* Role of distal and proximal histidine in Hemoglobin and Myoglobin :-

The proximal histidine residue offers its imidazole moiety to bind the fifth co-ordination site of heme unit. The distal histidine residues in the region of sixth co-ordination site, but it does not co-ordinate with iron in both oxy- and deoxy-forms. The imidazole group from the proximal histidine residue acts as a good σ-donor to facilitate the central metal to act as a better π-donor towards the π-acid ligand (O_2) at the trans-position (i.e sixth position) (e.g O_2). This largly helps O_2 to act as a better π-acid ligand (i.e π-acceptance) to induce the spin pairing at iron i.e O_2 acts as a relatively strong field ligand. Thus the proximal and distal histidine residues also plays a very important role in hemoglobin and Myoglobin.

* Role of protein chains: CO and CN$^-$ poisoning and treatment :-

CO is a powerfull poison to Hb and Mb, as the heme group has a very high affinity for the π-acid ligand like CO. It has been noticed that an isolated heme unit in sol^n binds CO about 2.5×10^4 times as strongly as O_2. Astonishingly, for Hb and Mb, the binding affinity for CO is only 2×10^2 times as strong as for O_2. Thus the globin protein drastically diminishes the CO affinity of Hb and Mb. In this regard, the distal histidine plays the crucial role. Because of the presence of imidazole moiety from the distal histidine residue in the region of sixth coordination site, it does not allow CO to form the linear $Fe-C \equiv O$ bond and CO is forced to make a bent bond. The isolated heme unit which binds CO very strong forms the linear bond. In Hb and Mb, the CO affinity

* Non- porphyrin systems :-

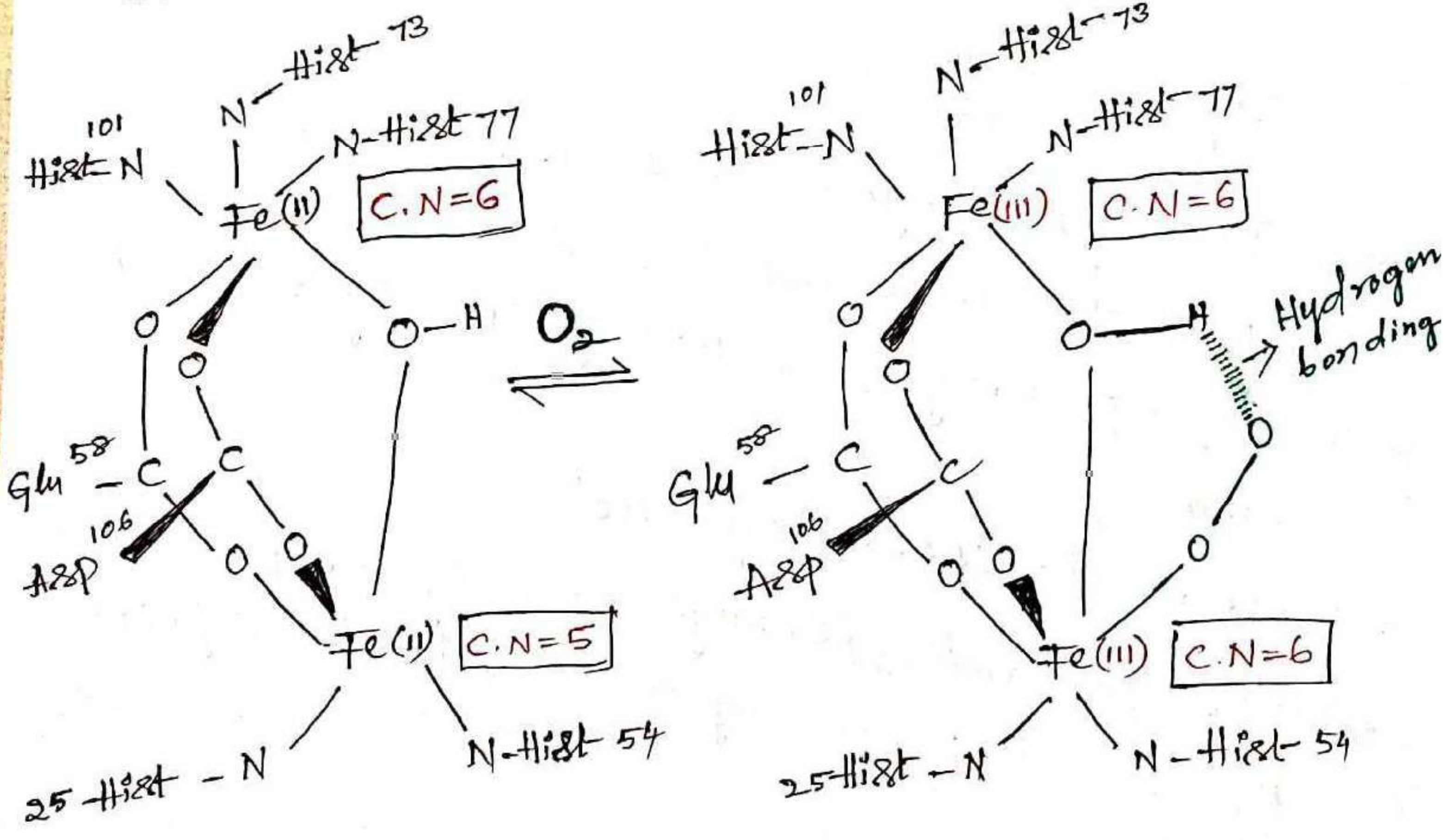
1 HEMERYTHRIN :-

Hemerythrin is an oxygen uptake metalloprotein and no porphyrin skeleton in oxygen transport

⇒ It is a non- hemeprotein

⇒ Its molecular wt 1,08,000

Structure of hemerythrin :- → Deoxyhemerythrin
→ Oxyhemerythrin



DEOXY-HEMERYTHRIN

OXY-HEMERYTHRIN

* Deoxyhemerythrin :-

=> In deoxy form both Fe atoms are +2 oxidation State and It is non-hemeprotein.

=> The two Fe-atoms are commonly bound by Glutamic and Asparatic acid

=> The two Fe-atoms commonly bridged by -OH group ∴ one Fe atom has a C.N is 6 and another Fe-atom has a C.N is 5

* oxy-hemerythrin :-

=> In oxyhemerythrin both atoms are +3 O.S

=> Both Fe-atoms has 6-co-ordinated

=> O_2 uptaking Fe(II) through the hydrogen-bonding

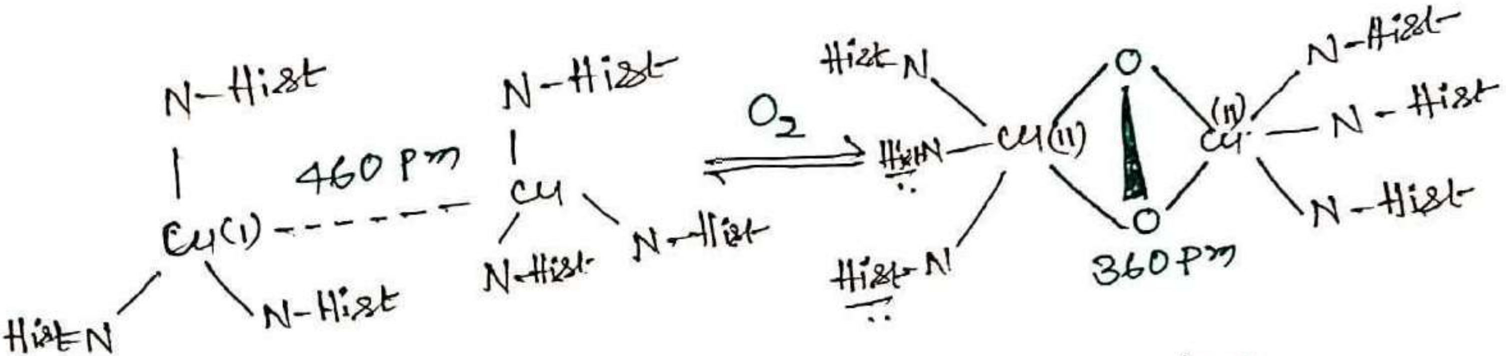
=> It is "Antiferromagnetic"

=> The peroxide(O_2^-) linkage at only one Fe-atom this is supported by a Massbour spectral data.

2. HEMOCYANINE :-

Hemocyanines are copper containing O_2 uptake proteins occuring in a number of invertebrates.

Structure of Hemocyanine :- → Deoxy Hemocyanine
→ oxy Hemocyanine



Deoxy Hemocyanine   oxy Hemocyanine

* Deoxy Hemocyanine :-

⇒ Both cu atoms are +1 oxidation state.
⇒ Each cu bond with three Histidine ligands
⇒ cu – cu bond distance is 460 pm
⇒ Deoxy Hemocyanine is diamagnetic, colourless.

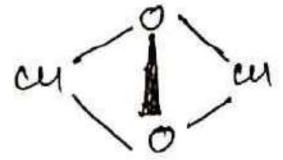
* oxy Hemocyanine :-

⇒ oxygenation provides copper with four co-ordi-nated structure.
⇒ Both cu ions are +2 O.S

⇒ oxy Hemocyanine is blue

⇒ Both d–d transition and charge transfer responsible for colour spectra (blue)

⇒ The two Cu ions are bridged by a peroxide ion (O_2^{2-}) with unusual "$\mu-\eta^2:\eta^2$" bond
μ → indicates "bridging", η^2 → indicates "No of bonds".

⇒ 

O_2^{2-} peroxide linkage

* PHOTOSYNTHESIS :–
AND
*. CHLOROPHYLL :–

photosynthesis is a redox reaction where "H_2O is oxidised to O_2" and "CO_2 is reduced to CH_2O"

$$2H_2O \xrightarrow{\text{Light}} 4[H] + O_2$$

$$x\,CO_2 \xrightarrow{\frac{x}{2}4[H] \overset{\text{Light}}{\uparrow}} (CH_2O)_x + \frac{x}{2}O_2$$

In photosynthesis, when x moles of CO_2 used, $\frac{x}{2}$ moles of O_2 will be liberated.

In this process, "Solar energy" is stored as "chemical energy." In the respiration, the reverse reaction operates. photosynthesis in green plants occurs in chloroplasts which possess chlorophylls to absorb light. Then the "light energy is converted into chemical energy" through a series of reaction.

* Light and dark reaction in photosynthesis :-

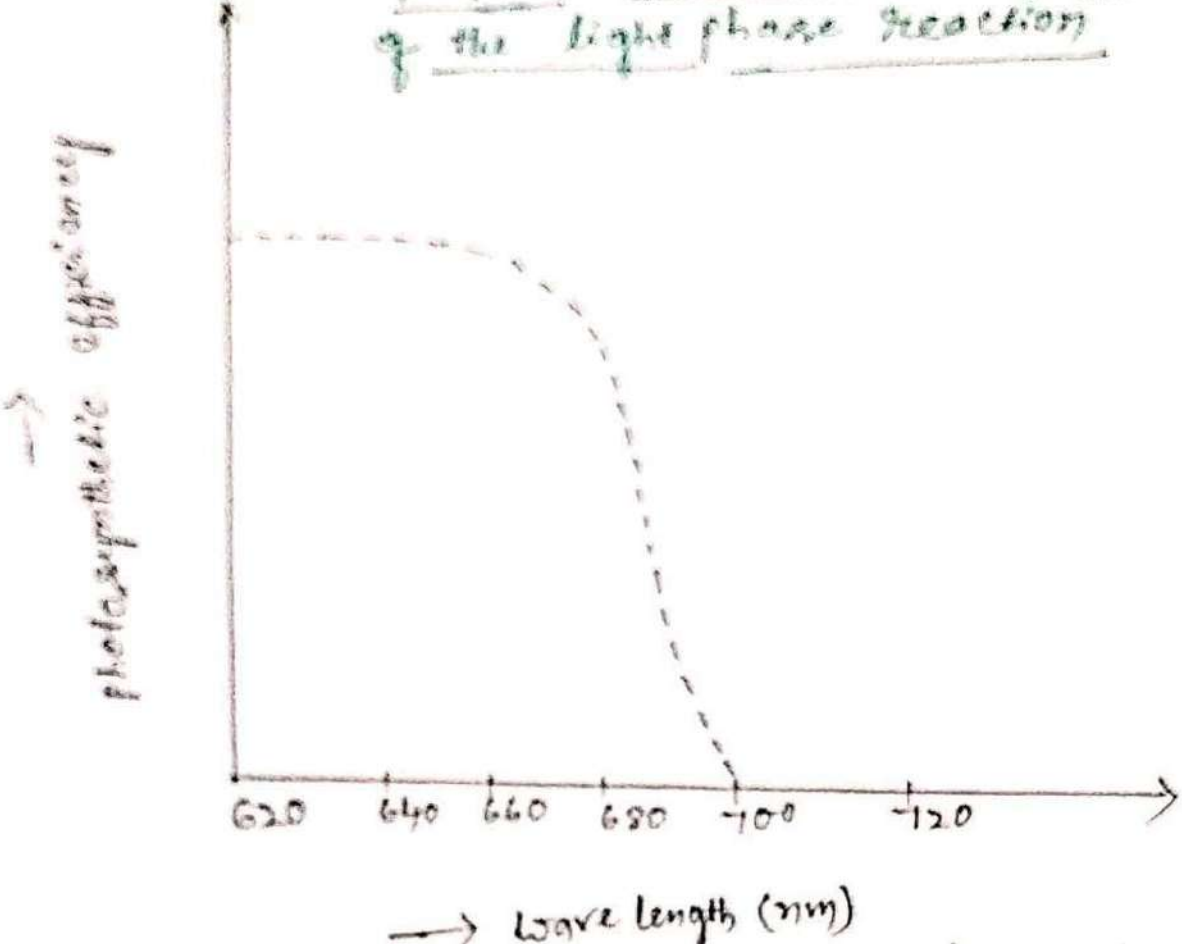
1) Light Reaction :-

The overall photosynthesis reaction takes place in two phases. The light phase reaction involves the capture of light by light absorbing pigments which consequently lead to Oxidation of H_2O to O_2 with the concomitant reduction of $NADP^+$ to NADPH [reduced nicotinamide adenine dinucleotide phosphate]. It is also lead to the synthesis of ATP.

$$\boxed{2H_2O + 2NADP^+ + (2ADP + 2P_i) \xrightarrow[\text{(8 photons)}]{\text{light}} O_2 + 2NADPH + 2H^+ + 2ATP}$$

continued →

Graphical representation of efficiency of the light phase reaction



From graph the efficiency of the light phase reaction measured by quantum yield for O_2 evolution does not vary significantantly with the wavelength of illumination in the range of 400 to 675 nm but it abruptly decreases for the light of wavelength above 680 nm (as shown in Fig). This phenomenon is described as red drop. This red drop is quite unexpected as chlorophyll-a is known to absorb light in the region of 700 nm (i.e. far-red light). However, the efficiency of the process for the light 700 nm increases synergitically in the presence of shorter wavelength (such as yellow-green). This observation indicates that "The two reaction centers are involved in the overall process!"

Dark Reaction:-

In the dark phase, "NADPH reduces CO_2 to carbohydrates with simultaneous consumption of ATP." This dark phase reaction is a complicated one and very often described by Calvin cycle. The overall dark-phase reaction is:

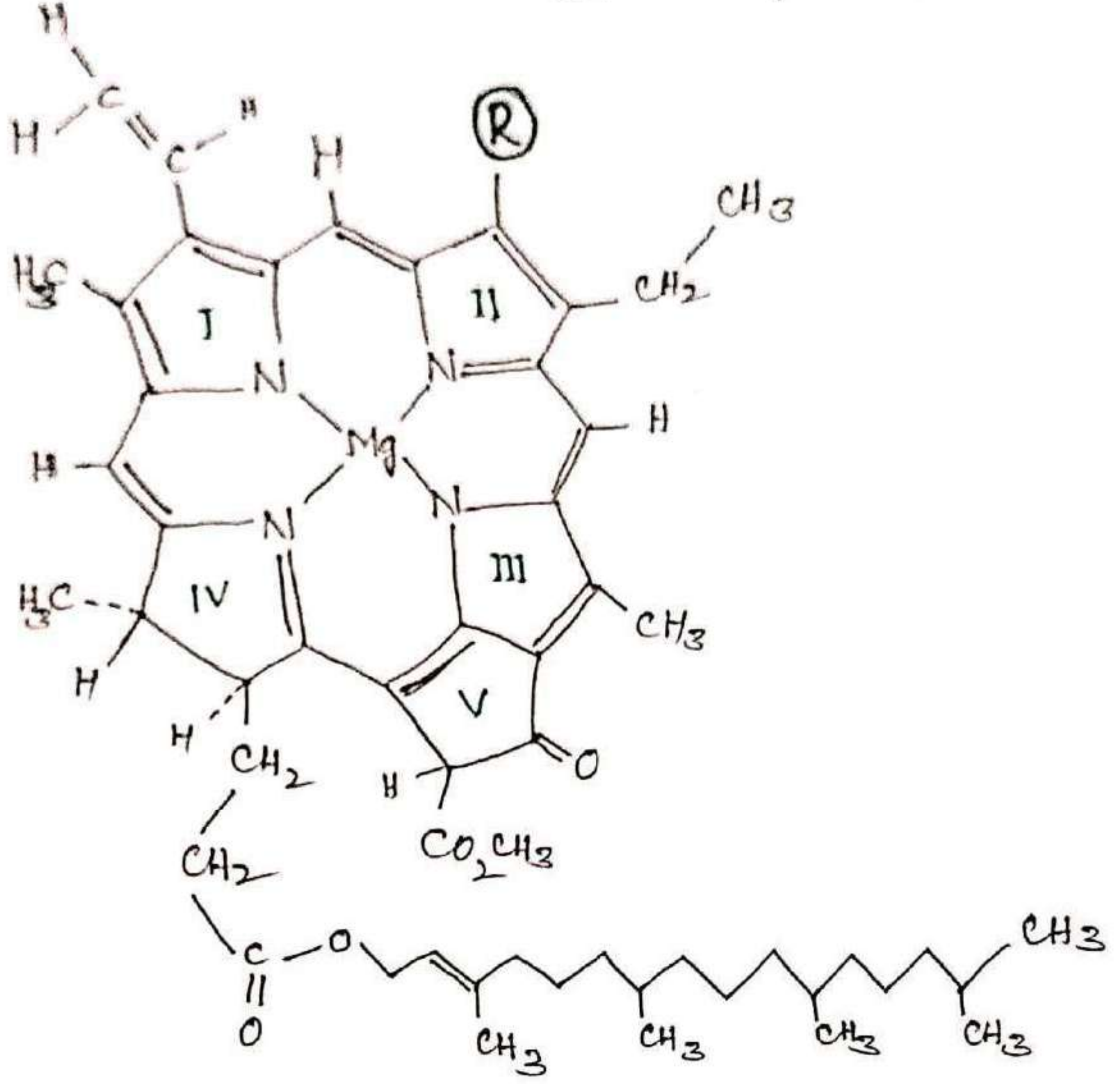
$$\boxed{6CO_2 + 12NADPH + 12H^+ + 18ATP \rightarrow C_6H_{12}O_6 + 12NADP^+ + 6H_2O + (18ADP + 18P_i)}$$

* Chlorophylls: Structural features:-

In the photosynthetic systems, the active component is the green pigment, chlorophyll is a macrocyclic complex of Mg(II). Chlorophyll consists of a macrocyclic tetrapyrrole system. The macrocyclic ring in chlorophyll is reffered to as "chlorin ring".

* Structure :-

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



The long alkyl chain at the bottom is called - phytyl group.

Features :-

⟹ i) one double bond in pyrrole ring (denoted by IV) is reduced; porphyrins with the reduced tetrapyrrole ring systems are in general known as "Chlorins"

⇒ ii) a porphyrin ring is fused to one pyrrole ring (denoted by III);

⇒ iii) both acid chains are <u>esterified</u>. One side chain (attached with the cyclopentanone ring) <u>is a</u> <u>"methyl ester"</u> while other chain (attached with the [illegible] is partially reduced) <u>is an</u> <u>"ester</u> <u>of</u> <u>phytol</u> <u>($C_{20}H_{39}OH$)"</u>. <u>This</u> <u>long</u> <u>chain</u> <u>alcohol</u> <u>is</u> "tetra<u>isop</u>renoid <u>alcohol"</u>

⇒ iv) In fact, <u>presence</u> of <u>this</u> <u>phytol</u> <u>chain</u> <u>makes</u> <u>chlorophyll</u> <u>highly</u> <u>hydrophobic</u> and <u>soluble in</u> <u>non-polar</u> <u>media</u>

⇒ v) In ring II, R differs for chlorophyll-a ($\underline{R = -CH_3}$) and chlorophyll-b ($\underline{R = -CHO}$)

⇒ vi) <u>Mg(II)</u> sits at the <u>centre</u> of <u>chlorin ring</u> and it lies above <u>the</u> <u>macrocyclic</u> <u>plane</u> <u>by</u> ≈30 <u>to 50</u> <u>pm</u>. Sometimes chlorophyll is described as a <u>magnesium</u> <u>porphyrin</u>.

⇒ vii) The chlorophyll acts as the <u>chromophore</u> <u>in</u> <u>photosynthesis</u>. The extensive conjugation in the chlorin ring allows the electron transition, "$\underline{\pi(HOMO) \longrightarrow \pi^*(LUMO)}$" in the visible region. The peaks are highly intense [extinction coefficient = 10^5.]