Production of Assimilatory Power in PS

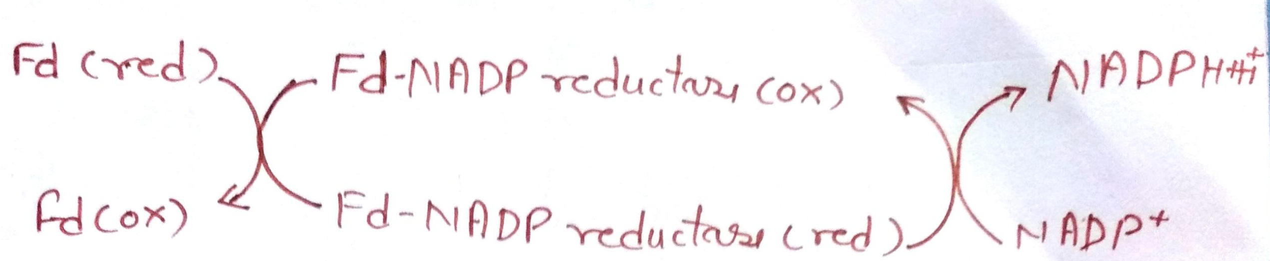
ATP & ADP

Arnon (1956) used the term assimilatory powers to Refer ATP (adenosine triphosphate) and NADPH 2 (reduced Nicotinamide adenine dinucleotide phosphate). The process of reduction of NADP into NADPH + H^+ may be denoted as Electron transport system in Photosynthesis or Reduction of NADP while the formation of ATP from ADP and Inorganic phosphate (Pi) utilising light energy is called Photophosphorylation

i.e.

(a) Electron transport system in Photosynthesis or reduction of NADP
(Transport of electron from water to NADP

(b) Phosphorylation of or formation of ATP in PS.



Ferredoxin reduces $NADP^+$ by providing two electrons, one at a time.
All this can be better explained using Z-scheme model as proposed by Hill and Bendal (1960). In view of recent researches, it has been partly modified. Fig

. The term photolysis of water been used but it is confusing as photolysis not the primary photochemical reaction occuring under the direct influence of light. It is actually due to pulling apart of electrons by the oxidised PS II from OH ions. The proton (H^+) are released in the system and are used for reduction of NADP while OH radicals react to form H_2O_2 which because of its unstable nature breaks up to produce water and evolve oxygen.

$$4OH \rightarrow 2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$$

Thus in reduction of NADP, the source of electron is Chlorophyll molecule and for protons is the water molecules

NADPH + ATP = assimilatory process

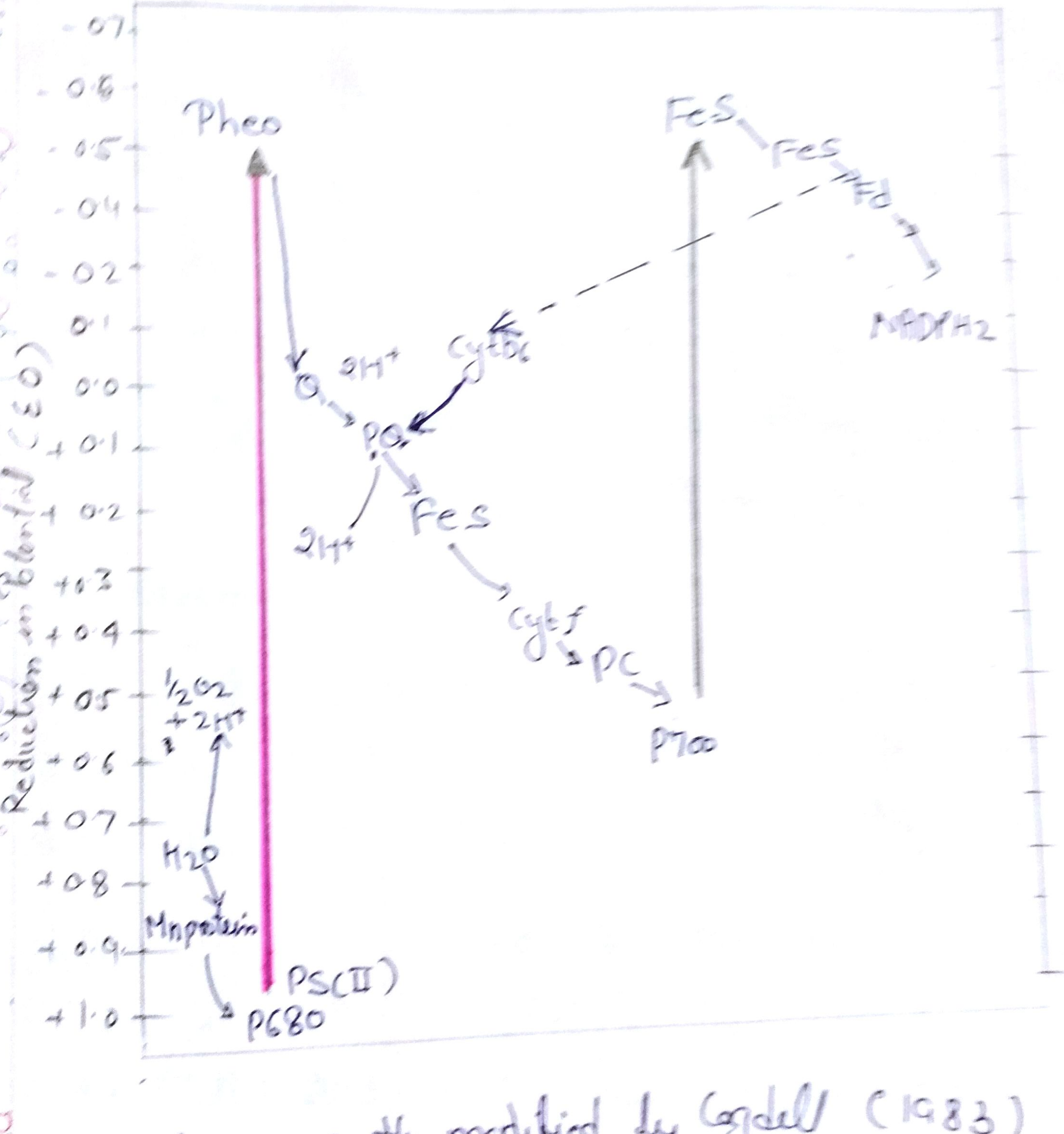
Electron Transport system (ETS)
or
Reduction of NADP

when a proton is absorbed by a pigment in a the light harvesting complex associated with PS II, its energy is transferred by inductive resonance to P680 which is removed by Pheo (Pheophytin). So Pheo is the first electron acceptor. Loss of electron from P680 causes it to become positively charged. It then attract an electron from P680 an adjacent Mn-protein. As the Mn-protein becomes oxidised by losing one electron, it in turn it strongly attract an electron from water. This pulling apart of electron from water molecule has been imperfectly referred to as Photolysis of water. On the other hand, electron from Pheo is used in reduction of plastoquinone (PQ to PQH). This reduction step requires two electrons & and two protons

$$\left[PQ \underset{-2e^-, -2H^+}{\overset{+2e, +2H^+}{\rightleftharpoons}} PQH_2 \right]$$

At least Four types of Plastoquinones have been reported from chloroplast, three are tocopheryl quinones and one is Vit K (1,4-naphthoquinone acetate).
From PQH_2, electron move, one at a time, to cytochrome b_6 to cytochrome f to plastocyanin (PC). PC moves along the edge of membrane to PS I where P700 accepts the electron. P700 cannot accept the electron unless it has previously lost one which can occur by light excitation

Excited P700 gives its electron to Fe^{3+} in one of the Fe-S proteins which may be called Ferredoxin reducing substance (FRS). The exact reducing potential and chemical composition of FRS is still unknown. However, electron from P700 either through FRS or directly reduces ferredoxin.
So the electron required to reduce ferredoxin (Fd) is provided by photoexcited P700 and thus Ferredoxin (or FRS) becomes the primary electron acceptor of PS I.



Z scheme (partly modified by Cogdell (1983)

Steps between Cyt b6 to Cyt f & P700 to FeS are called Down hill & Up hill reactions respectively on the left reduction potential values are given

Photophosphorylation

Arnon and his associates (1954) were first to show that isolated chloroplast can produce ATP when exposed to light, i.e.

$$ADP + P_i \xrightarrow[\text{Chlorophyll}]{\text{Light}} ATP$$

They called this kind of phosphorylation as Photophosphorylation which is different from the oxidative phosphorylation found in mitochondria in suspect that it requires light as a source of energy and is independent of oxygen.

The role of ATP in Photosynthesis is essential at 2 steps

Firstly. It supplements energy for the reduction of CO_2 utilizing $NADPH + H^+$ which is the end-product of light reaction.

$NADPH + H^+$ is helped by the energy of ATP to move the electrons to Phosphoglyceric acid (PGA) and into the carbon cycle.

Secondly, ATP is used in phosphorylation of ribulose-5-phosphate into ribulose-1,5-diphosphate during its regeneration in Calvin cycle.

Ribulose-1,5-disphosphate is the CO_2 acceptor of C_3 plants. Thus at both these steps, the role of ATP is quite necessary. In general for every glucose molecule synthesized 18 ATP are required in C_3 plants and 30 ATP in C_4 plants.

So far three different kinds of Photophosphorylation have been recognised:

I. Non-cyclic Photophosphorylation.

II. Cyclic Photophosphorylation.

III Pseudocyclic Photophosphorylation.

I. Non-cyclic Photophosphorylation

It occurs among the green plants and involves both PS I & PS II. As the energy-rich electron passes through the electron Transport system, at every step it releases energy generally equal to the difference between the energy levels of donor and acceptor. At steps of transfer where the released energy is not sufficient to bind inorganic phosphate with ADP, it is wasted in the form of heat or fluorescent light but at steps, where this released energy is sufficient to bind inorganic phosphate with ADP, the ATP synthesis is coupled with energy released. During the passage of excited electron from PS II to PS I, the ATP synthesis is presumed to occur between cytochrome b_6 ($E_0' = 0.03V$) and cytochrome f ($E_0' = 0.36V$) As the difference between the redox potentials of the cytochromes amounts to 0.33 eV, it is more than enough to accomodate phosphorylation of ADP.

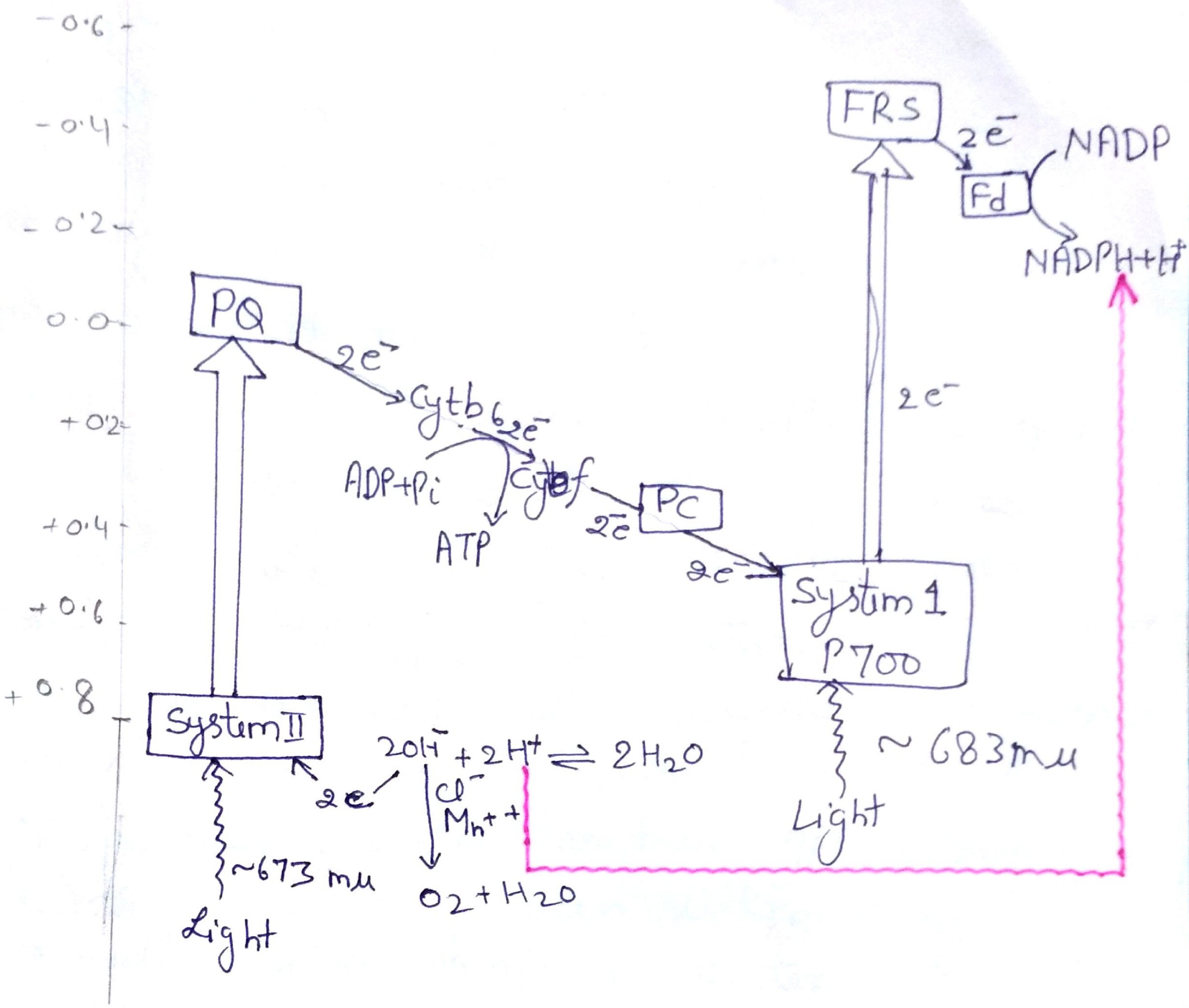


Figure: Schematic representation of Photo induced electron transport in Photosynthesis showing Non-cyclic photophosphorylation.

In noncyclic photophosphorylation, the flow of electron is unidirectional, that is electron donated by PS II after passing through plastoquinones, cyt b6, cyt f, plastocyanin and PS I eventually reaches ferredoxin which in turn donates to reduce NADP. The reduced NADP (NADPH+H+) is utilised for the reduction of CO_2 to carbohydrate level. The electron doesn't complete the cycle. It starts from PS II and is drained off in the carbohydrates produced by CO_2 reduction. So the ATP synthesis resulting from this type of non-cyclic electron transport chain is known as non-cyclic photophosphorylation. Water molecule is utilised as a source of electron in this system. In this process, two molecules of ATP are formed per two molecules of $NADP^+$ reduced or one molecule of oxygen evolved or two molecules of water oxidised

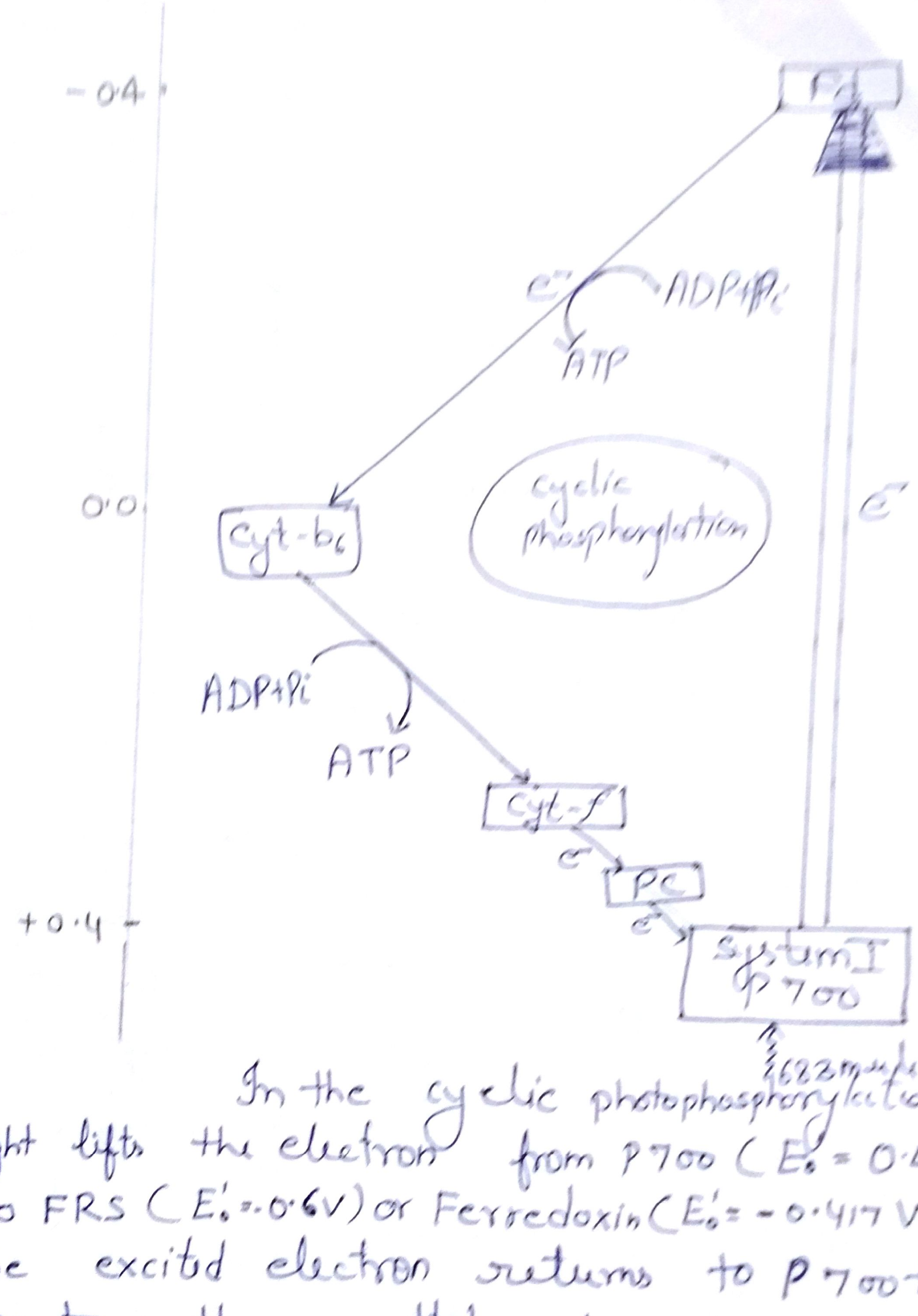
$$2ADP + 2Pi + 2NADP + 2H_2O \rightarrow 2NADPH + H^+ + O_2$$

During light reaction, the Protons (H^+) accumulate inside the thylakoid membrane resulting in a Proton Gradient. The energy released by the Protons when they diffuse across the thylakoid membrane into the stroma. (along the proton concentration gradient) is used to produce ATP. The process is similar to the production of ATP by ATP by F_0-F_1 particles of mitochondria.

II Cyclic Photophosphorylation

In addition to non-cyclic photophosphorylation, there is another pathway of ATP formation which involves only PS I and wavelength of light greater than 680 nm is used. It has been referred as cyclic photophosphorylation.

During photosynthesis this type of ps photophosphorylation was demonstrated by Frenkel in the isolated chromatophore from the bacterium Rhodospirillum rubrum. The reaction in cyclic process resembles those seen in mitochondria but here initially energy is provided from absorbed light quanta instead of glucose. Electrons used in the cyclic photophosphorylation do not come from water. i.e. water is not oxidised and oxygen is not evolved in the process.



In the cyclic photophosphorylation; light lifts the electron from P700 ($E'_0 = 0.42V$) to FRS ($E'_0 = -0.6V$) or Ferredoxin ($E'_0 = -0.417V$). The excited electron returns to P700 through two to three H-transfer steps to decreasing redox potentials. It is during such a downhill migration of the electron that enough energy is released for ATP synthesis. The potential gap between FRS to P700 is nearly one volt which is sufficient to produce at least 2 ATP molecules per electron transfer, or four ATP molecules per 2 electron transfer. In the process, ATP can be formed between cytochrome b_6 ($E_0' = 0.03V$) and cytochrome f ($E_0' = 0.36V$) and between ferredoxin and cytochrome b_6, the potential gap between those 2, being more than ~ 0.32 V.

The concept about its site, rate and mechanism is not yet very clear. The pathway of cyclic electron ~~incl~~ includes a part of electron transport chain that connects PS II to PS I (two phosystems). What is the exact point of entrance of cyclic electron after the ferredoxin is debatable. The studies so far made reveals that it may enter at plastiquinone, cytochrome b_6, cytochrome f or plastocyanin level. The reason is that PS I mediated cyclic photophosphorylation in some cases requires plastoquinone and in other cyt b_6 or cyt f or plastocyanin.