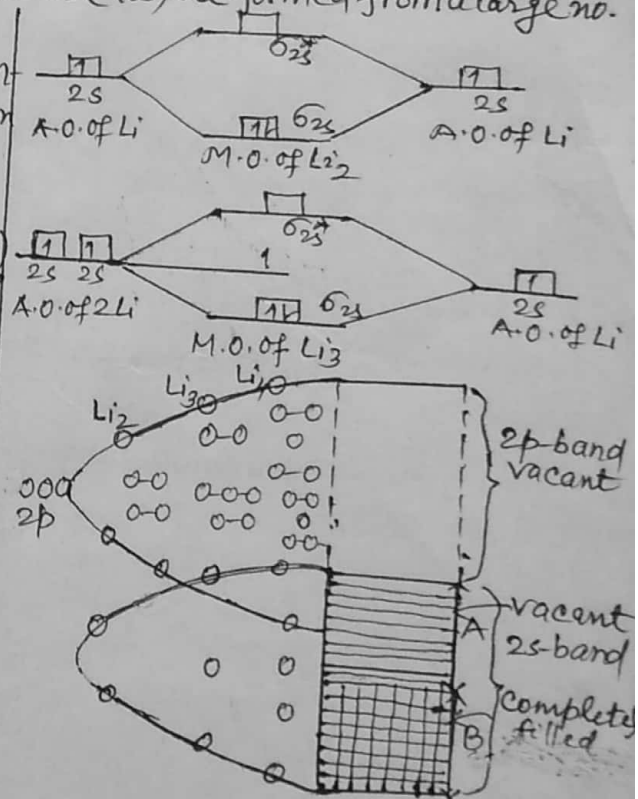
- Factors affecting metallic bond:
- (i) Ionisation energy of the metals should be low so that the valence electrons of the metal are loosely held by the nucleus and thus become mobile.
 - (ii) The metal should have low electronegativity so that they do not accept electrons.
 - (iii) The number of vacant orbitals in a metal should be more than the number of valence electrons in it so that the mobile electrons easily move into the vacant orbitals.

- Features of metallic bond:
- (i) It is weaker bond than ionic & covalent bonds.
 - (ii) It is non-directional
 - (iii) It is electrostatic nature, i.e. electrostatic force of attraction acting between kernels (metal cations) and mobile electrons.

→ Theories of Metallic bond: To explain nature of metallic bond, following theories have been proposed: 1. Electron sea theory 2. Valence bond theory 3. Molecular orbital theory or Band model: The smallest piece of a metal would contain about 10^{20} atoms, a large number of molecular orbitals (MOs) are formed from a large no. of atomic orbitals (AOs).

Let us consider an idealised one dimensional lattice of Li-atom (Li-Li-Li-...) In the formation of this chain, first of all two Li-atoms will form a Li_2 molecule. In the formation of Li_2 , the two 2s atomic orbitals, having unpaired electron ($2s^1$) undergo linear combination to give two MOs. The lower energy MO (σ_{2s}^+) is completely filled and the higher energy MO (σ_{2s}^-) is vacant. Attaching another Li-atom to Li_2 molecule gives the linear Li_3 molecule (hypothetical).

Now, as the length of the chain increases by increasing no. of Li-atoms we get a large no. of MOs closely spaced together. No. of MOs is the same as that of AOs. As the number of Li-atoms increases, the energy levels get closer & closer and ultimately become continuous. Such a group of continuous energy levels is known as a band and consequently, the MOI is called band model. Here A is the upper half of the 2s-band (vacant) and B is the lower half (completely filled). Small circles indicate AOs & MOs. This can readily explain the metallic properties.



Superconducting materials / Superconductivity?

Kammerlignh Onnes (1913) observed for the first time superconductivity phenomenon in Helium (He). The materials which offer no resistance to the passage of electricity through them at temperature lying between 2K & 5K (i.e., low temp.) are called Superconducting materials, and phenomenon exhibited by them is called superconductivity. Such substances become diamagnetic at this temperature, and hence are repelled by magnets.

He, most metals and mixed metal oxides are examples of superconducting materials. Recent discoveries have shown that many mixed oxides become superconducting at fairly high temperatures. For examples, $\text{La}_{1.5}\text{Ba}_{1.5}\text{CuO}_4$, $\text{Ba}_{0.7}\text{K}_{0.3}\text{BiO}_3$ (at 30K), $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ (at 40K), $\text{YBa}_2\text{Cu}_3\text{O}_7$ (at 90K), $\text{Ba}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$ (at 105K), $\text{Th}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (at 125K) etc.

Applications: Superconducting materials are used in (i) electronics (ii) building super magnets (iii) Levitation transportation (iv) power transmission.

Group-8: Unit-3. General Chemistry of f-block elements

→ What are f-block elements/Inner transition elements?

Those elements in which last or differentiating electron enters in antepenultimate, i.e. (n-2) f orbitals are called f-block elements. These elements are also known as inner transition elements due to last electrons in them enters into (n-2) f orbitals, i.e. inner to the penultimate energy level. They have ele. Conf. [Noble gas] (n-2) f^{1-14} (n-1) d^{0-1} ns² (where n=6 or 7). These are elements of Group-3 and shown in two series/horizontal positions, below main part of Periodic table. f-block elements are of two series: (i) 4f series/Lanthanides: Ce₅₈ to Lu₇₁ (ii) 5f series/Actinides: Th₉₀ to Lr₁₀₃.

→ What are Lanthanides?

Those elements in which last electron enters in 4f-orbitals are called 4f or first inner transition series. 4f series elements are called Lanthanides or Lanthanones since they follow Lanthanum (La₅₇). They are also called rare earths as found in earth crust in very small amounts. Outer ele. Conf. of Lanthanides is $4f^{1-14} 5d^{0-1} 6s^2$. These are elements of Group-3, Period-6 (shown in 1st horizontal row below main part of PT). They are Ce₅₈ to Lu₇₁.

1. Electronic Configuration: General ele. Conf. of Lanthanides is [Xe]₅₄ $4f^{1-14} 5d^{0-1} 6s^2$.

In Lanthanides, 4f orbitals/subshell gradually filled. Since the energies associated with 4f & 5d subshells are very close, there are some doubts regarding their ele. Conf. because the electrons can exchange their positions. The commonly accepted ele. Conf. of Lanthanides are given in Table-1.

Table-1

Element	Symbol	At. No.	Ele. Conf.	Oxidation states
Cerium	Ce	58	[Xe] $4f^1 5d^1 6s^2$	+3, +4
Praseodymium	Pr	59	[Xe] $4f^3 5d^0 6s^2$	+3, +4
Neodymium	Nd	60	[Xe] $4f^4 5d^0 6s^2$	+2, +3, +4
Promethium	Pm	61	[Xe] $4f^5 5d^0 6s^2$	+3
Samarium	Sm	62	[Xe] $4f^6 5d^0 6s^2$	+2, +3
Europium	Eu	63	[Xe] $4f^7 5d^0 6s^2$	+2, +3
Gadolinium	Gd	64	[Xe] $4f^7 5d^1 6s^2$	+3
Terbium	Tb	65	[Xe] $4f^9 5d^0 6s^2$	+3, +4
Dysprosium	Dy	66	[Xe] $4f^{10} 5d^0 6s^2$	+3, +4
Holmium	Ho	67	[Xe] $4f^{11} 5d^0 6s^2$	+3
Erbium	Er	68	[Xe] $4f^{12} 5d^0 6s^2$	+3
Thulium	Tm	69	[Xe] $4f^{13} 5d^0 6s^2$	+2, +3
Ytterbium	Yb	70	[Xe] $4f^{14} 5d^0 6s^2$	+2, +3
Lutetium	Lu	71	[Xe] $4f^{14} 5d^1 6s^2$	+3

It is clear from table that (i) Lu₇₁ has completely filled f-subshell while others are incomplete f-subshell (ii) Ce₅₈, Gd₆₄ & Lu₇₁ have single electron in d-subshell (i.e. d¹ Conf.) (iii) Lanthanides (Eu₆₃, Yb₇₀) are relatively more stable since they are either half filled or completely filled f-subshell.

2. Oxidation states: Lanthanides show variable oxidation states. Oxidation states exhibited by Lanthanides are shown in Table-1. From table, it is evident that (i) the most common & stable oxidation state of Lanthanides (Nd, Sm, Eu, Yb, Lu) is +3. (ii) Some Lanthanides occasionally exhibit oxidation state +2 also (iii) Some Lanthanides (Ce, Pr, Tb) occasionally exhibit O.S. +4 also. Sm²⁺, Eu²⁺, Tm²⁺ & Yb²⁺ exist in aqueous solution. Ce⁴⁺, Pr⁴⁺, Nd⁴⁺, Tb⁴⁺ & Dy⁴⁺ (only oxide) exist in aqueous solution. Lanthanides in O. state +2 act as reducing agent while O. state +4 act as oxidising agent.

3. Atomic & Ionic radii (Lanthanide Contraction): The atomic & ionic radii in lanthanides show a regular change (decrease) in the size of atoms/ions with the increase in atomic number. The regular (steady) decrease in the size of lanthanide atoms/ions with the increase in atomic number (i.e., La_{57} to Lu_{71}) is known as Lanthanide Contraction.

Table-2

Element	La_{57}	Ce_{58}	Pr_{59}	Nd_{60}	Pm_{61}	Sm_{62}	Eu_{63}	Gd_{64}	Tb_{65}	Dy_{66}	Ho_{67}	Er_{68}	Tm_{69}	Yb_{70}	Lu_{71}
Atomic radius (Å)	187	183	182	181	181	180	199	180	178	177	176	175	174	173	172
Ionic (Ln^{3+}) radius (Å)	106	103	101	100	98	96	95	94	92	91	89	88	87	86	85

Cause of Lanthanide Contraction: Lanthanide contraction, i.e. decrease in size (atomic/ionic) from La to Lu, is due to poor shielding effect of antepenultimate, i.e. $(n-2)$ f orbitals. On moving along lanthanide series, the nuclear charge increases due to increase in number of protons as well as one electron increases in $(n-2)$ f-orbital. The shielding effect is poor in case of $(n-2)$ f orbital (order of shielding effect: $s > p > d > f$) as well as it becomes very less effective if shielding is by f orbitals as they are more diffused. Evidently, the increase in nuclear charge (no. of proton) with increase in atomic number predominates over decrease in nuclear charge due to shielding effect & thus valence or outermost shells are pulled more effectively towards nucleus to show decrease in atomic/ionic size.

Consequences of Lanthanide Contraction: Some of the important consequences/effects of Lanthanide Contraction are -

- (i) In Lanthanide contraction (La^{3+} to Lu^{3+}) average decrease in atomic size is about 14 pm, which is responsible for a small decrease in electronegativity and standard oxidation potential along the series (La to Lu). So lanthanides are chemically similar in properties.
- (ii) The basic character of oxides and hydroxides decreases from La_2O_3 to Lu_2O_3 / $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. Due to smaller size of Lu, the Lu-OH bond acquires more covalent character.
- (iii) Lanthanides have similar chemical properties and it is therefore difficult to separate from each other, but ability to form complexes varies slightly which helps in their separation by ion-exchange method.
- (iv) The closer values of atomic radii for Zr-Hf, Nb-Ta & Mo-W pairs of elements of fourth and fifth d-series of a subsequent group. Here increase in size down group is cancelled by decrease in size due to Lanthanide contraction. This is the reason that members of 4d & 5d series of a group resemble more closely in comparison to 3d members.

Table-3

Group →	4	5	6
3d-series	Ti (132 pm)	V (122 pm)	Cr (130 pm)
4d-series	Zr (160 pm)	Nb (146 pm)	Mo (139 pm)
5d-series	Hf (159 pm)	Ta (146 pm)	W (140 pm)

4. Magnetic properties: We know that magnetic behaviour in ^{chemical} substances arises due to the presence of

(3) unpaired electrons. An electron may be regarded as an elementary or tiny magnetic. The origin of magnetism is most easily described in pre-wave mechanical terms where we make picture the electron as negatively charged particle, possesses both spinning motion on its axis and revolving motion about a nucleus. The former motion gives rise to spin moment and the later to orbital moment. The combination of these two moments results in the paramagnetic moment (i.e., paramagnetism) for certain atom/ion.

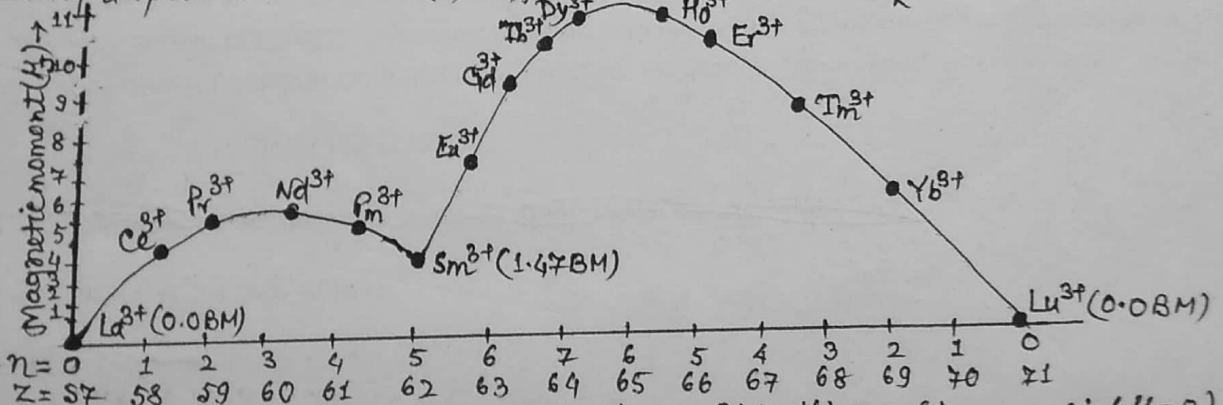
In the 4f series (i.e., lanthanides), La^{3+} ion is empty (i.e., $4f^0$ conf.) and Lu^{3+} is completely filled (i.e., $4f^{14}$ conf.). These ions are diamagnetic as there is no unpaired electron. The remaining M^{3+} ($4f^1 - f^{13}$ conf.) ions are paramagnetic, since they are partly filled, i.e., presence of one or more unpaired electrons.

The magnetic behaviour of the f-block elements (lanthanides/actinides) is fundamentally different from that of d-block elements (transition metals). The reason for the difference is that the electrons responsible for the properties of the M^{3+} ions are 4f or 5f orbital which are effectively shielded from the influence of external forces by overlain s & p-orbitals. Due to this, it is not possible to explain the magnetic moment in term of unpaired electron atom. The orbital contribution which is ignore in the case of d-block elements, cannot be ignored in the case of f-block elements.

The simple relation for calculating magnetic moment is given by $\mu = \sqrt{n(n+2)} \text{ BM}$ (where n = no. of unpaired electrons) cannot be valid in f block elements. In the case of f block elements, the total paramagnetism is due to both spin^(S) & Orbital^(L) moments, given as $\mu_{\text{eff}} = g \sqrt{J(J+1)} \text{ BM}$ (where g = a constant, called Lande Splitting factor = $1.5 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$; J = total or resultant angular momentum). μ_J values of M^{3+} ions calculated from above formula, e.g., for Ce^{3+} ($4f^1$ conf.) ground state term is $^2F_{5/2}$, $S = 1/2$, $L = 3$, $J = 5/2$, $g = 6/7$

μ_J or $\mu_{\text{eff}} = g \sqrt{J(J+1)} \text{ BM} = \frac{6}{7} \sqrt{5/2(5/2+1)} = 2.54 \text{ BM}$. Experimental value lie in the range 2.3-2.5 BM.

The experimental values of μ_J (in BM) of M^{3+} ions are plotted against their atomic nos./ number of unpaired electrons (n) in f-orbitals for lanthanides as shown below:



From the graph, it is evident that La^{3+} ($4f^0$) & Lu^{3+} ($4f^{14}$) are diamagnetic ($\mu_J = 0$). μ_J values increase upto Nd^{3+} and then decreases to Sm^{3+} ion. It starts rising again and becomes maximum at Dy^{3+} (10.5 BM) and then decreases to Lu^{3+} (0.0 BM).

⇒ What are Actinides?

Those elements in which the last electron enters in 5f orbitals are called 5f or second inner transition series. They are called actinides or actinones since they follow Actinium (Ac_{89}). Outer ele. conf. is $5f^{0-14} 6d^{0-1} 7s^2$. These are elements of Group 3 and Period 7 (shown in 2nd horizontal row below main part of PT). They include 14 elements from Th_{90} to Lr_{103} . They are radio active elements. First three elements (Th_{90} , Pa_{91} , & U_{92}) are natural and last 11 elements (Np_{93} to Lr_{103}) are artificial (man made), called transuranic elements.

1. Electronic Configuration: The general electronic conf. of actinides is $[Rn] 5f^{1-14} 6d^{0-1} 7s^2$. From Th_{90} onwards 5f subshell gets progressively filled. However, there are some doubts regarding the filling of 5f & 6d subshells due to their comparable energies. The commonly accepted ele. conf. of actinides are given in the table-4.

Table-4

Element	Symbol	At. No.	Electronic Conf.	Oxidation states
Thorium	Th	90	$[Rn] 5f^0 6d^2 7s^2$	(+3), +4
Protoactinium	Pa	91	$[Rn] 5f^2 6d^1 7s^2$	(+3), (+4), +5, (+6)
Uranium	U	92	$[Rn] 5f^3 6d^1 7s^2$	+3, +4, +5, +6, +7
Neptunium	Np	93	$[Rn] 5f^4 6d^1 7s^2$	+3, +4, +5, +6
Plutonium	Pu	94	$[Rn] 5f^6 6d^0 7s^2$	+3, (+4), +5, +6
* Americium	Am	95	$[Rn] 5f^7 6d^0 7s^2$	+3, (+4)
Curium	Cm	96	$[Rn] 5f^7 6d^1 7s^2$	+3, +4
Berkelium	Bk	97	$[Rn] 5f^9 6d^0 7s^2$	+3
Californium	Cf	98	$[Rn] 5f^{10} 6d^0 7s^2$	+3
Einsteinium	Es	99	$[Rn] 5f^{11} 6d^0 7s^2$	+3
Fermium	Fm	100	$[Rn] 5f^{12} 6d^0 7s^2$	+3
Mendelevium	Md	101	$[Rn] 5f^{13} 6d^0 7s^2$	+3
* Nobelium	No	102	$[Rn] 5f^{14} 6d^0 7s^2$	+2, +3
Lawrencium	Lr	103	$[Rn] 5f^{14} 6d^1 7s^2$	+3

2. Oxidation states: Actinides generally show variable O. states from +2 to +7 (Table-4). This is due to comparable energies of 5f, 6d & 7s subshells. The common O. state is +3. The elements in first half of the series show higher O. states. O. states of f^0, f^7, f^{14} conf. are relatively more stable. Oxidation states shown by () are less stable.

⇒ Comparative study of Lanthanides & Actinides:

Lanthanides (4f-series)	Actinides (5f-series)
1. They show variable O. states (+2 to +4).	1. They show variable O. states (+2 to +7)
2. They show lanthanide contraction	2. They also show actinide contraction (same).
3. Most ions of lanthanides (Ln^{3+}) are coloured	3. Most ions of actinides are coloured (due to f-f trans.)
4. These are referred as rare earths	4. Elements beyond U_{92} are called transuranic elements.
5. They are natural & non-radioactive. Pm is a radioactive element.	5. They are mostly artificial. Th, Pa & U are radioactive.
6. Their oxides, hydroxides are less basic in nature.	6. Their oxides, hydroxides are more basic in nature.
7. They do not form oxo-cations	7. They form oxo-cations, e.g. UO_2^{2+} .
8. They show ion-exchange behaviour & so they are separated by ion-exchange method.	8. They also show ion-exchange behaviour.
9. Their mag. prop. (Paramagnetism) can be easily explained	9. Their mag. prop. cannot be easily explained.
10. Their physical & Chem. properties have been thoroughly studied.	10. Physical & chemical properties beyond U_{92} have not been studied thoroughly.

Group C: Unit - 2

Bioinorganic Chemistry

[By Dr. Birendra Kumar, Mahareja College]

Bioinorganic Chemistry is a branch of Chemistry in which we make study of significant role of metal ions in biological system (animals & plants). The metal ions are responsible for initiating or inhibiting reactions in biological systems.

→ Essential & trace elements in Biological System: Elements which are required for the maintenance of life and essential for life processes in plants and animals are called essential elements. They may be metallic or non-metallic. There are 30 such elements, e.g. Na, K, Ca, Mg, N, P, etc.

Elements which are present in trace amounts in biological systems are called trace elements. e.g., Fe, Cu, Co, Zn, Cr, Mn, Ni etc. All essential and trace elements are not required by every animal or plant.

→ Role of metal/ionic in biological systems:

1. Sodium (Na or Na^+): It is common & essential cation present in extra-cellular fluids of plants & animals. It present to a good extent in bones as phosphate (PO_4^{3-}), and mainly exists as Chloride (Cl^-) and bicarbonate (HCO_3^-). In human, it present 90 gm/70kg of its weight. The main functions/role are: (i) It activates certain enzymes in animal body. (ii) It regulates acid-base equilibrium in biological systems. (iii) The intake of Na^+ ions in excess amounts may cause hypertension. Excessive Na^+ is harmful to plants & aquatic life. (iv) It is essential for the formation of HCl in stomach and conduction of nerve impulses & muscle contraction. (v) It is responsible for the transport of glucose & amino acids into cell. (vi) It play major role in preservation of normal irritability of muscle & permeability of the cell. (vii) It is important in nerve action and in the function of heart.

2. Potassium (K or K^+): It is also common & essential cation, mostly present in intra-cellular fluid as well as extra-cellular fluid of biological systems. In human, it present 140 gm/70kg of its weight.

The main functions/role are: (i) It activates a variety of enzymes, such as glycolytic enzyme pyruvate kinase. (ii) It promotes oxidation of glucose into ATP, which is source of energy. (iii) It is also responsible for the transmission of nerve signals. (iv) Certain enzymatic reactions controlled by Na^+/K^+ . [The Na^+ & K^+ ions differ in concⁿ on the opposite sides of the cell membranes. The ratio of Na^+ & K^+ concⁿ is called concⁿ or ionic gradient. Sod. - potassium pump operates across the cell membranes to maintain concⁿ gradient in cells] (v) It play important role in metabolic functions like protein biosynthesis by ribosomes. (vi) It controls osmotic pressure and water retention. (vii) It influences acid-base equilibrium like Na^+ in extra-cellular fluid. (viii) It is essential for nerve impulses & muscle contraction.

3. Magnesium (Mg or Mg^{2+}): It is very important essential element for biological systems. The main role/functions are: (i) Mg^{2+} is present in chlorophyll, a green pigment of plants, as Mg-Complex. It absorbs light from Sun & brings about the process of photosynthesis in plants to CO_2 & H_2O to glucose. (ii) It plays important role in many metallo-enzymes. (iii) Mg^{2+} salts serve as remedies for constipation, obesity, liver & gall bladder disorders. (iv) It forms a complex with ATP, which required for most enzymatic reactions within the cell. (v) Mg^{2+} ions are present in enzyme phosphatase which acts upon organic phosphates to hydrolyse them into free phosphates. (vi) Intra-cellular fluid has high concⁿ of Mg^{2+} . It combines with ATP^{4-} & ADP^{3-} ions to form $[\text{Mg}(\text{ATP})]^{2-}$ & $[\text{Mg}(\text{ADP})]^-$. Thus, ATP & ADP exist as these forms in intra-cellular fluid at biological pH (7.0 to 7.5). (vii) Mg^{2+} present in the enzyme aminopeptidase which hydrolyses polypeptides the free amino acid end of the chain to form lower peptides and sometimes free amino acids.

4. Calcium (Ca²⁺ or Ca): Calcium is a major constituent of bones & teeth, ^{is} present as phosphates in the bones of human beings and animals. Large amounts of Ca are present in the bone tissues as Ca₁₀(PO₄)₆(OH)₂. The enamel on teeth is a double salt of Ca, 3Ca₂(PO₄)₂CaF₂.

Roles of Ca: (i) Ca²⁺ plays an important role in muscle contraction (ii) It acts as an agent of blood coagulation (iii) It plays an important role in biological processes, enzymatic systems & in skeletal formation. With phosphorus in the mineral hydroxyapatite [Ca₅(PO₄)₃(OH)], it is a major constituent of bone, teeth & shells (iv) It acts as a messenger for hormonal actions trigger for muscular contraction (v) It also plays a role in the stabilization of protein ~~structure~~ structure and helps in the maintenance of rhythm of hearts (vi) Deficiency of Ca²⁺ ions causes tetany, while excess of it causes Calcification.

5. Iron (Fe): Iron (Fe) is an essential trace metal in biological systems. Egg, milk, white grain, spinach have moderate amount of Fe. It is essential for all forms of life.

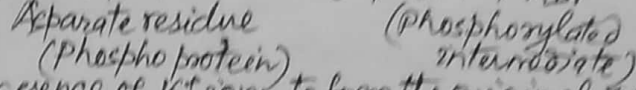
Roles of Iron: (i) In plants & bacteria, iron present as cytochromes & ferridoxin which are responsible for electron transfer reactions in biological systems (ii) It is an important component of nitrogenase (a nitrogen fixing enzyme) which are required by some plants for fixation of atmospheric N₂, (iii) It is also essential for the synthesis of haemoglobin, myoglobin, cytochrome etc, stored as ferritin and transported as transferrin, (iv) The excessive intake of iron can cause siderosis and can damage organs excess iron is not excreted but remains deposited in livers, spleen & skin.

6. Cobalt (Co): Cobalt (Co) is an essential trace element for many organisms.

Roles of Co: (i) It is required for the synthesis of Vit B₁₂ (ii) It activates a number of enzymes (iii) It is essential for healthy growth of animals (iv) When injected intravenously, it is highly toxic to plants and moderately to mammals (v) Deficiency of Cobalt in soil adversely affects the health of grazing animals.

⇒ Sodium (Na⁺) - K⁺ pump: Na⁺ & K⁺ are chemically similar but biologically different. Na⁺ ions are pumped out of cytoplasm while K⁺ ions are pumped in. This transport of ions is called Na⁺-K⁺ pump or simply Sodium pump. The difference in concⁿ of two ions (Na⁺ & K⁺) inside & outside the cell membrane produces an electrical potential, which is crucial for the functioning of nerve and muscle cells. The ratio of Na⁺ & K⁺ concentrations is called ionic or concⁿ gradient in cells. This pump operates across the cell membranes to maintain concⁿ gradient in cells.

Mechanism: The mechanism of sodium pump is that Na⁺-K⁺ATPase is phosphorylated by ATP (Adenosine triphosphate) in presence of Na⁺ & Mg²⁺ ions to form phosphorylated intermediate (E-P).

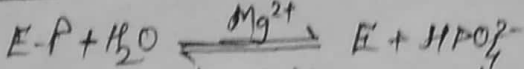


(E-P) formed is hydrolysed in presence of K⁺ ions, to form the original E as a result of dephosphorylation. E-P + H₂O $\xrightarrow{K^+}$ E + HPO₄²⁻

It is electrogenic in nature. During this process, 3Na⁺ & 2K⁺ ions transported per ATP.

⇒ Calcium pump: Ca²⁺ plays an important role in muscles. It triggers a signal that stimulates muscles to contract. In normal state, the concⁿ in the intracellular fluids is very low (10⁻⁷ times that of extracellular fluids). The maintenance of low Ca²⁺ concentration in the intracellular fluids is done by biochemical process known as Ca²⁺ pump or simply Calcium pump.

Mechanism: E + ATP $\xrightarrow{Ca^{2+}, Mg^{2+}}$ ADP + E-P (Intermediate)



During the cycle, two Ca²⁺ ions are transported for each ATP hydrolysed,