→ Essential and Trace elements in biological processes:-

→ Biochemistry:→

- The study of chemisty of living organism or biological study (plants and animal both) is known as biochemistry. Thus biochemistry is the chemisty of life.

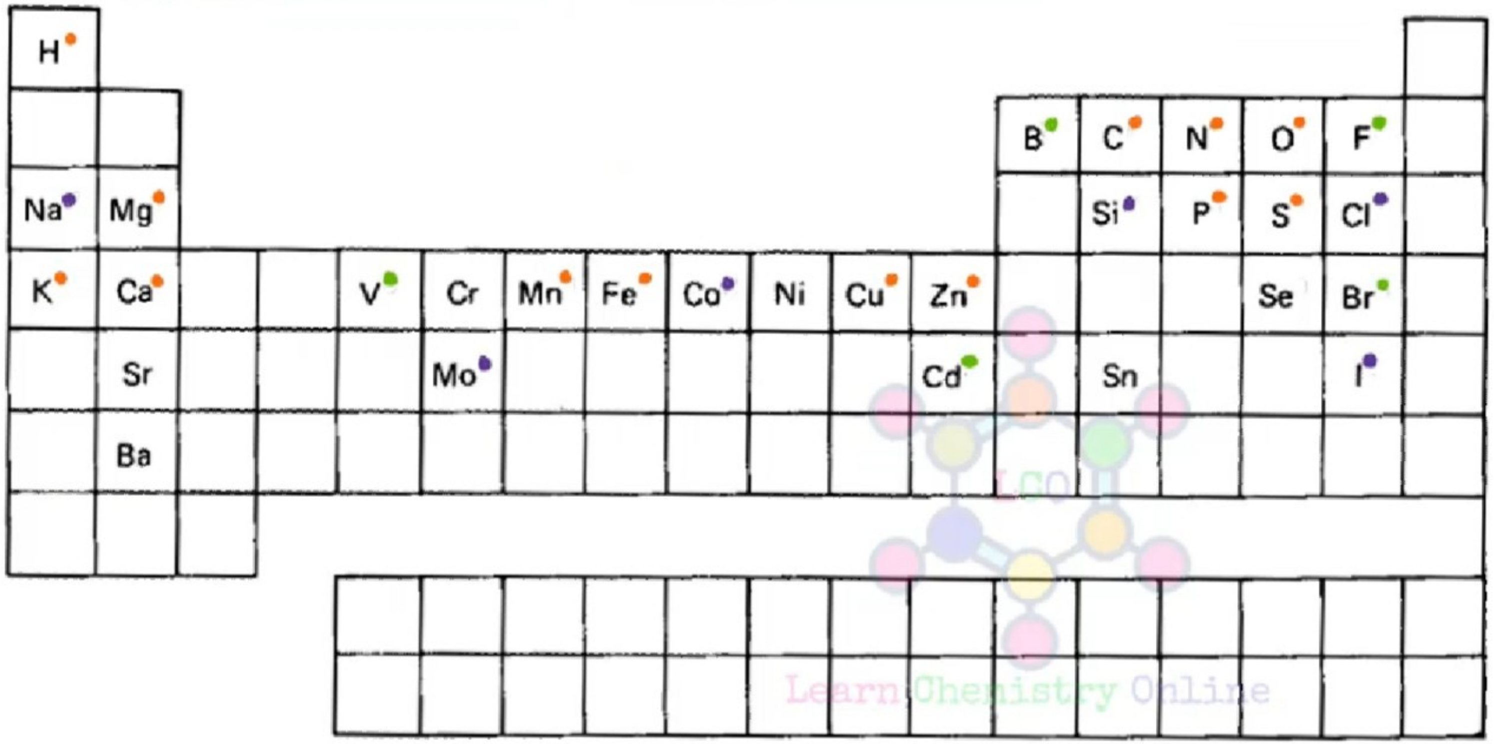
→ Bioinorganic chemistry:→

- Bioinorganic chemistry is the branch of chemistry in which we study about the significant role of metal ion in biological systems.
- These metal ions are responsible for initiating or inhibiting reactions in biological systems.

→ Essential and Trace elements:→

- An essential element is that which is required for the maintenace of life.
- 30 elements are recognized as essential for life processes in plants and animals.
- The elements whose ions are present in biological system in bulk amounts are called bulk elements. e.g. C, H, N, O, Na, K, Ca, Mg, P, S and Cl.
- The elements whose ions are present in biological system in trace amounts are called trace elements. e.g. Trace metals :- V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Mo.
  Trace non metals :- B, Si, Se, F and I.

- Essential elements of life are given below



- ● Essential to all animals and plants
- ● Essential to several class of animals and plants
- ● Essential to a wide variety of species in one class

- All the essential and trace elements are not required by every plants or animal.
  e.g. Na is essential for humans and animals but not for bacteria. some plants require Al, B and V but human do not require these elements.
- Some essential elements prove to be toxic, even fatal, when taken in higher concentration.

- Biological role of trace elements are given below -

Metal	Mass/mg*	Biological roles
V	0.11	Enzymes (nitrogenases, haloperoxidases)
Cr	14	Claimed (not yet proven) to be essential in glucose metabolism in higher mammals
Mn	12	Enzymes (phosphatase, mitochondrial superoxide dismutase, glycosyl transferase); photoredox activity in Photosystem II
Fe	4200	Electron-transfer systems (Fe–S proteins, cytochromes); O_2 storage and transport (haemoglobin, myoglobin, haemerythrin); Fe storage (ferritin, transferritin); Fe transport proteins (siderophores); in enzymes (e.g. nitrogenases, hydrogenases, oxidases, reductases)
Co	3	Vitamin B_{12} coenzyme
Ni	15	Enzymes (urease, some hydrogenases)
Cu	72	Electron transfer systems (blue copper proteins); O_2 storage and transport (haemocyanin); Cu transport proteins (ceruloplasmin)
Zn	2300	Acts as a Lewis acid (e.g. in hydrolysis processes involving carboxypeptidase, carbonic anhydrase, alcohol dehydrogenase); structural roles
Mo	5	Enzymes (nitrogenases, reductases, hydroxylases)

* Trace metal present in an average 70kg human.

→ Metalloporphyrins:→

- Porphine ligand is a ring system which contains four pyrrole rings.
- These pyrrole rings are linked together through methene (=CH−) bridges.
- Porphine has conjugated double bonds.
- Porphine has four N-atoms. These N-atoms present in pyrrole rings. Two N-atoms are present as NH-groups and two are as N-atoms.
- If two protons present in NH-groups are removed then all four N-atoms can coordinated to M^{+2} metallic ions ($M^{+2} = Mg^{+2}, Fe^{+2}, Ni^{+2}$) to form complexes which are called Metalloporphyrins.
- These complexes are neutral complexes and in these complexes, porphine acts as tetradentate dinegative ligand.
- Metalloporphyrines are bioinorganic compounds and play a vital role in biological system.
- The size of central hole in the centere of porphine is ideal for accomandation of M^{+2} ions of the elements of first transition series and higher alkaline earth metals.

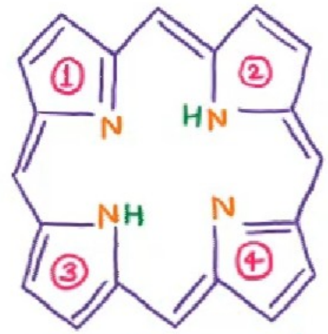


fig:- structure of porphine containing four pyrrole ring 1,2,3,4

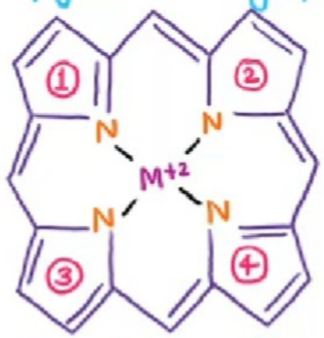


fig. structure of Metalloporphyrine

- M^{+2} ions of appropriate size are surrounded by four N-atoms of porphyrine ring in a square planar geometry and other axial positions are avaliable for other ligands.
- If the size of M^{+2} ion is smaller than the size of the hole, the porphine ring becomes ruffed.
- If the size of M^{+2} ion is larger than the size of the hole, it cannot fit into the hole and stays out of square planar containing four atoms. In such case metal ion sets above the porphine ring which becomes domed and acquires pyramidal structure.

→ Examples of Metalloporphyrine :→

① Heme :→

- Heme is Fe(II) porphyrine complex in which Fe(II) coordinated throught four N- atoms of phorphine in square planar geometry
- Fe(II)–N bond length → ~ 2.2 A°

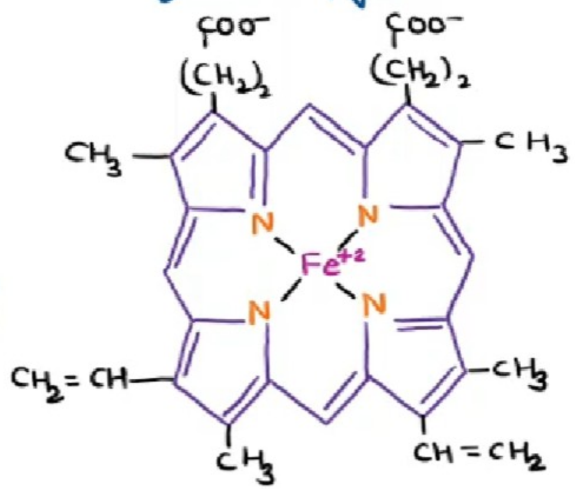


fig:- structure of Heme
(Iron (II) porphyrine complex)

② Chlorophyll :→

- Photosynthetic cells contain green pigments which can absorb solar energy. These light absorbing pigments are called chlorophylls.
- Photosynthetic cells contain two types of chlorophylls.
  ① Chlorophyll a → $R = CH_3$
  ② Chlorophyll b → $R = CHO$
- Both chlorophylls are planar complexes of Mg(II) with four nitrogen sitting at the corners of a square planar. These N-atoms are part of pyrrole rings.
- Chlorophyll a and b can be isolated using chromatographic technique.
- Chlorophyll a and b are green but their absorption spectra are slightly different.

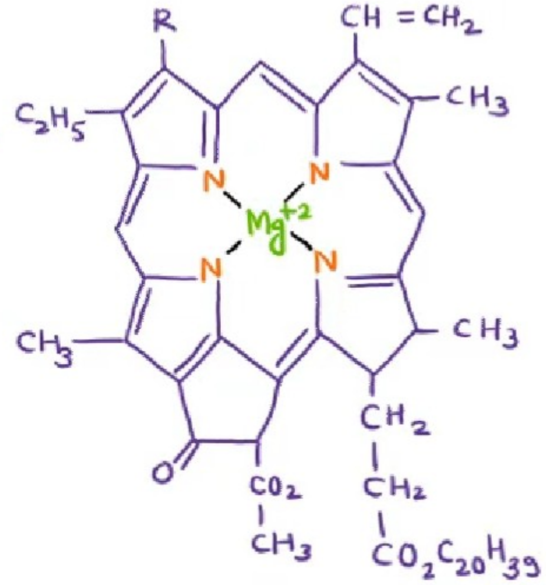


fig:- Chlorophyll a : $R = CH_3$
Chlorophyll b : $R = CHO$

→ Myoglobin (Mb) :→

- Myoglobin is a heme containing protein or metallo-protein or metalloporphyrine.
- Mb may be viewd as a monomer of hemoglobin (Hb) and is made up of one heme unit connected to one globin (polypeptide chain).
- In Mb, heme group is embedded in the cracks formed by the coiling of its polypeptide chain.
- The polypeptide chain in Mb contains 15 to 160 amino acid residues.
- The polypeptide chain in Mb is coordinated to iron atom of the heme group through N-atom of histidine.
- Molar mass of Mb is about 17000
- Mb which has not taken up oxygen is called deoxy-myoglobin (deoxy-Mb) or simply myoglobin. while the myoglobin which has taken up O_2 is called oxygenated myoglobin or oxymyoglobin (oxy-Mb).

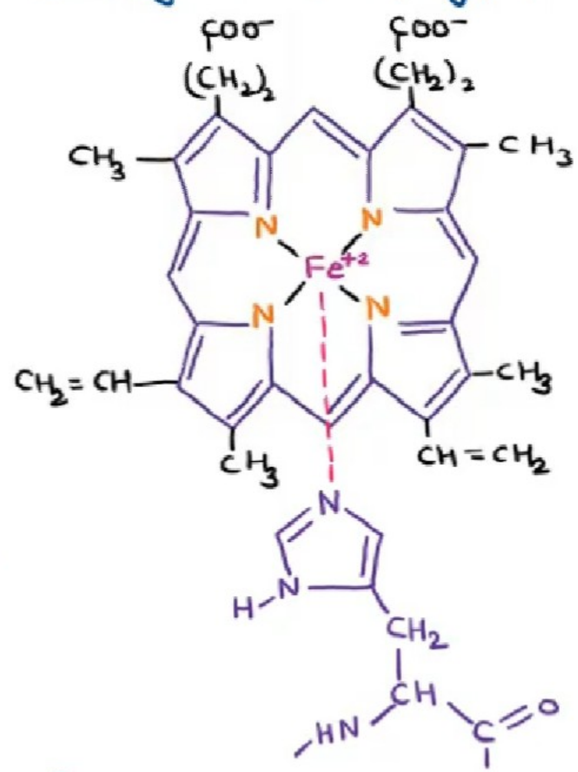


fig:- Deoxy-myoglobin

(i) Deoxy-Mb :→

- Deoxy-Mb is a five coordinated molecule and has square pyramidal geometry.
- Four coordination positions are occupied by four porphyrin N-atoms & fift coordination position is occupied by N- atom of imidazole of a histine residue which is linked with protein.
- Deoxy-Mb has weak field and High spin complex. This complex has paramagnetic nature due to 4 unpaired electrons.
- The Fe-N atom distance (218pm) larger than the central hole of porphyine ring. Therefore, Fe lies above the plane of four N- atoms.

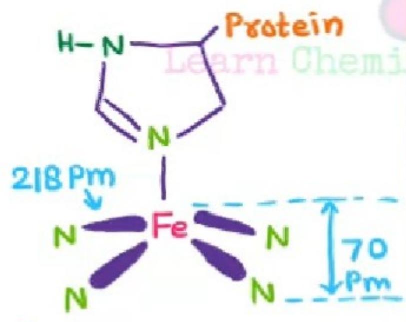


fig:- Deoxy-Mb

(ii) Oxy-Mb :→

- Oxy-Mb is a six coordinated molecule and has octahedral geometry.
- Five coordination positions are similar to deoxy-Mb and sixth coordination position is occupied by O_2.
- Oxy-Mb has strong field and low spin complex. This complex has diamagnetic nature due to no unpaired electrons.
- The Fe-N atom distance (200 pm) matches the size of central hole of porphyine ring. hence Fe(II) becomes coplanar.
- The release of strain energy of S.P. structure compensates the loss of pairing energy in going from C.N. 5 to C.N. 6

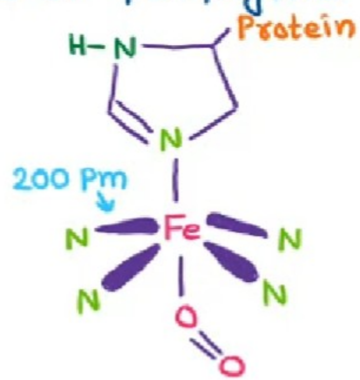


fig:- oxy-Mb.

→ Oxygen-binding curve for Myoglobin:→

- The graph between present oxygen of Mb and partial pressure (Torr) of O_2 in lungs and muscle is called oxygen-binding curve.
- This graph shows that at high pressure Mb is good O_2 binder and prevailing in lungs and much poorer binder at low pressure and prevaling in muscles.

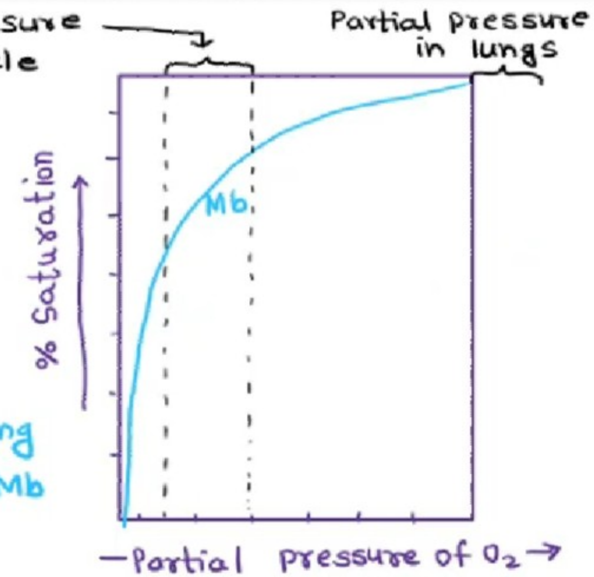


fig. oxygen binding curve for Mb

→ Role of Mb in biological system:→

- The O_2 librates by Hb is taken up by Mb to form oxy-Mb (MbO_2). This is called oxygenation of Mb.

$$Mb + O_2 \xrightarrow[\text{of Mb}]{\text{Oxygenation}} MbO_2$$

- As the blood runs in arteries to the tissues, O_2 bind with MbO_2 is becomes free. This free O_2 is used in the combustion (oxidation) of food (Glucose).

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 38ATP \text{ (In form of energy)}$$

- These ATP molecule provides energy to the living organism to perform metabolic activities and to maintain body temp. H_2O is retained by the body and CO_2 is combined with hemoglobin to carb-amino hemoglobin, which decomeposes to give CO_2 and hemoglobin.

→ Hemoglobin (Hb) :→

- The human contains about 4g of iron. About 70% of this is found as hemoglobin. Most of the rest is found as ferritin.
- Hb is a Fe(II) porphyrine. Hb contains four identical units arranged roughly tetrahedrally. Each unit has one heme group. (fig. 1)
- Molar mass of Hb is 65000.
- In the Hb structure (fig. 2), four heme groups are represented as heme-1, heme-2, heme-3 and heme-4 which are bound to globin protein on its surface. Thus Hb is Heme containing protein. The four heme groups are subunits of Hb.
- Hb is an octahedral complex of Fe(II). Fe(II) occupies the central position and the four corners of the square are occupied by N-atom of heme group. one axial position is occupied by N-atom of histidine and other axial position is occupied by H_2O molecule.
- The four subunits are linked through salt bridges present b/w the four polypeptide chains. These salt bridges indroduce strain in Hb molecule.

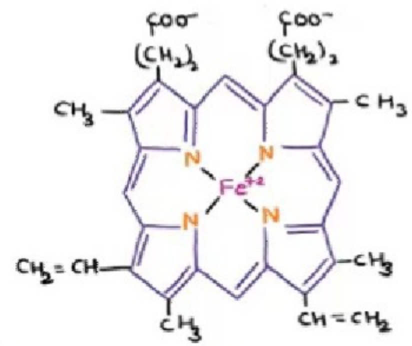


fig. 1 - Heme group

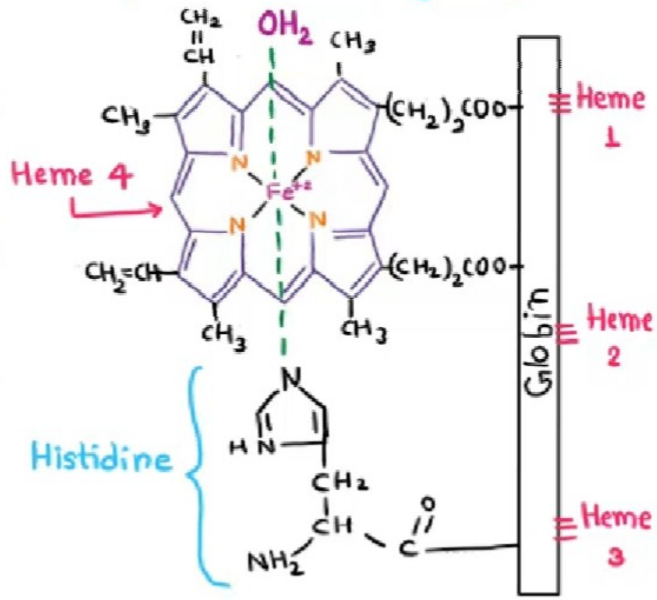


fig:- 2 - Structure of Hb

- Hb which is not taken up O_2 is called deoxy-hemoglobin (deoxy-Hb) or simply hemoglobin while the hemoglobin which has taken up O_2 is called oxygenated hemoglobin or oxyhemoglobin (oxy-Hb).

→ Comparison between Hb and HbO_2 :→

deoxy-hemoglobin (deoxy-Hb) or Hb	Oxyhemoglobin (oxy-Hb) or HbO_2
– High spin complex of Fe(II)	– Low spin complex of Fe(II)
– No. of unpaired $e^- = 4$	– No. of unpaired $e^- = 0$
– Paramagnetic	– Diamagnetic
– In Hb, since Fe(II) is HS, Fe(II) has larger radius (0.9A°). Being larger in size, Fe(II) just does not fit in the centre hole of porphyrine ring. Thus Fe(II) lies above the plane of the four N-atoms of porphyrine ring and tilted towards N-atom of histidine.	– In HbO_2, since Fe(II) is LS, Fe(II) has smaller radius (0.75A°). Being smaller in size, Fe(II) fits in the centre hole of porphyrine ring. Thus Fe(II) lies in the plane of the four N-atoms of porphyrine ring.

- When Hb coordinated to O_2, it converted in to HbO_2. Thus Fe(II) of Heme unit will changes from HS (paramagnetic) to LS (diamagnetic).

→ oxygen-binding curve for Hemoglobin :→

- The graph between present oxygen of Hb and partial pressure (Torr) of O_2 in lungs and muscle is called oxygen-binding curve.
- This graph shows that at high pressure Hb is good O_2 binder and prevailing in lungs and much poorer binder at low pressure and prevaling in muscles.

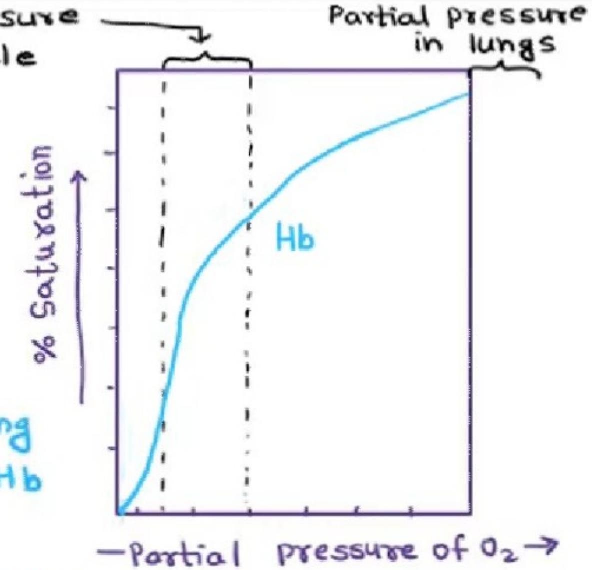


fig. oxygen binding curve for Hb

→ Role of Hb in biological system:→

- O_2 is inhaled in the lungs. In human lungs, since partial pressure of O_2 is high, the inhaled O_2 is binds Hb present in blood in lungs to form oxygenated hemoglobin (HbO_2), called oxyhemoglobin.
- When Hb bind to O_2, H_2O present in Hb is replaced by O_2. this reaction is reversible.

$$\text{Hemoglobin} + O_2 \rightleftharpoons \text{oxyhemoglobin} + H_2O$$

or $$\text{Hb (containing } H_2O) + O_2 \rightleftharpoons HbO_2 + H_2O.$$

- As HbO_2 runs to the muscular tissue through arteries, the partial pressure of O_2 in muscule tissue decreases and HbO_2 liberates O_2 which is further proceeds by Mb.

$$HbO_2 \longrightarrow Hb + O_2$$

- Fe(II) present in Hb can be oxidised to Fe(III) under controlled conditions to form Fe(III) protein called met-hemoglobin. Fe(III)-protein is responsible for brown colour of old meat and dried blood.

→ Bohr effect :→

- Oxygen affinity of Mb and Hb varies with pH value of medium. The variation of oxygen affinity of Mb and Hb with pH of medium is called Bohr effect.
- In other words the effect of pH on O_2 uptake of Mb and Hb is called Bohr effect.

→ Comparison b/w Hb and Mb :→

- Hb and Mb both are Heme proteins.
- Both are metalloporphyrins.
- Both are good O_2 binder at high partial pressure of O_2. but in case of low partial pressure of O_2, Hb is far poorer binder.
- In Hb and Mb, Fe(II) ion is lies above the plane of four N-atoms of porphyrine ring.

→ Biological role of alkali and alkaline earth metal ions with special reference to Ca^{+2}.

1. Role of Na^+ ion:→

- Na^+ ion is a major cation present in extra-cellular fluids of animals and human beings.
- sodium is present to a good extent in bones as phosphate.
- Sodium mainly exist as chloride and bicarbonate.
- Na^+ ion used to activate certain enzymes in animal body.
- The excess intake of Na^+ ion may cause hypertension. The saline water containing excessive amount of NaCl is harmful to plants and aquatic life because of toxicity of Na^+ ion.
- Na^+ ion regulates acid-base equilibrium.
- Na is essential for the formation of HCl in stomach and conduction of nerve and muscle contraction.
- Herbivorous animals look out for salt-lick to make up their Na requiremet because they do not get required amout of Na from vegetables.
- It also helps in maintaining osmotic pressure of the body fluid, thereby protecting the body against fluid loss.
- It has a role to play in preservation of permeability of the cell.
- The injectable medicines are dissolved in sodium chloride before they are injected into human body.

- Na^+ ion is important in nerve action and in the the function of heart.
- Na^+ ion is responsible for the transport of glucose and amino acid in the cell.

2. Role of K^+ ion:→

- K^+ ion is mostly present in intra cellular fluid and in extra cellular fluid.
- K^+ ion is essential for nerve impluse and muscle contration.
- K^+ ion is essential for all organism except blue green algae.
- It is moderately toxic to mammals but only when injected intravenously.
- It regulates acid-base equilibrium.
- It controls osmotic pressure and water retention.
- It is important for metabolic functions, protein synthesis and enzyme activity.

- $Na^+ - K^+$ pump or sodium-potassium pump or sodium pump:→

- Although Na^+ and K^+ ions are chemically similar, yet biological response for these ions is different. Na^+ ions are pumped out of cyto-plasm and K^+ ions are pumped in cyto-plasm. This transport of ions is called $Na^+ - K^+$ pump or simply sodium pump.
- This pump involves the active take up of K^+ ion and expulsion of Na^+ ion.
- The difference in concentration of the two ions inside and outside the cell membrane produces an electrical potential, which is essential for the functioning of nerve and muscle cells.

- Higher intake of Na^+ is risky but there is no such risk from higher intake of K^+ ions.
- Na^+ and K^+ are present in the red blood cells. The ratio of these ion in human, rabbits, rats and horses is 1:7. In cats and dogs this ratio is 15:1.
- The energy for the transport of Na^+ and K^+ ion is provided by the hydrolysis of ATP molecules. Kidney and brain cells use about 70% of the energy from ATP for the transport of ions. For each hydrolysed ATP molecule, $3Na^+$ ions are transport out of the cell and $2K^+$ ions are transported inside the cell.

$$3Na^+ (\text{inside}) + 2K^+ (\text{outside}) + H_2O + ATP^{-4} \longrightarrow 3Na^+ (\text{outside}) + 2K^+ (\text{inside}) + ADP^{-3} + H_2PO_4^-$$

The net result in movement of one positive charge outward per cycle and hence sodium pump is electrogenic in nature.

③ Role of Mg^{+2} ion :→

- It is essential to all organism and present in greater concentration in red cells than plasma.
- Mg^{+2} plays important role in many metallo-enzymes.
- Mg^{+2} is present in chlorophyll and Chlorophyll plays a major role in photosynthesis.
- Mg^{+2} salts are used as remedies for costipation, obesity, liver and gall bladder disorders.
- Mg^{+2} is required for many enzyme activities.

- Mg is present in many enzymes like phosphotase, aminopeptidase etc.
- Whole grains, fruits and vegetablse are rich in Mg.
- Mg defficiency in plants destroys the green colour of leaves.
- Mg defficiency in human is indicated by tetanus like cramp and swelling of arterial walls.
- Mg^{+2} ion combines with ATP and ADP to form $[Mg(ATP)]^{-2}$ and $[Mg(ADP)]^{-}$. These complex ions are present in intra-cellular fluid.

(4) Role of Ca^{+2} ion :→

- Ca is a major constituent of bones and teeth.
- The teeth enamal is a double salt of calcium, $3Ca_3(PO_4)_2 \cdot CaF_2$
- Ca is present in bones of humans and animals as calcium phosphate.
- This ion is play an important role in muscle contraction.
- The malnutrition in children is due to Ca^{+2} ion.
- 99% of the body calcium is found in bones and 1% is found in the body fluids. calcium in body fuild is of great importance in blood coagulation, in excitation of muscles, nerves and in maintaining membrane permeability.
- Calcium ion plays an important role in blood clotting and heart beat.

- Calcium present in bones in both crystalline and amorphous forms. amorphous form is predominant in early life but later on the crystalline form takes over in adult life.
- Deficiency of Ca^{+2} ion causes tetany, while excess of its causes calcification.
- Ca^{+2} ions also important for stabilisation of protein structure, as a messenger for hormonal action, as a trigger for muscular contraction etc.
- Ca rich foods are spinach, egg, milk and other dairy products.
- When we consume ca, it absorbed into the blood in small intestine. The absorbed Ca is deposited on the bones or excerted.
- Calcium pump:→
- The maintenance of low concentration of Ca in the intracellular fluids is done by biochemical process known as calcium pump or Ca^{+2} pump.

→ Nitrogen fixation:→

- The conversion of free atomospheric nitrogen into useful nitrogenous compounds is called Nitrogen fixation.
- Nitrogen present in nitrogenous compounds is called fixed or combined nitrogen.
- Following method are used for nitrogen fixation –

① Artificial methods ② Natural methods

① Artificial methods:→

ⓐ Haber's process:→

$$N_2 + 3H_2 \xrightleftharpoons[\text{550°c, 200-500 atm}]{\text{Fe + Mo}} 2NH_3 \text{ (Ammonia)}$$

ⓑ Ostwald's process:–

$$4NH_3 + 5O_2 \xrightarrow[\text{1070 K}]{\text{Pt}} 4NO + 6H_2O$$

$$2NO + O_2 \text{(Excess)} \longrightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \text{(Excess)} \rightarrow 4HNO_3 \text{ (Nitric acid)}$$

(c) Birkland-Eyde process :→

$$N_2 + O_2 \rightleftharpoons 2NO \text{ (Nitric oxide)}$$

$$2NO + O_2 \longrightarrow 2NO_2 \text{ (Nitrogen peroxide)}$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3 \text{ (Nitric acid)}$$

(d) synthesis of ammonium salts and nitrates :→

- NH_3 obtained from Haber's process and HNO_3 obtained from Ostwald's process and Birkland-Eyde process can be used for the preparation of ammonium salts and nitrates which are used as fertilizers.

(e) Synthesis of calcium cyanamide :→

$$CaC_2 + N_2 \xrightarrow{800-1000^\circ C} \underbrace{CaCN_2 + C}$$

mixture of calcium cyanamide and carbon is called Nitrolim and used as fertilizer.

(f) Synthesis of Nitrides :→

$$3Mg + N_2 \longrightarrow Mg_3N_2 \text{ (Magnesium nitride)}$$

$$2Al + N_2 \longrightarrow 2AlN \text{ (Aluminum nitride)}$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

(2) Natural methods :→

(a) By lightning discharges :→

- Due to lightning discharges (electrical disturbance) O_2 and N_2 combine to form NO

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

$$\underset{\text{present in soil}}{2HNO_3 + CaCO_3} \longrightarrow \underset{\text{stored in soil as plant food}}{Ca(NO_3)_2} + CO_2 + H_2O$$

(b) By symbiotic bacteria :→

- Nitrogen fixing bacteria, called symbiotic bacteria live in the roots of leguminous plants. These bacteria convert the atomspheric N_2 into nitrogenous compounds which are consumed directly by the plants. In return of this, bateria get their own food from the plant.

(c) By nitrogenase enzyme salts :→

- In nature, the fixation of N_2 takes place at the soil temp (ordinary temp.) and atomspheric pressure through metalloenzyme namely nitrogenase. (Fe-Mo-S protein)

$$N_2 + 8H^+ + 8e^- \longrightarrow 2NH_3 + H_2$$

$$N_2 + 10H^+ + 8e^- \longrightarrow 2NH_4^+ + H_2$$

The energy required to break $N \equiv N$ bond is provided by ATP molecule. After supply of energy ATP is converted in to ADP.

Electrons are supplied by reductase (Fe - S protein). These electrons are used by nitrogenase to reduce N_2 to NH_3 or NH_4^+.

NH_3 obtained above is converted into nitrate or nitrite or may be used directly in the synthesis of amino acids or other essential compounds.