* Role of Magnesium (II) in Chlorophyll:—

⇒ Mg(II) sits at the chlorin ring and it lies above the macrocyclic ring by ~ 30 to 50 pm.

⇒ The Mg(II) in chlorophyll is really unique. In fact, without magnesium the chlorin ring is "flourescent". But, after incorporation of Mg(II) chlorophyll becomes "phosphorescent". This change (due to metal incorporation), i.e flourescent to phosphorescent is biologically very important, if the flourescence occurs exclusively, the absorbed light energy is lost immediatly and it will not be available for chemical transformation in chemical reaction. Hence, the absorbed light energy must be stored for some while so that it can be utilised in a chemical reaction for the Conversion of light energy to chemical energy. For this phosphorescence behaviour, there must be an excited state of finite life-time. probably, mixing of the excited singlet and triplet states through spin-orbit coupling in magnesium gives relatively stable triplet excited state. In fact, triplet to singlet transition is not allowed and it makes the triplet excited state stable.

⇒ Mg(II)(d^0-system) does not have any crystal field stabilisation energy to prefer the "square planar geometry", rather it prefers the "tetrahedral geometry." Consequently, the "Mg(II) – N bonds remain in strained" condition, and the electrons constituting the bonds can, ∴, be readly excited by the absorption of light energy. This absorbed energy can be used in the desired chemical reaction.

⇒ Through co-ordination bond by chlorophyll to the Mg(II) - centre, rigidity of the macrocyclic structure is further strengthened. It may be noted that the macrocyclic ring experiencing conjugation or delocalisation of π - electron cloud is itself sufficiently rigid. The rigidity of the system minimises the energy loss due to molecular Vibrant-

⇒ The water molecule co-ordinated to the Mg(II) -centre, in the axial direction in the chlorophyll of active reaction centre, (i.e Chl.H_2O·Chl) experiences the photoinduced splitting to generate the H atom that provides the electron for the photosynthetic process. Thus coordination of water molecule to the Mg(II)-centre plays an excellent role.

⇒ Here it is interesting to note that for the electron transfer process, not the metal (Mg(II)) but the macrocycle is involved

* PS-I OR P-700:— [P-stands for Pigment]

The process of photosynthesis is carried out by two kinds of photosystems. Existance of such two photosystem was established by considering the phenomenon of reddrop and the dependence of photosynthetic efficiency on the wave length of light.

* The photosystem I (PS-I), which is excited by the light wavelength in the region 700 nm (or lower) generates a strong reductant to bring about the "reduction of NADP$^+$ to NADPH"

* PS-I utilises Chlorophyll-a. The photosystem (PS-I) contains ~250 light harvesting pigments [~200 chlorophylls and ~50 carotenoids]

* PS-II OR P-680:

* The photosystem-II (PS-II), which uses the light of wavelength 680 nm or lower to produce a very strong oxidant to oxidise H_2O to O_2.

* PS-II uses chlorophyll-b. The photosystem (PS-II) contains ≃ 250 light harvesting pigments [≃ 200 chlorophylls and ≃ 50 carotenoides]

* Z-scheme of photosynthesis,

Chlorophyll catalyses the reduction of $NADP^+$ (to NADPH) and oxidation of H_2O (to O_2) in the presence of light. The electron flows from H_2O to $NADP^+$ through an electron transport chain (P-680 to P-700*), which looks like letter Z when the electron carriers are placed in the order of their reduction potentials. This is known as Z-scheme of photosynthesis.

The photosynthesis process is carried out by two kinds of photosystems namely PS-I and PS-II. Each photosystems contains ~250 light harvesting pigments, in addition to different electron carriers. In terms of the std reduction potentials of the involved couples, i.e O_2/H_2O ($E_0' = 0.82V$) and $NADP^+/NADPH$ ($E_0' = -0.34V$), the electron flow from H_2O to $NADP^+$ to produce NADPH is thermodynamically uphill process. But photoexcitation of PS-I and PS-II can make the electron flow down hill as shown is Z-scheme.

when the chlorophyll (present in PS-I and PS-II) is excited, its electron distribution pattern changes. On excitation, it can act both as a better reducing agent and also a better oxidising agent. Thus the excited chlorophylls can intiate a series of redox reactions.

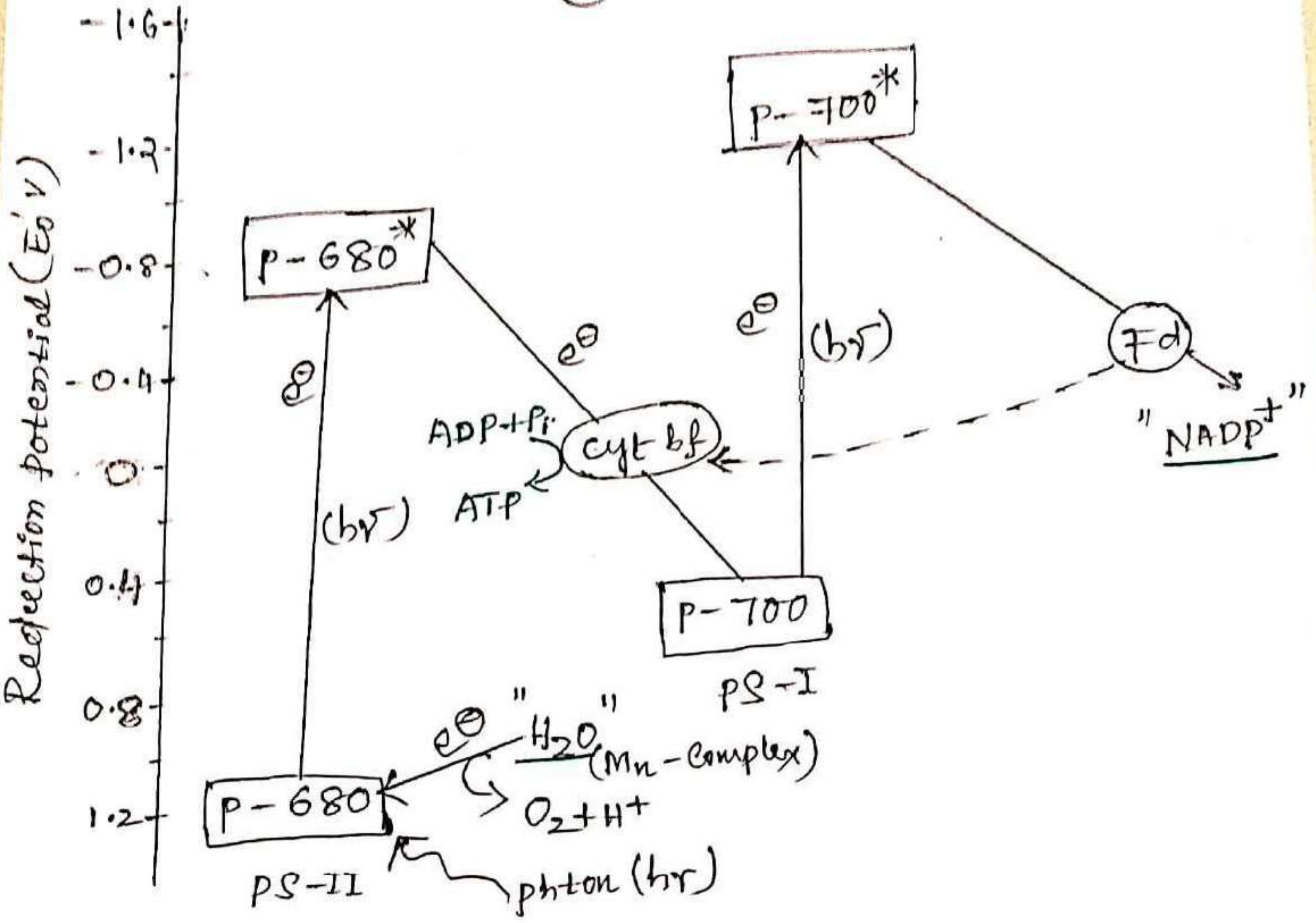
when P-700 (PS-I) is excited to $P-700^*$, its reduction potentials changes from +0.4 V to about -1.3 V. In fact, the

The uphill reaction is favoured by the absorption of 700 nm photon ($\equiv 171$ kJ mol^{-1}) and photon energy is utilised to elevate the electron. "Thus P-700* becomes a better reducing agent" and it transfers its electron to its primary electron acceptor P-430. It is a membrane bound ferrodoxin of the Fe_4S_4 type characterised by an strong absorption maxima at 430 nm in the reduced form. Then the electrons flow the downhill and ultimately reach $NADP^+$ through a series of electron carriers arranged in the increasing order of their reduction potentials. This electron transport chain is shown below.

P-700* ⟶ P-430 (Fe_4S_4 protein) ⟶ Fd (Fe-S protein)

↓

$NADP^+$ ⟵ FP (flavoprotein)



NOTE: (a) The electron flows from H_2O to $NADP^+$

(b) The electron flow from P-680 to P-700* interms of the redox potentials diagram looks like the letter Z.

* Oxygen evolving complex [OEC] :-

To sustain the process, the oxidised species $Chl\text{-}a_1^{\cdot +}$ (a cation radical) in P-700 must be reduced to $Chl\text{-}a_1$ so that it may again participate in a catalytic process. The std reduction potential of $O_2|H_2O$ couple ($E_0' = 0.82V$) is too high to reduce $Chl\text{-}a_1^{\cdot +}$ in P-700. To perform the task, PS-II (P-680) is linked with the PS-I (P-700). When P-680 is excited to P-680*, the reduction potential changes approximatly from +1.2V to about -0.8V. A P-680 nm photon is possessing an energy of 1.82 eV which is used to change the reduction potential. Thus P-680*, acts as a better reducing agent. In P-680*, the excited $Chl\text{-}a_2^*$ transfers its electron to pheophytin (Ph). Then electrons flow the downhill to reach $Chl\text{-}a_1^{\cdot +}$ (in PS-II). After transferring electron to pheophytin, $Chl-a_2^{\cdot+}$ is produced in PS-II. This oxidised species $Chl-a_2^{\cdot+}$ is then brought to $Chl-a_2$ by water. In this event, O_2 evolution occurs and the process is catalysed by a polynuclear manganese protein called "oxygen evolving complex (OEC)". The electron transport chain from pheophytin to $Chl-a_1^{\cdot+}$ is shown below where the electron carriers are arranged in the increasing order of their reduction potential.

$P-680^*$ (PS-II) → pheophytin → cyt-b → (PQ) plastoquinone

↓

(PS-I i.e P-700) $Chl-a_1^{\cdot+}$ ← plastocyanin (PC) ← cyt bf complex

The overall reaction catalysed by PS-II is:

$$2H_2O + PQ \xrightarrow{h\nu} O_2 + 2PQH_2 : (\Delta E_0' = -0.72V)$$

PQ = plastoquinone

PQH_2 = plastoquinol.

Then the electron reach to plastocyanin (PC) through the cytochrome - bf complex. Considering reduction potentials (E_0') for the $PQ|PQH_2$ and $O_2|H_2O$ couples as +0.10V and +0.82V respectively, the std free energy change ($\Delta G_0'$) becomes +ve. This uphill reaction is favoured by the absorption of photons of 680 nm ($\equiv$ 171 KJ mol^{-1}) in PS-II.