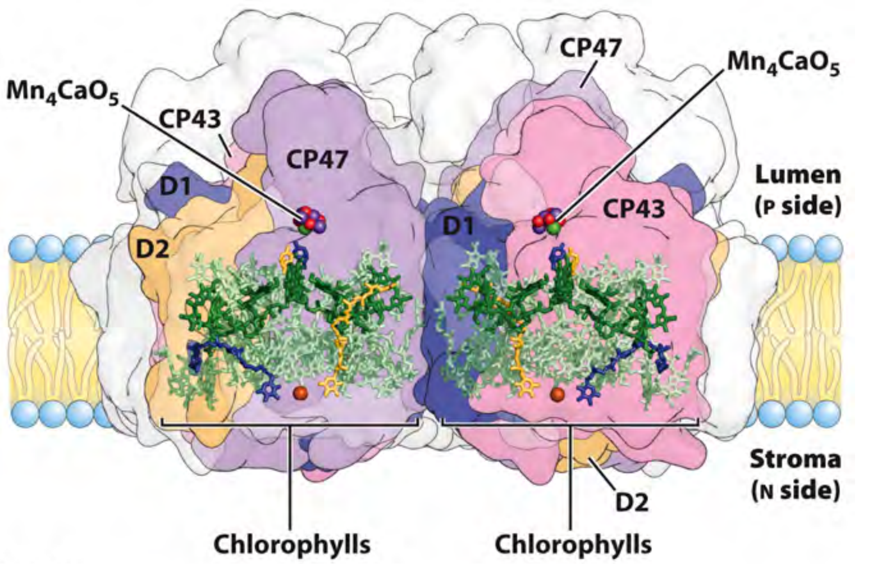
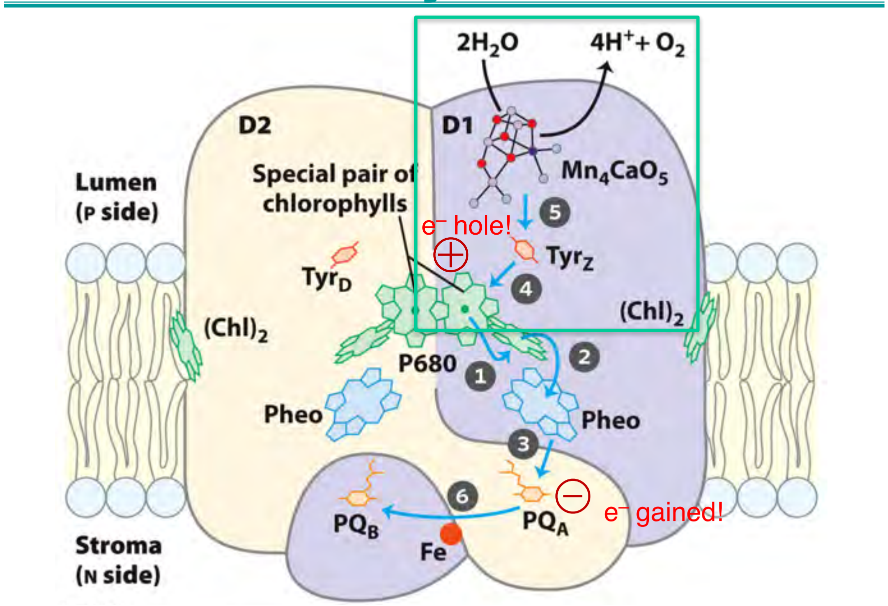
Photosynthesis



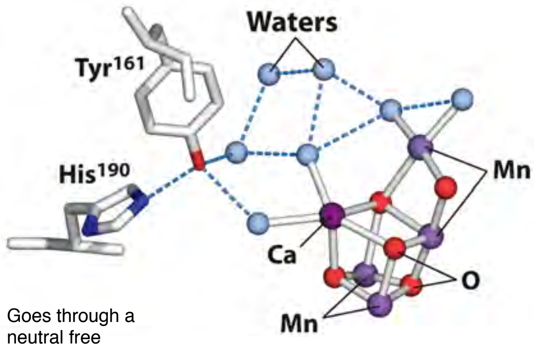
Photosystem II (P680)

Photosynthesis



Photosystem II Evolves Oxygen from Water

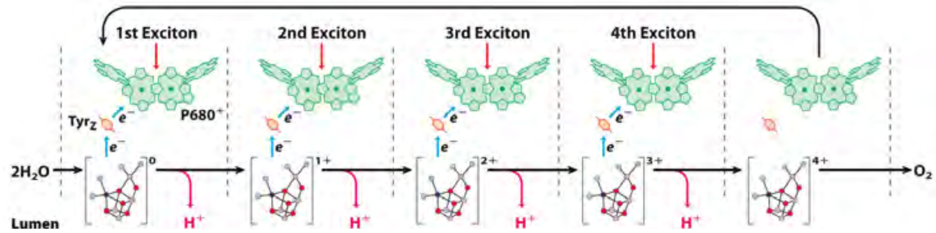
Photosynthesis



The water-splitting complex offers single electrons to photosystem II to fill the hole after charge separation. After four electrons are freed from two waters, a single O_2 is released.
Overall reaction:

$2H_2O \rightleftharpoons O_2 + 4e^- + 4H^+$

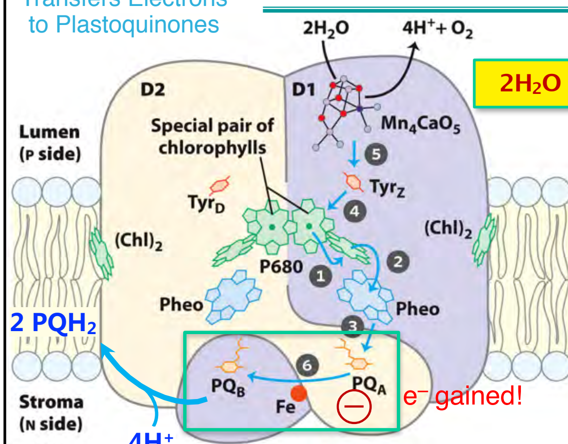
Goes through a neutral free radical: Y-O• + H•



Photosynthesis

Photosystem II Transfers Electrons to Plastoquinones

$2H_2O \rightleftharpoons O_2 + 4e^- + 4H^+$ (2NADPH + 2H+)

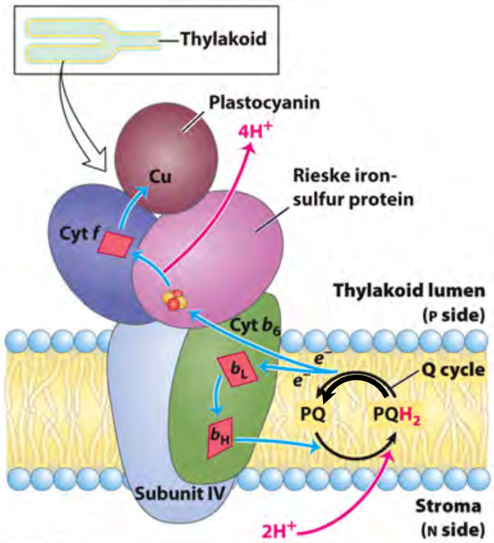


Recall that the ΔE_o is enough to provide an electron hole deep enough to dissociate water (E'_o +1.45V), but not a reductant with the ability to reduce NADP+ (PQ, like CoQ, likes e– more than NADH).

Plastoquinones are structurally and functionally similar to ubiquinones (CoQ) found in the mitochondria.

These lipid-soluble small molecules transport two electrons to the cytochrome b_6f complex.

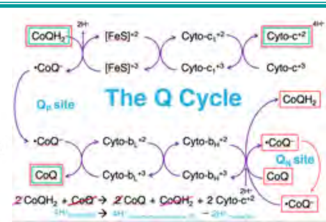
Photosynthesis

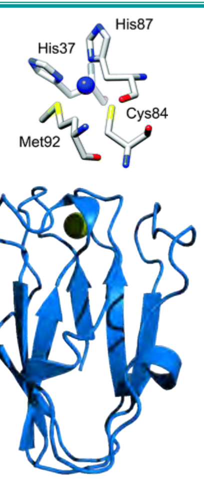


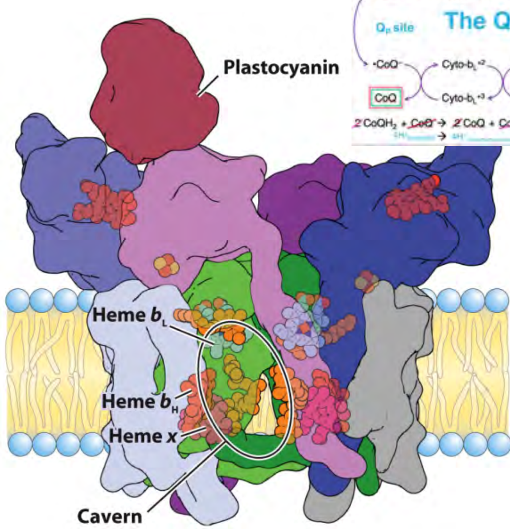
- Structurally and functionally similar to Complex III in the electron-transport chain
- Protons are removed from plastoquinones (PQH_2) as plastoquinones are oxidized (PQ).
- The PQ cycle is similar to the Q cycle in the ETC.
- Electrons are funneled to plastocyanin, a single electron carrier, which carries the electron to PS-I.

Cytochrome b_6f Complex Translocates Protons into the Lumen

Photosynthesis





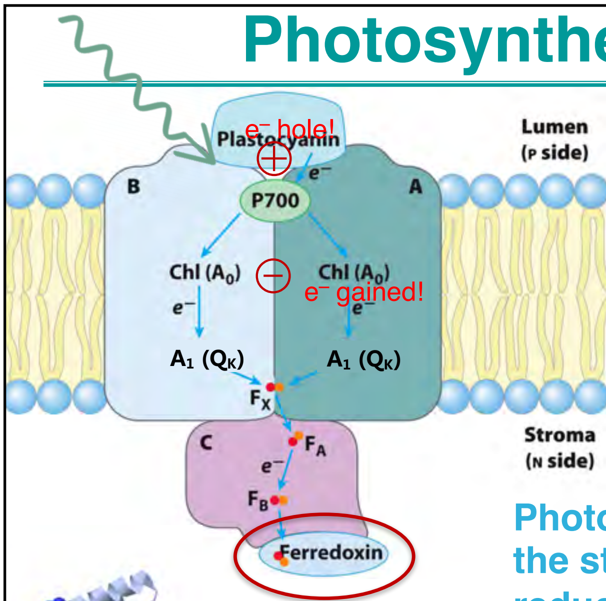


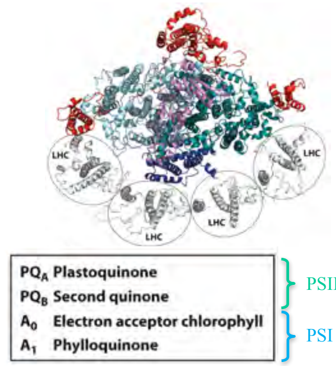
Plastocyanin
(E'_o is +0.37)

What do we do with all the reduced Plastocyanin?

Cytochrome b_6f Complex Translocates Protons into the Lumen

Photosynthesis





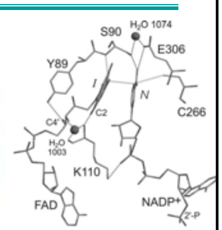
Photosystem I creates the strongest biological reductant known: A_0^-

(E'_o is ~⁻1.4)

Photosystem I (P700)

Photosynthesis

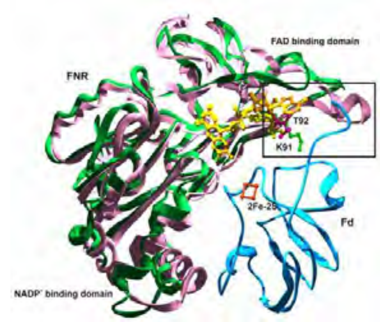
NADPH is produced by the NADPH Reductase in the Stroma



Photosystem I created reduced ferrodoxin (F_d)

(E'_o is –0.4)

F_d is a 1-e⁻ carrier, so 2 F_d transfer their electrons, one at a time, to the FAD cofactor in the reductase. The fully reduced $FADH_2$ then transfers 2e⁻ to $NADP^+$ to make each NADPH.

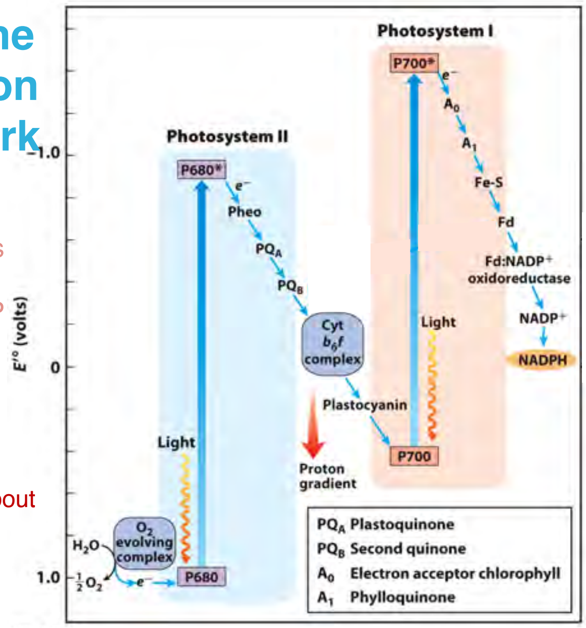


Photosynthesis

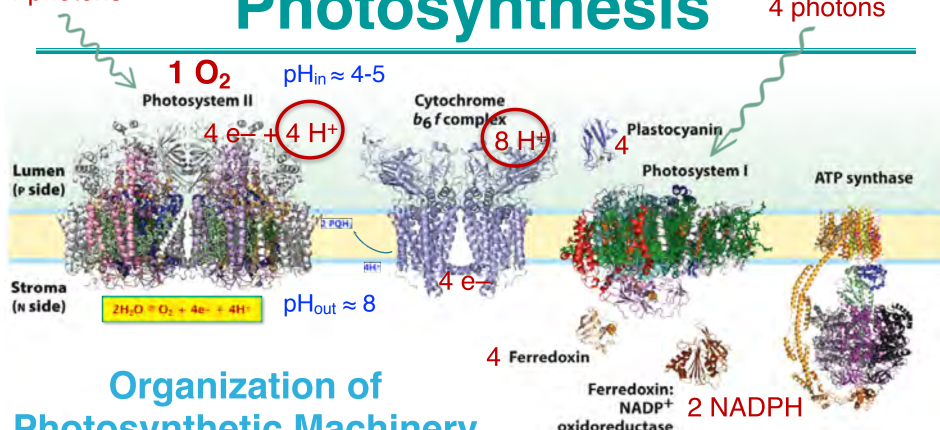
In Plants, the Two Reaction Centers Work Together

Cyclic Photosynthesis Can Be Utilized to Generate Excess ATP

This explains the energetics, but what about the stoichiometry?



Photosynthesis



Organization of Photosynthetic Machinery in the Thylakoid Membrane

$$\Delta G' = RT\,ln\,\frac{[H^+]_{out}}{[H^+]_{in}} + z\mathscr{F}\Delta\psi$$

$= RT2.3(pH_{in} - pH_{out}) + (+1)(96480)(+0.05)$

$= 5.9(3) + 4.8$ kJ/mol

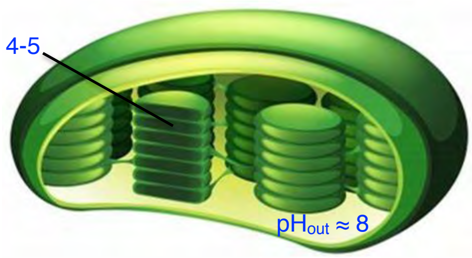
$= 17.7 + 4.8$ kJ/mol

$= 22.5$ kJ/mol per proton

per 12 H^+ = 12x22.5 kJ/mol

= 270 kJ/mol

Photosynthesis



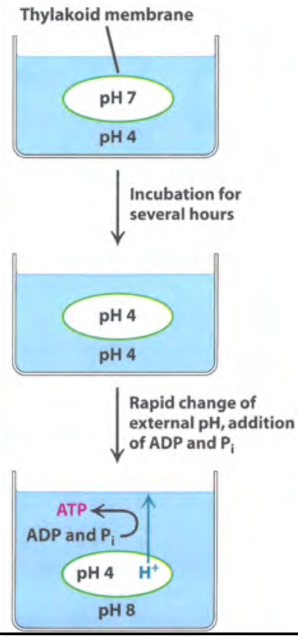
André Jagendorf

$$\Delta G' = RT\ln\frac{[H^+]_{out}}{[H^+]_{in}} + z\mathscr{F}\Delta\psi$$

$= 17.7$ kJ/mol $+ 4.8$ kJ/mol

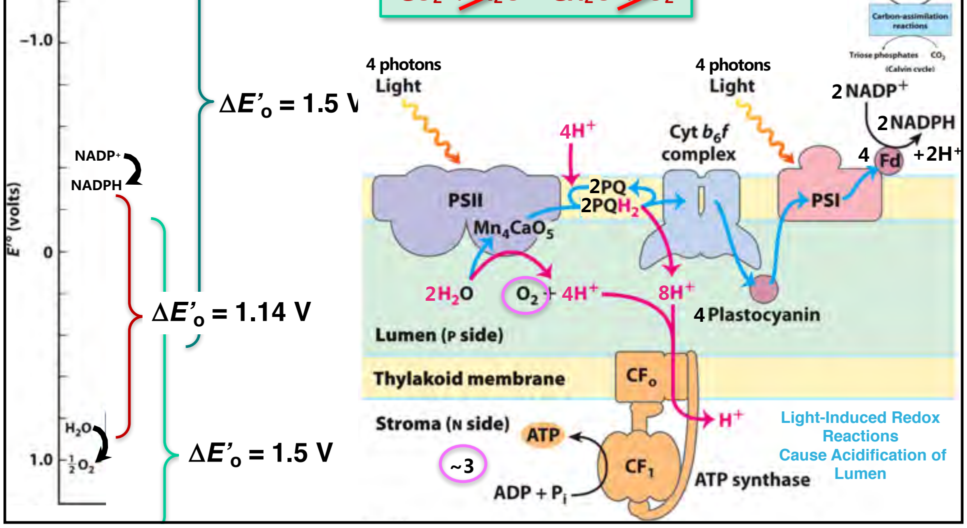
pH gradient

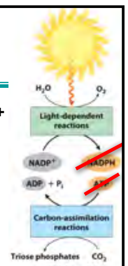
Membrane potential



Photosynthesis

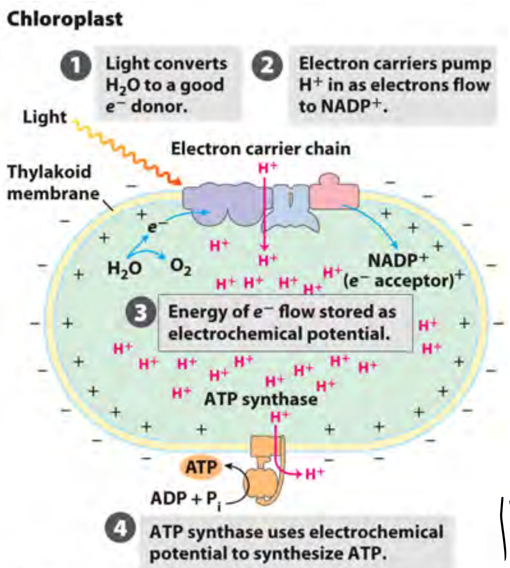
Net equation: $2\ H_2O + 2\ NADP^+ + 8$ photons → $O_2 + 2\ NADPH + 2\ H^+$

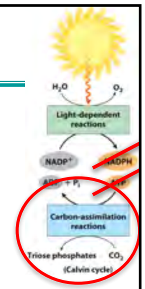




Photosynthesis

Light Energy is Converted to ATP





- In contrast to oxidative phosphorylation, protons are pumped into the lumen, building up a large concentration gradient quickly in the small space.
- The proton-motive force across the thylakoid membrane drives the synthesis of ATP.
- The F_0-c-rings are larger ~14 in chloroplasts, so synthesis of ATP costs more H^+ per ATP (~4-5) than in oxidative phosphorylation. ATP:NADPH
- For the same light, there is a 3:2 ratio of ~~NADPH to AT~~P synthesis

Photosynthesis

Summary of light reactions:

- Photosynthetic organisms capture energy from light at a variety of wavelengths using accessory pigments and funnel it via excitons to reaction centers: P680 & P700.
- In plants, electrons are freed from H_2O, which generates O_2 and H^+. These electrons are excited and moved through the photosynthetic electron-transport chain (cytb$_6$f).
- Per oxygen produced from 4 photons in PS-II, 12 H^+ are mobilized into the lumen from the H_2O and cytb$_6$f.
- The final electron acceptor for linear photosynthesis is $NADP^+$, which requires two electrons for conversion to NADPH. Per 8 photons, 2 NADPH are produced.
- When ATP stores are low, the electrons can be transported to cytochrome *b$_6$f* and cycled through the second half of photosynthesis. This cyclic photosynthesis resulting in an increased proton gradient and more ATP.

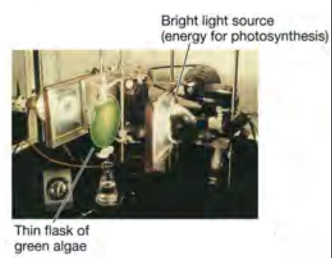
ANABOLISM I
Carbohydrates

Photosynthesis and Carbohydrate Synthesis in Plants

Photosynthesis

Assimilation of CO_2 by Plants

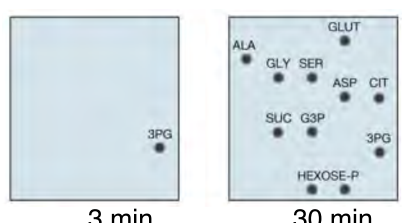
- Taking CO_2 into biological, more reduced, carbon intermediates is ***CO_2 assimilation***.
- Question was: What was the first compound made by plants when they assimilated ***CO_2***?



Melvin Calvin, 1911–1997

Calvin and Benson used the ^{14}C radioisotope to determine the sequence of reactions in CO_2 fixation.

They exposed *Chlorella* to $^{14}CO_2$, then extracted the organic compounds and separated them by paper chromatography.



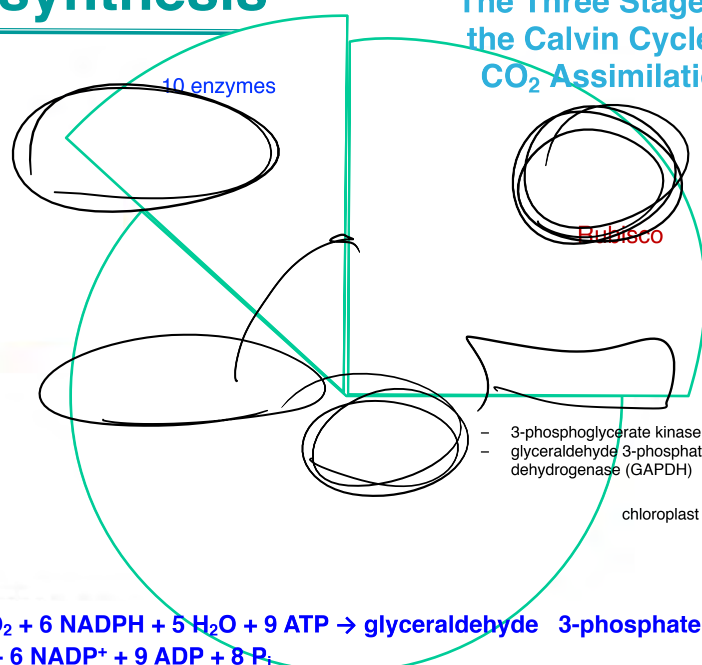
3PG ~ 3-phosphoglycerate

Photosynthesis

- Plant cells: can also *make* 3-C intermediates for further synthesis
  - made from CO_2, H_2O, plus ATP and NADPH from photosynthesis
- It occurs in the stroma of chloroplasts via a cyclic process known as the Calvin cycle.
- Key intermediate **ribulose 1,5-bisphosphate** is constantly regenerated using energy of ATP.
- It produces **3-phosphoglycerate,** which is rapidly converted to **glyceraldehyde 3-phosphate** (G3P) & **dihydroxyacetone phosphate** (DHAP), which are important intermediates for all other compounds.
- The net result is the reduction of CO_2 with NADPH that was generated in the light reactions of photosynthesis.

Photosynthesis

The Three Stages of the Calvin Cycle of CO_2 Assimilation



- 3-phosphoglycerate kinase (3PGK)
- glyceraldehyde 3-phosphate dehydrogenase (GAPDH)

chloroplast isoforms

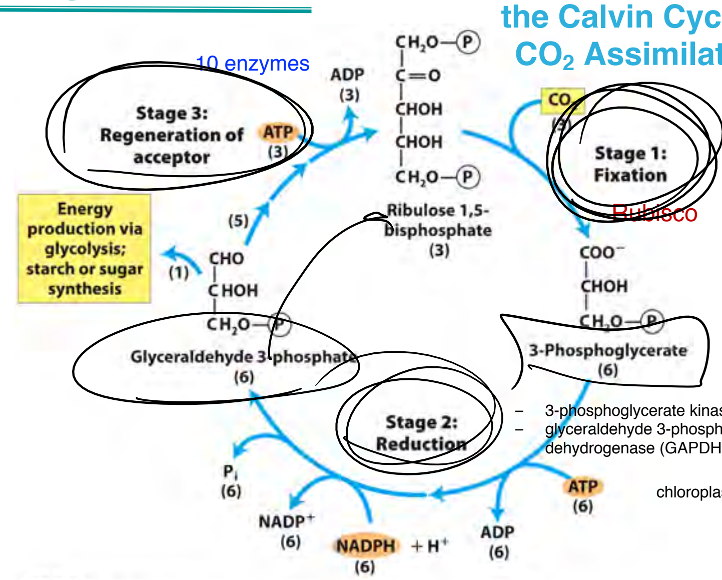
Overall: $3\ CO_2 + 6\ NADPH + 5\ H_2O + 9\ ATP \rightarrow$ glyceraldehyde 3-phosphate (G3P) $+ 2\ H^+ + 6\ NADP^+ + 9\ ADP + 8\ P_i$

*Ribulose 1,5-bisphosphate carboxylase/oxygenase (also RuBisCo)

Photosynthesis

The Three Stages of the Calvin Cycle of CO_2 Assimilation

10 enzymes



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chloroplast isoforms

Overall: 3 CO_2 + 6 NADPH + 5 H_2O + 9 ATP → glyceraldehyde 3-phosphate (G3P) + 2 H^+ + 6 $NADP^+$ + 9 ADP + 8 P_i

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