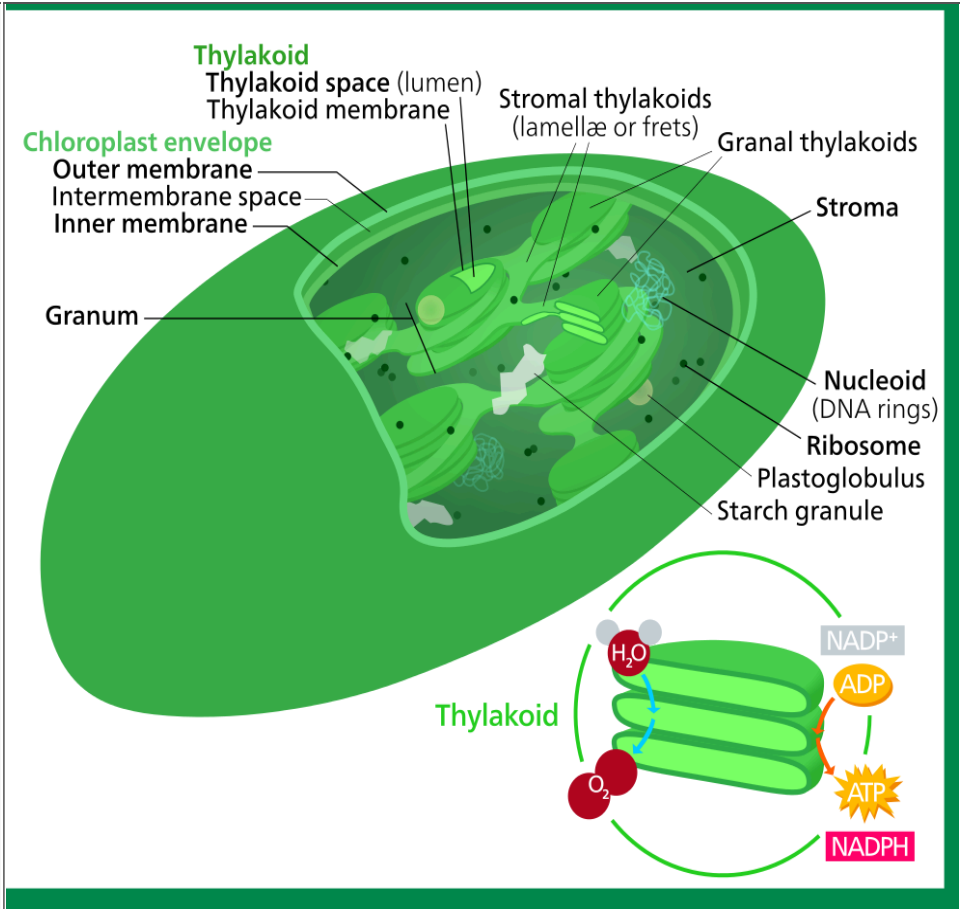


PHOTOSYNTHESIS

These are my brief notes on the processes of electron transport that are the foundation of photosynthesis in green plants and cyanobacteria (previously called blue green algae)

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Chloroplast of a green plant. The reactions discussed in this page occur on the membranes of the thylakoid. The reactions involved in conversion of carbon dioxide to sugars are located in the surrounding stroma.

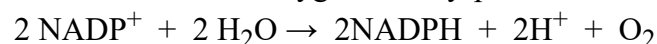
Summary
Photosynthesis is the sythesis of complex carbon compounds from CO₂ using energy from the sun. The process requires adenosine triphosphate (ATP) as an energy provider and NADPH as a reductant.
ATP is the energy ‘currency’ in living things. The free energy (ΔG) required to drive biosynthetic reactions becomes available when

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its terminal phosphate is removed, giving adenosine diphosphate (ADP). ATP regeneration from ADP involves a membrane enzyme, ATP synthase. The energy required is provided by an electrochemical gradient of protons. When protons move down this gradient through the synthase enzyme a phosphate is added to ADP to make ATP. In mitochondria the electrochemical gradient is a mix of the membrane potential and the difference in proton concentration. In chloroplasts the predominant component is the proton gradient. The difference in proton concentration between the inside and outside of thylakoids is 3 pH units. The electrochemical gradient of protons is 'driven' by the flow of electrons down an electron transport chain in the membrane coupled to proton movement across the membrane.

The hydrogen carrier NADPH is made by reducing NADP^+ with a 'hydrogen donor' which is water during photosynthesis in green plants and cyanobacteria. Because oxygen is a 'by-product' this is called *oxygenic photosynthesis*.



Energy from the sun is used to split water (photolysis) into oxygen, and protons plus electrons which are used to reduce the NADP^+



In some bacteria the donor may be a reduced sulphur compound (eg H_2S), ferrous ions or organic reduced compounds; this is *anoxygenic photosynthesis* as no oxygen is produced..

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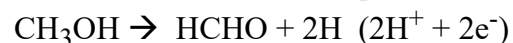
Oxidation and reduction, and redox potentials.

To understand the processes of photosynthesis it is helpful to understand redox reactions (oxidation and reduction reactions) and the importance of redox potentials. Oxidation is the loss of electrons. Reduction is the gain of electrons.

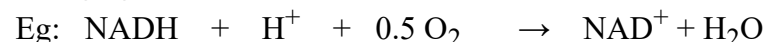
e.g. Ferrous iron Fe^{2+} can be oxidised to ferric iron Fe^{3+} by losing an electron. The reduced and oxidised forms are called a redox couple:



When organic molecules are involved protons are transferred at the same time as electrons, for example:



An oxidising agent accepts electrons; a reducing agent donates them. In the following reaction NADH is the reducing agent and oxygen is the oxidising agent:



The free energy available from redox reactions

The redox potential of a redox couple provides a measure of how effective it will be as an oxidising or reducing agent. The midpoint redox potential (E_m or E_o) is the potential when oxidised and reduced form are equal in concentration. The actual potential will be more +ve if the concentration of the oxidised form is higher, and vice versa. In a redox reaction electrons flow from the more -ve couple to the more +ve couple

A high -ve potential indicates a good reducing agent. A high +ve potential indicates a good oxidising agent.

Free energy is available from oxidation reactions (ΔG is negative) and how much is available can be calculated from the difference in redox potentials of the reacting couples (ΔE). $\Delta G = -nF\Delta E$

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For example: $\text{NADH}_2 + \text{O} \rightarrow \text{NAD}^+ + \text{H}_2\text{O}$

Em values: -320mV +880mV $\Delta E = 880 - (-320) = +1200 \text{ mV}$ So, $\Delta G = -180 \text{ kJ/mol}$ [Energy for synthesis of ATP is 30kJ/mol]

Some important Em values

Chlorophyll P680 Em = +1200mv

$\text{O}_2/\text{H}_2\text{O}$ Em = +880 mv

NADP/NADPH Em = -320 mv

Cytochrome c ($\text{Fe}^{3+} / \text{Fe}^{2+}$) Em = +260 mv

Ubiquinone (UQ / UQH_2) Em = +0.06 mv

$\text{CH}_3\text{OH}/\text{HCHO}$ Em = -0.182 mv

Electron transport reactions in photosynthesis

The production of ATP and NADPH involves operation of electron transport chains. A key fact needed to understand photosynthesis is that the light-harvesting chlorophyll can have 2 different redox potentials. It has a very positive potential so the oxidised form is a very strong oxidant; BUT the reduced chlorophyll absorbs energy from sunlight which decreases its redox potential making it a very strong reductant.

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Photosynthesis in green plants and cyanobacteria (blue-green algae)

This is the conversion of carbon dioxide to carbohydrate with 6 carbon atoms [eg glucose $(\text{CH}_2\text{O})_6$]:



The water provides the reductant ($12 \text{H}^+ + 12 \text{e}^-$); the oxygen is released as a 'waste product'.

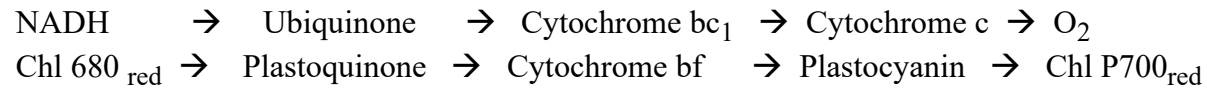
[NB: in some bacteria the H_2O is replaced by H_2S , releasing elemental sulphur; this led to the van Niel's suggestion that the oxygen produced by photosynthetic plants does not come from CO_2 as previously assumed, but comes from water.]

The photosynthetic process starts with the photolysis of water: $2 \text{H}_2\text{O} + 4 \text{Chl}_{\text{ox}} \rightarrow 4 \text{H}^+ + 4 \text{Chl}_{\text{red}} + \text{O}_2$
Em values +880 mv +1200mv

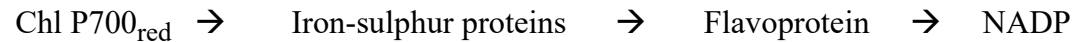
In this reaction the water is oxidised by the very strong oxidant, Chlorophyll. The protons are released on the inside of the thylakoid vesicle thus contributing to the gradient of protons across the thylakoid membrane. The volume of the thylakoid is very small and so a large proton gradient is 'easily' established.

Energy from sunlight decreases the Em of the reduced Chlorophyll from +1200 mv to -300 mv.

The reduced Chlorophyll is now oxidised by a membrane electron transport chain analogous to that in mitochondria for the oxidation of NADH by O_2 , producing an electrochemical gradient of protons, used to make ATP, the whole process being called photophosphorylation.

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The E_m of Chl P_{700} is about +300 mv. After irradiation of the reduced chlorophyll its E_m value decreases to about – 1200 mv. This reduced chlorophyll passes its electrons by way of iron-sulphur proteins and flavoproteins to NADP^+ to produce NADPH, protons being consumed in the process:



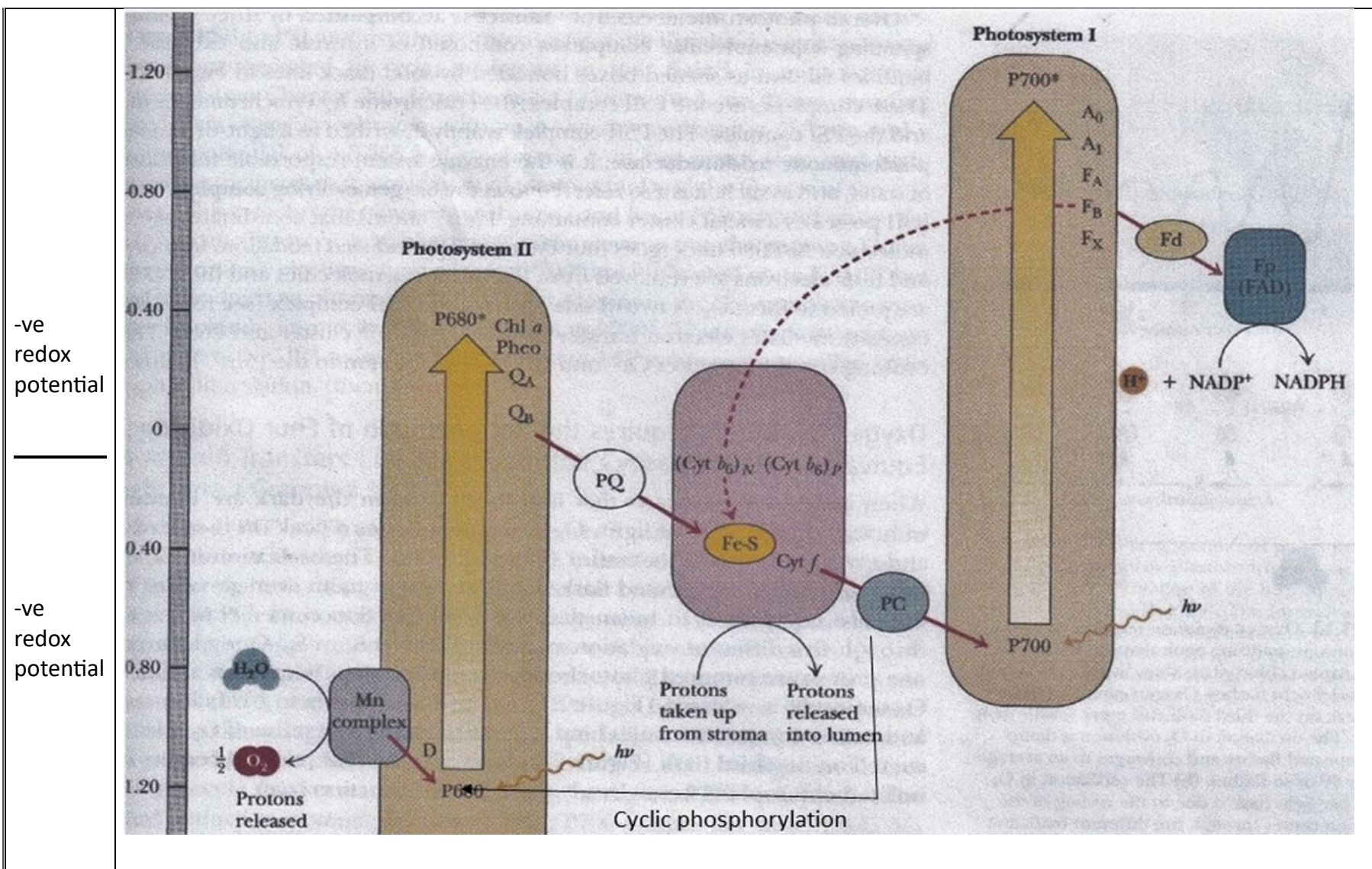
Cyclic photophosphorylation

This process, demonstrated by Arnon and Whatley, is necessary to balance the proportions of ATP and NADPH required for conversion of CO_2 to carbohydrates. The reduced plastocyanin produced by the first electron transport chain is used instead of water to reduce Chl P_{680} which then ‘recycles’ the electrons back to the first chain and its associated ATP synthesis. No water is used and no NADPH is produced.

The Z scheme of Hill and Bendall

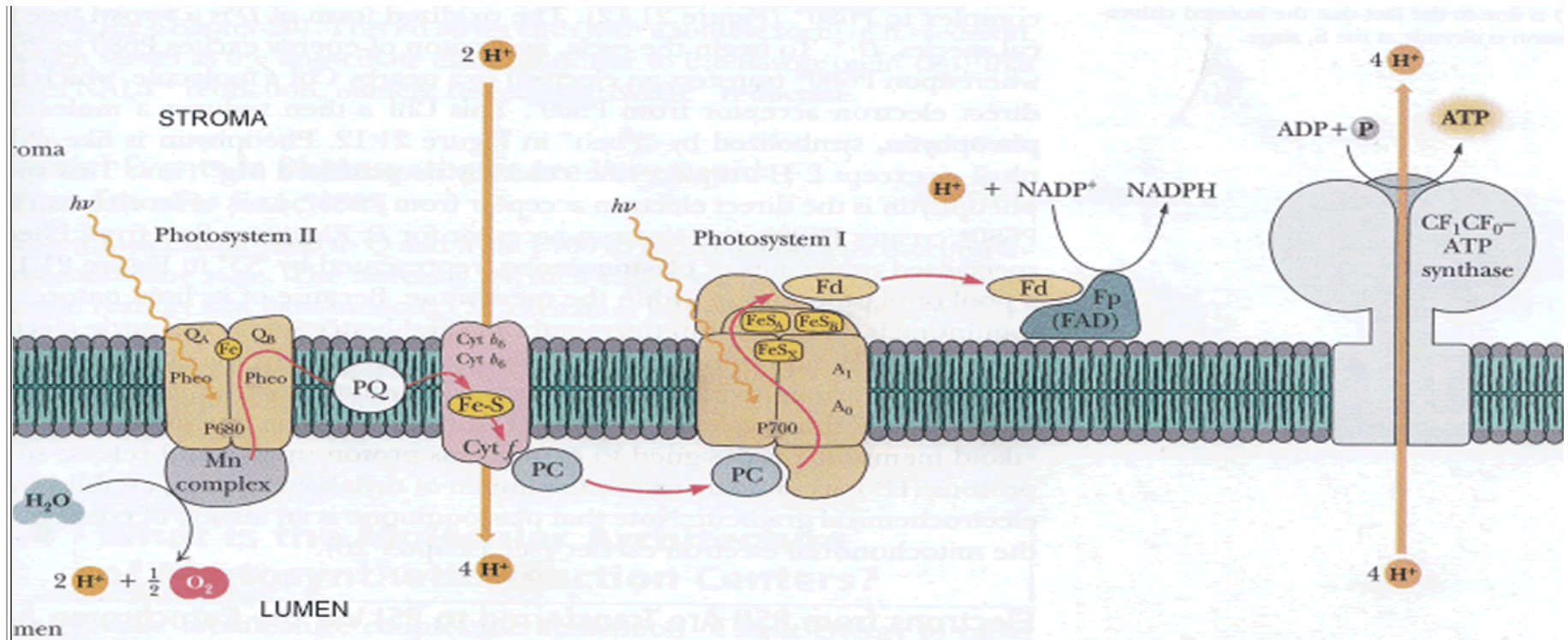
This scheme represents the electron transport systems in photosynthesis in a way that emphasises the relevance of the redox potentials of the components. *Picture from Garrett & Grisham 3rd Edition*

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Arrangement of the electron transport chains in the thylakoid membrane

The thylakoids are closed vesicles inside the chloroplast. The two photosystems are arranged so that photolysis of water and electron transport chains leads to proton accumulation inside the small volume of the lumen of the thylakoid. This gives a difference in pH of about 3 units between the inside and outside of the thylakoid. ATP and NADPH are synthesised on the outside of the thylakoids (the stroma of the chloroplast) for synthesis of carbohydrates from CO_2 . *Picture from Garrett & Grisham 3rd Edition*



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