

Photosynthesis & Chemical Conversion

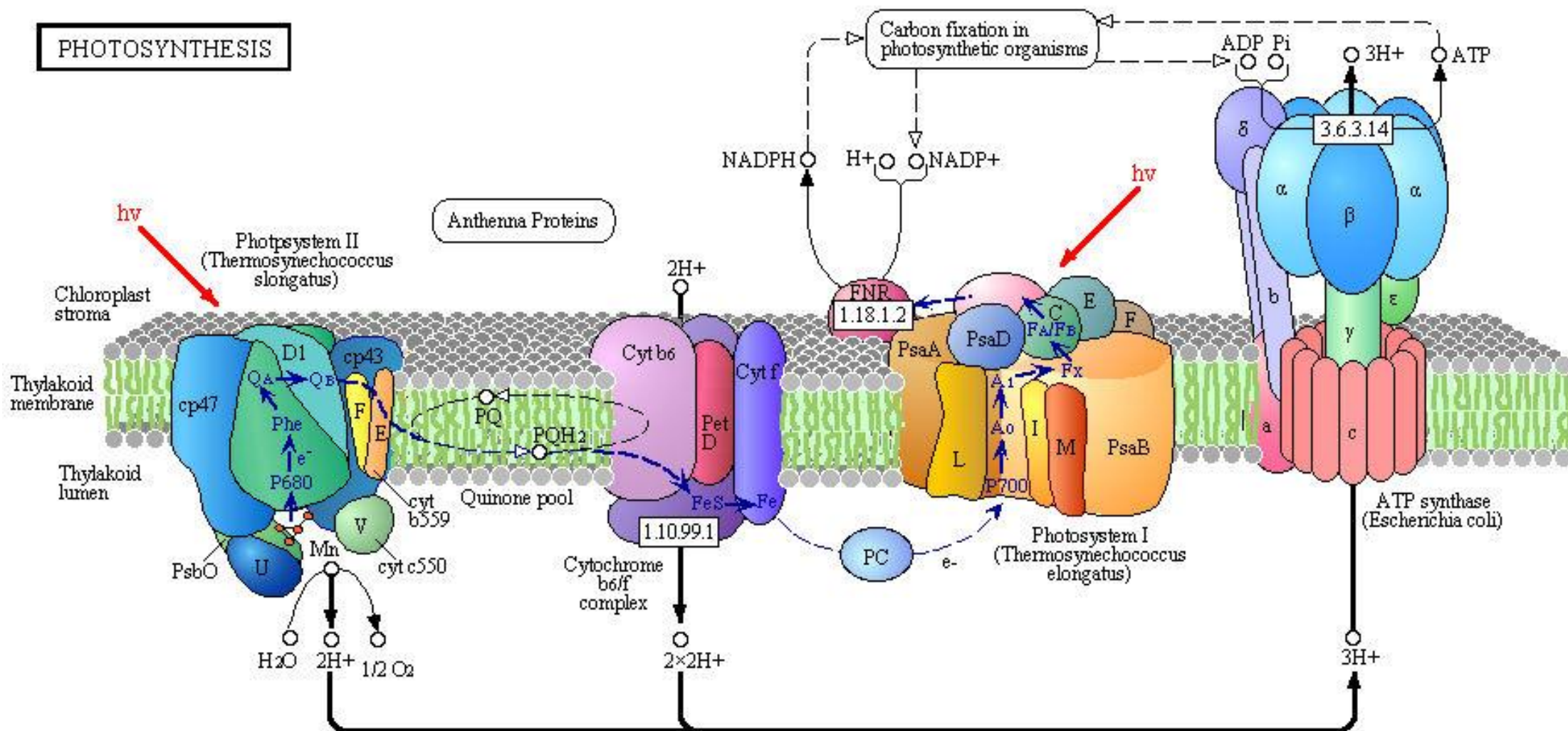


Lecture - Learning Objectives

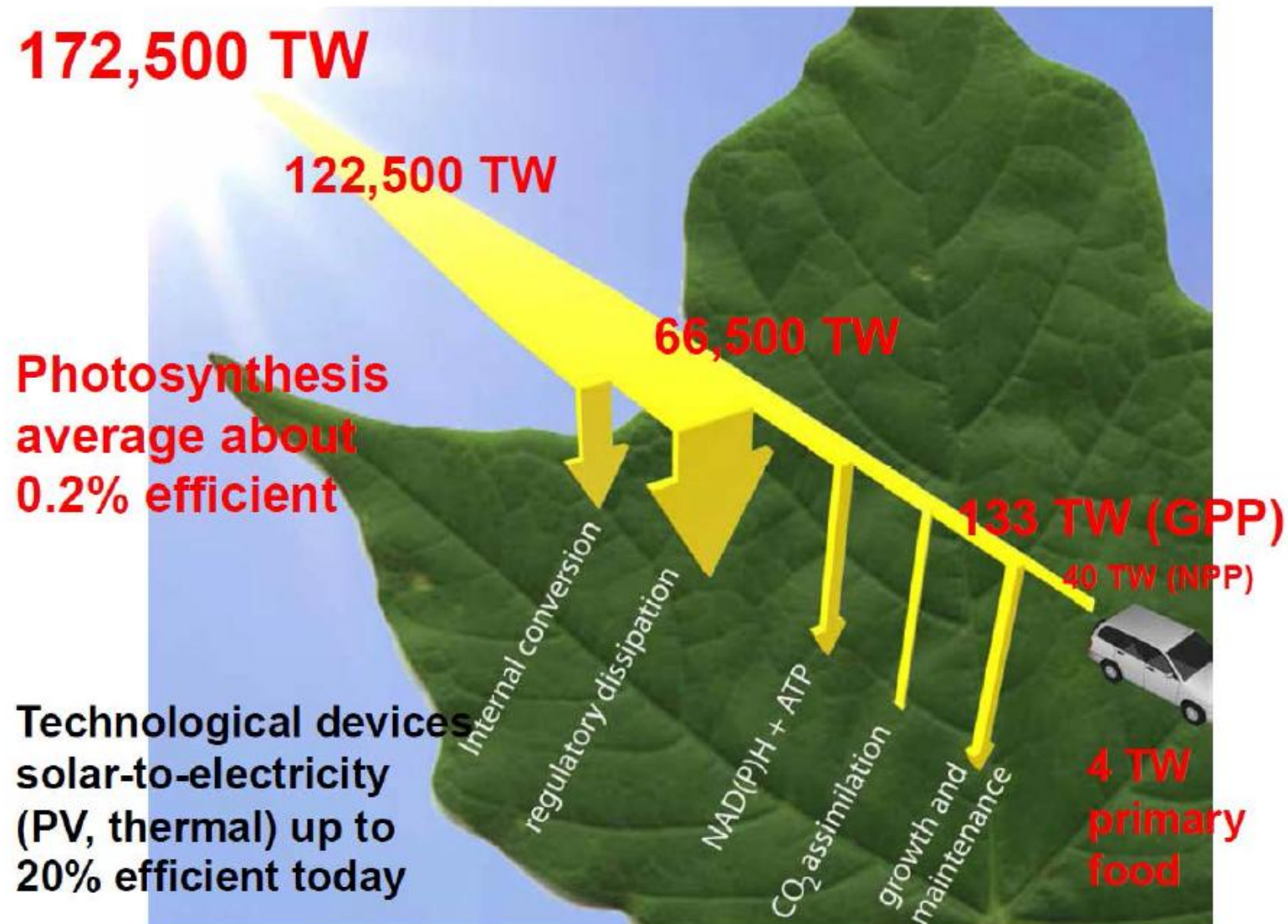
At the end of this lecture you should be able to:

- Understand the entire photosynthesis process and efficiency losses from light absorption to sugar production.
- Understand the Calvin Cycle.
- Understand the basic materials in biomass
- Know the major building block chemicals on which most of the chemistry industry is built on.

Photosynthesis



Graphical photosynthesis loss



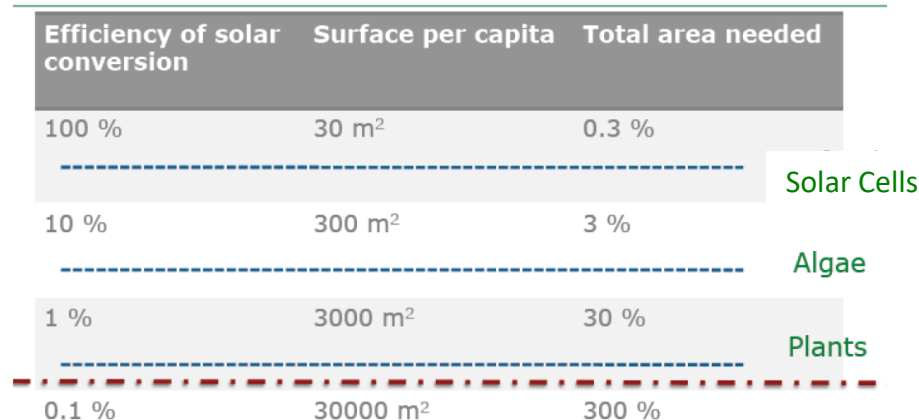
Adapted from Gust, Kramer, Moore, Moore & Vermaas, MRS Bulletin, 10

How much energy can this provide ?

- Photosynthesis actually produces 130 TW of energy.
- However plant respiration burns 63 TW, thus we are left with about 67 TW of net energy.
 - From this energy, basically all life forms are supported.
- Using 1% efficient biomass, we will need 50% of US cropland to convert this to enough ethanol to replace all of the US gasoline.

Europe in 2050:

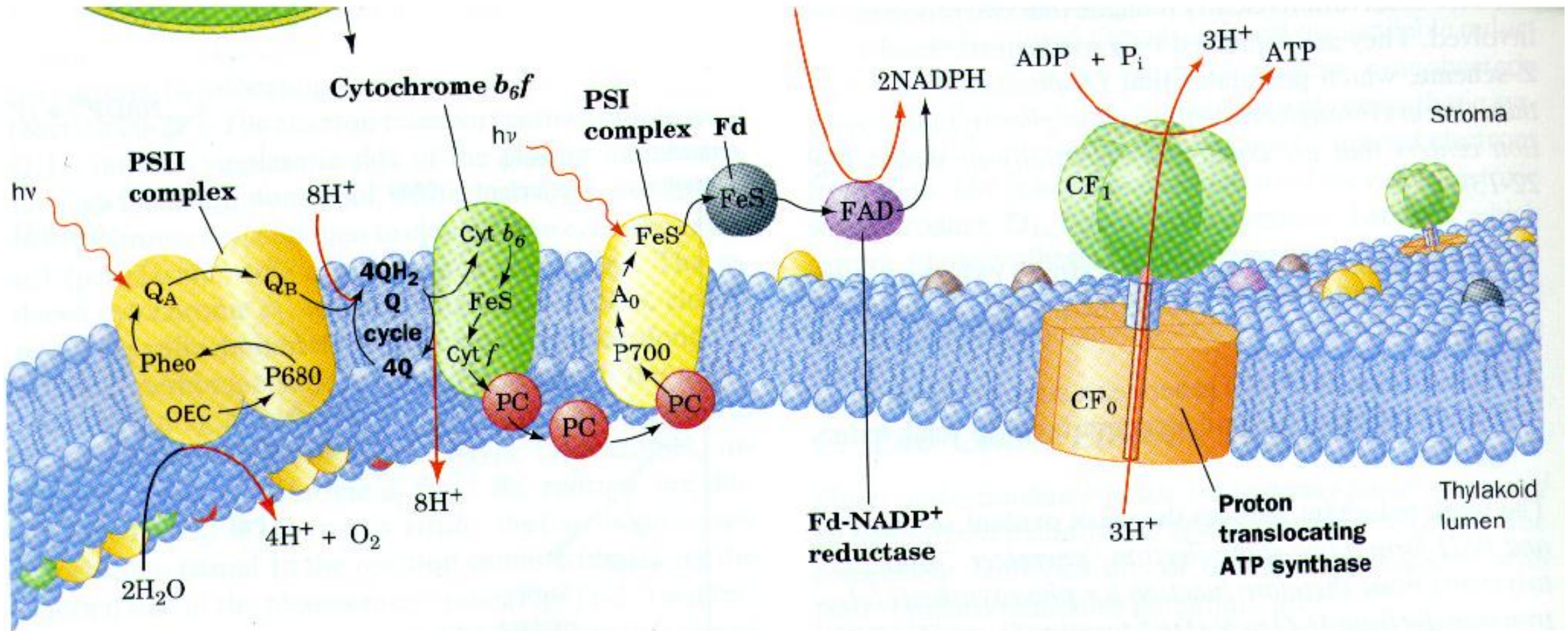
650 million people - 2 TW Power needed



Overall Efficiency

- 100% sunlight → non-bioavailable photons waste is 47%, leaving
- 53% (in the 400–700 nm range) → 30% of photons are lost due to incomplete absorption, leaving
- 37% (absorbed photon energy) → 24% is lost due to wavelength-mismatch degradation to 700 nm energy, leaving
- 28.2% (sunlight energy collected by chlorophyll) → 68% loss in conversion of ATP and NADPH to d-glucose, leaving
- 9% (collected as sugar) → ~40% of sugar is recycled/consumed by the leaf in dark and photo-respiration, leaving
- 5.4% net leaf efficiency
- In reality, the energy conversion efficiency is much less.
- Most photosynthetic processes are 0.1 %, with the most efficient at 1-3%.

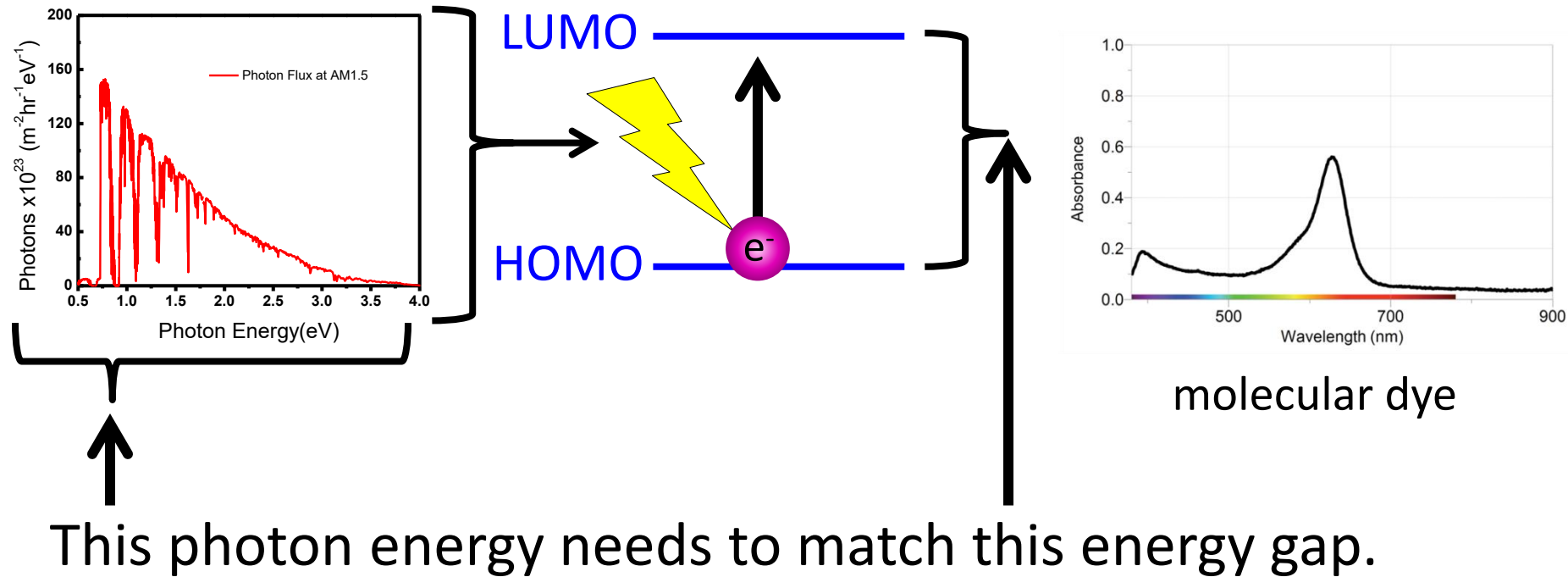
Basics of Photosynthesis



- There are 2 dominating factors that underlie photosynthesis:
 - Light absorption
 - How does the light absorb and create electron-hole pairs.
 - Electron and energy transfer
 - What are the physics behind transferring electrons and/ or energy.

Photoexcitation (in molecules)

- Molecular photoabsorbers have distinct energy levels.

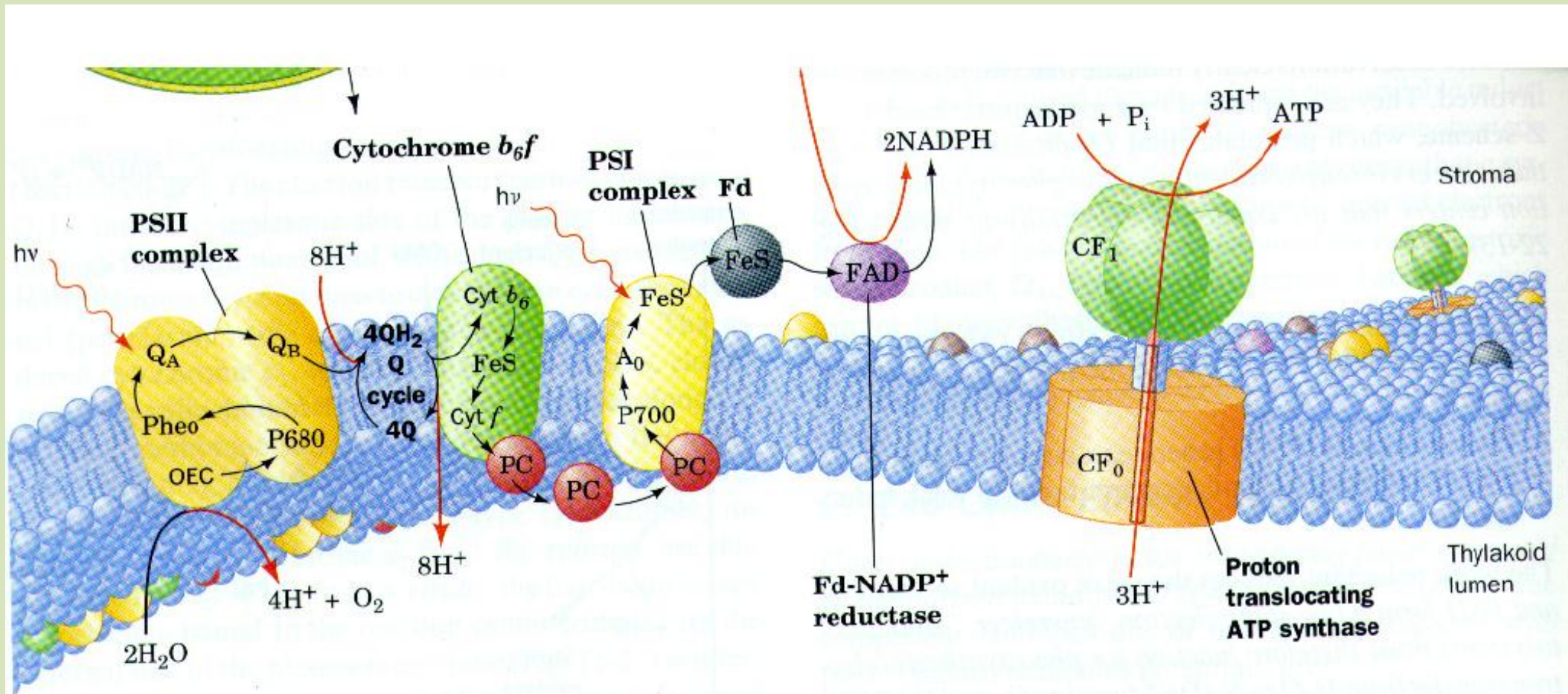
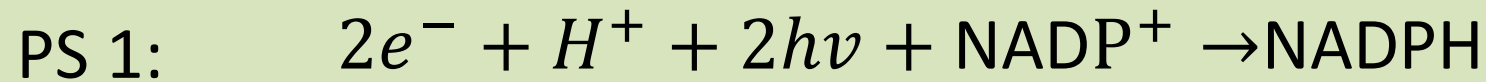
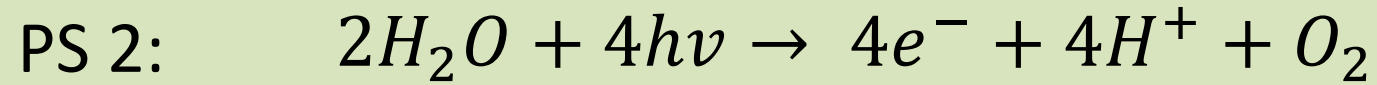


- Molecular photocatalyst only absorb efficiently at one wavelength.

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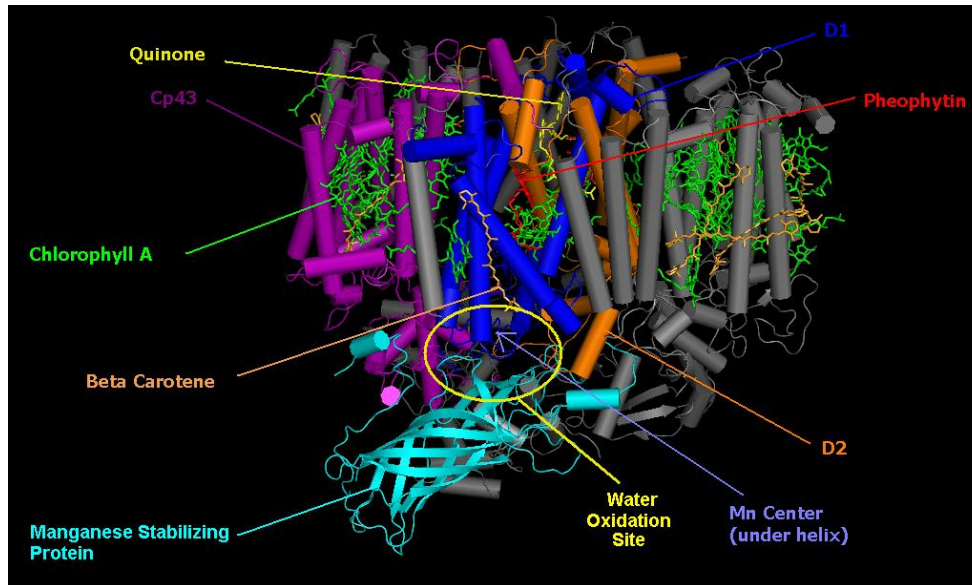
Basics of Photosynthesis



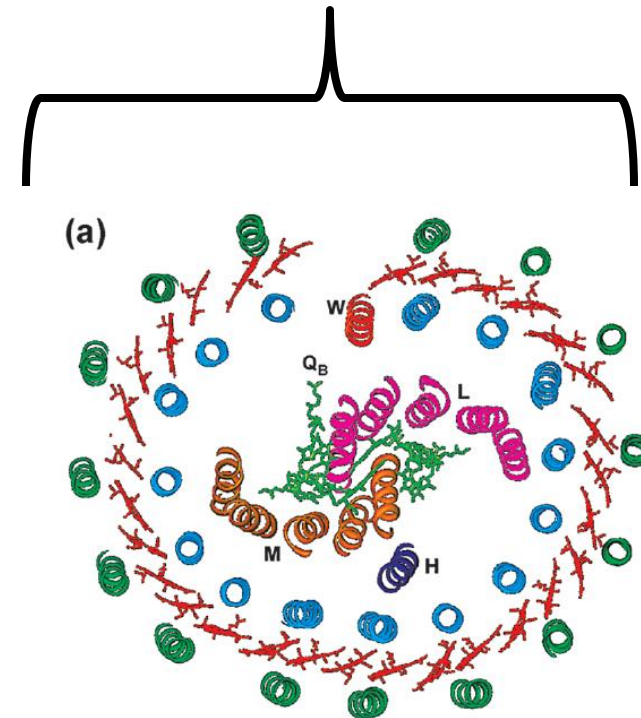
Photosystem II

- Photosystem II contains
 - 99 cofactors (random helper molecules)
 - 20 Protein subunits
 - 35 Chlorophyll
 - 12 beta-carotene
 - 25 lipids

- Many linked chlorophylls

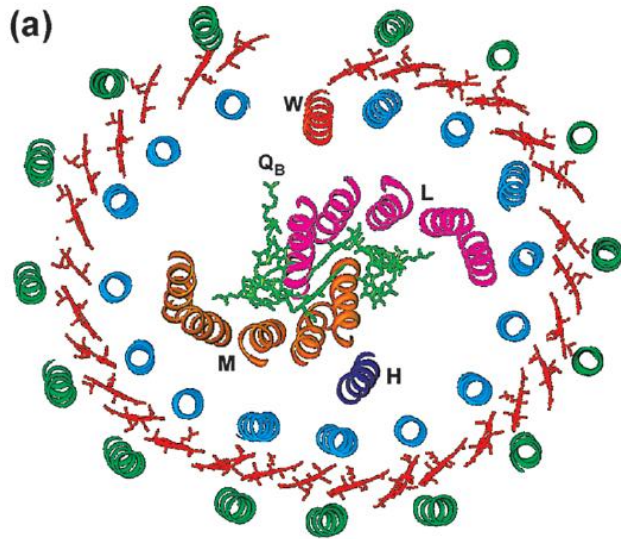


Photosystem II



Photosystem II- Interacting Molecules

- With chlorophylls next to each other they will have dipole-dipole interactions, which occur over 10 nm
- Thus any excited state will be a linear combination of the other chlorophyll states.

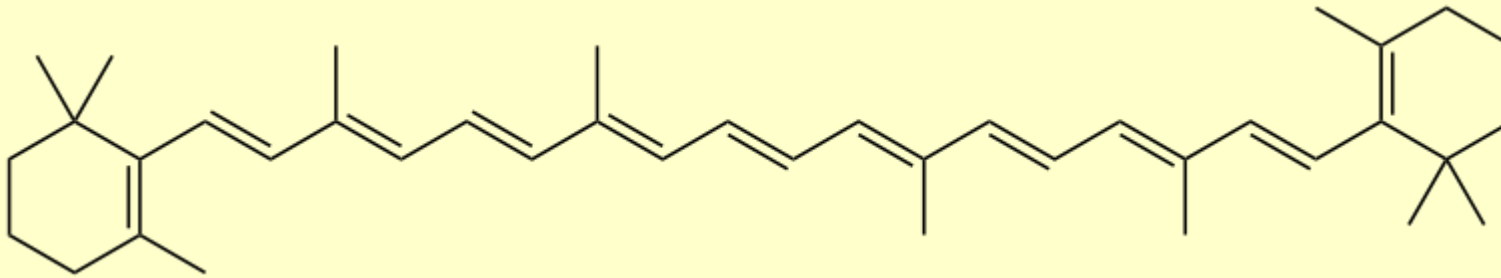


$$\psi_k = \sum_n C_{k,n} \phi_n$$

Percentage of exciton

- *This is photosynthesis's version of delocalized electrons*

Beta-Carotene



- What wavelength light does it absorb?
- β -Carotene has a mass of 9.1×10^{-31} kg and a length of 1.83 nm.
- Energy of a ground state electron is $E_0 = \frac{h^2}{8mL^2}$

Beta-Carotene

- Quantum mechanics allows us to calculate β -Carotene absorption.
- β -Carotene has 22 delocalized atoms, a mass of 9.1×10^{-31} kg and a length of 1.83 nm.
- This can be modeled as 1-D particle in a box.

$$E_n = n^2 E_0$$

$$E_{\text{photon}} = \Delta E = E_{12} - E_{11} = (144 - 121)E_0 = 23 \frac{h^2}{8mL^2} = 4.13 \times 10^{-19} \text{ J}$$

$$1 \text{ J} = 6.2 \times 10^{18} \text{ eV}$$

$$\lambda = \frac{hc}{E} = 480 \text{ nm}$$

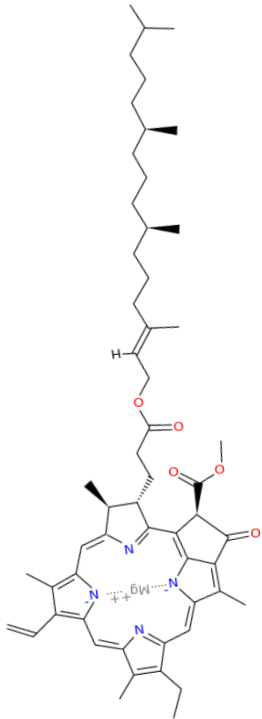
$$E_{12} = 144E_0 \quad \text{—————} \quad \text{LUMO}$$

$$E_{11} = 121E_0 \quad \begin{array}{c} \uparrow \downarrow \end{array} \quad \text{HOMO}$$

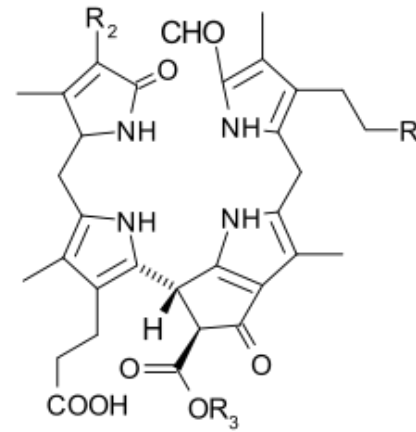
$$E_{10} = 100E_0 \quad \begin{array}{c} \uparrow \downarrow \end{array}$$

Side note

- In the autumn chlorophyll breaks down, thus causing a change in color.
- This is simply due to a modification of the delocalization of the molecule.



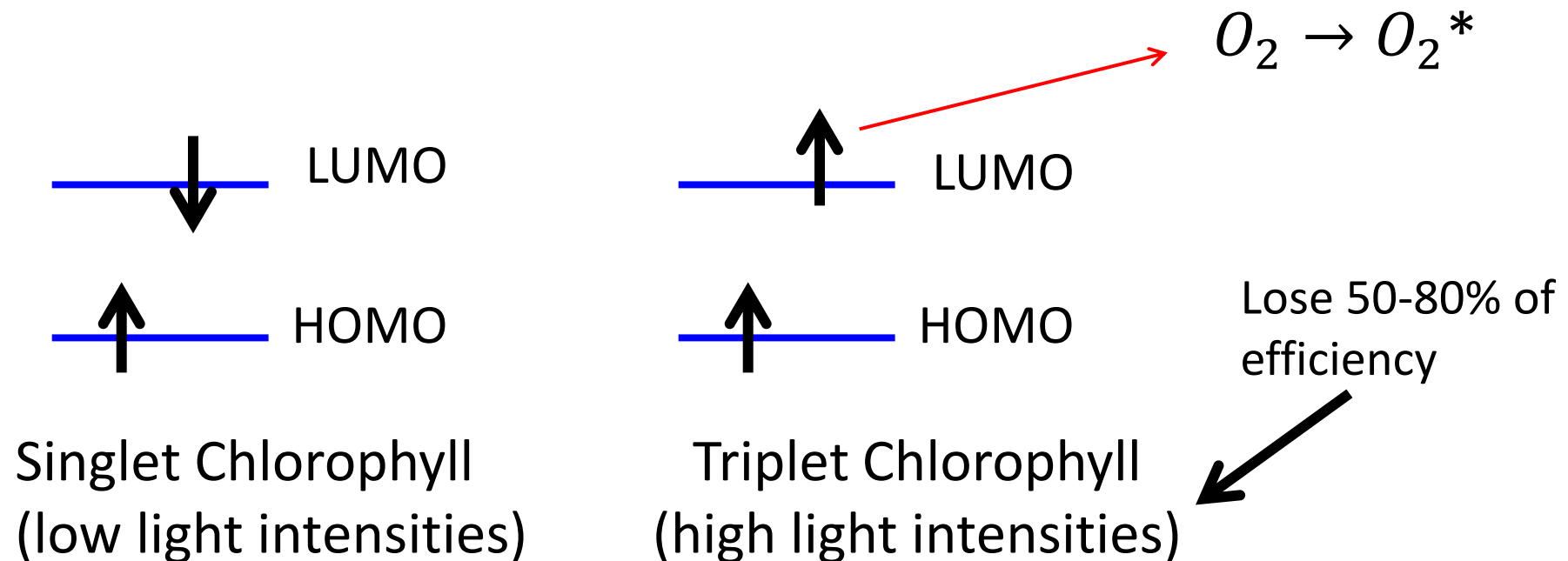
Chlorophyll a



Color change of
leaves in autumn

Beta-Carotene

- β -Carotene serves 2 purposes:
 - Absorb light and transfer it to the reaction center
 - Quench triplet chlorophyll, which can produce singlet oxygen.
- Singlet oxygen is highly reactive and destroys everything.



Beta-Carotene

- The β -Carotene easily accepts the electron.

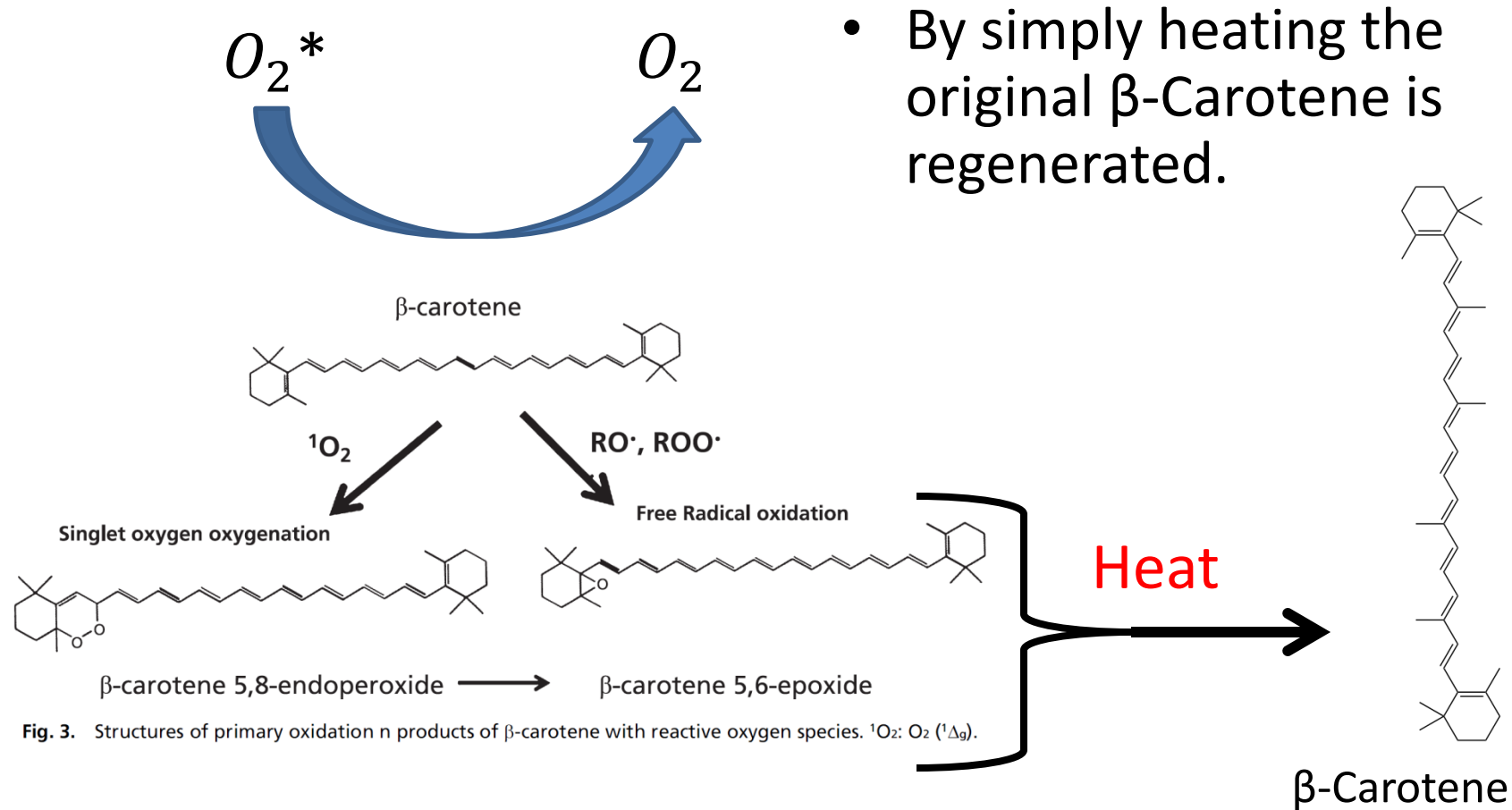
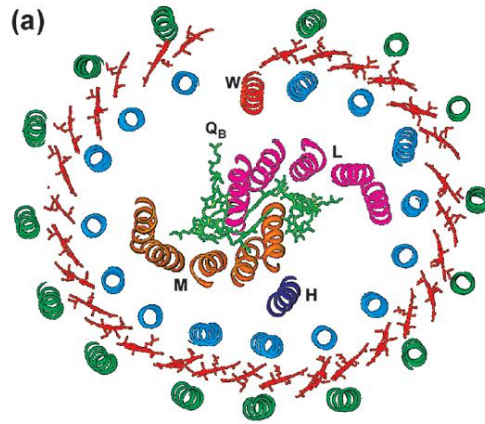
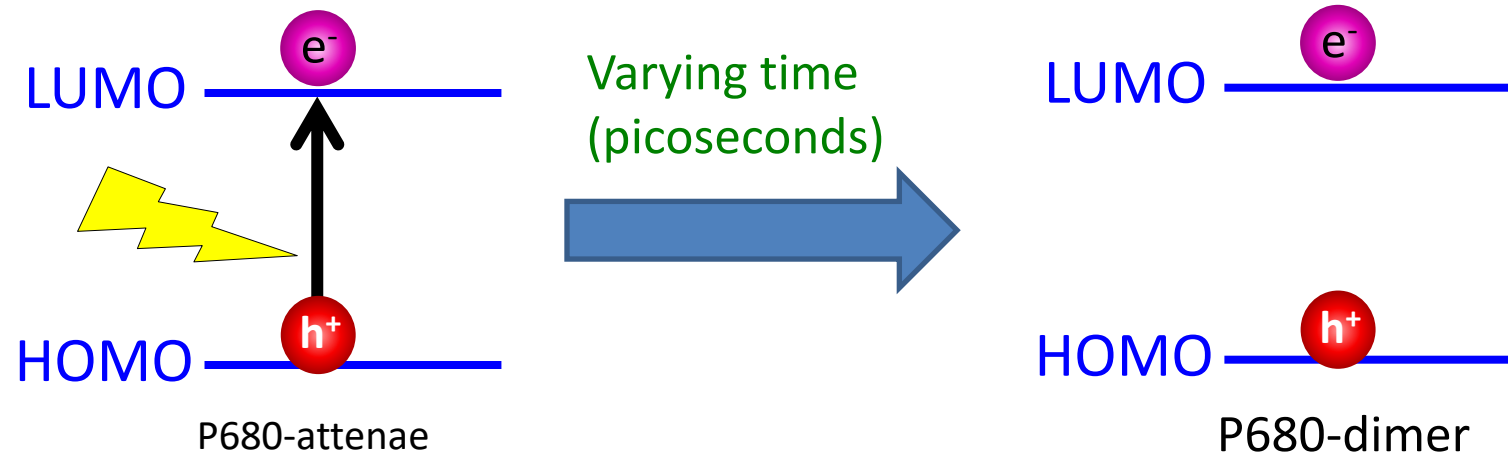
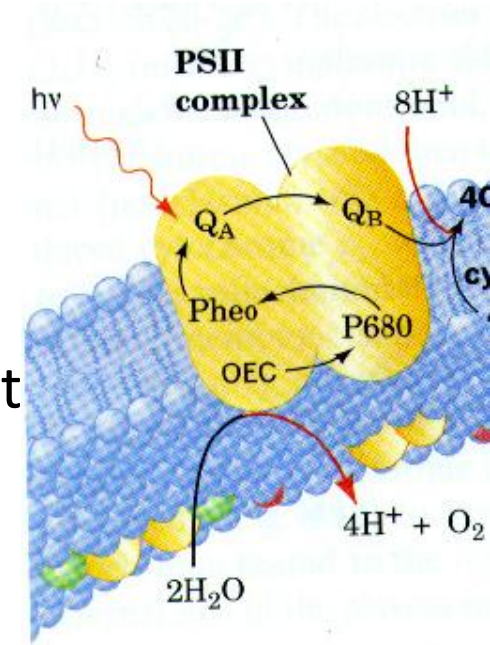


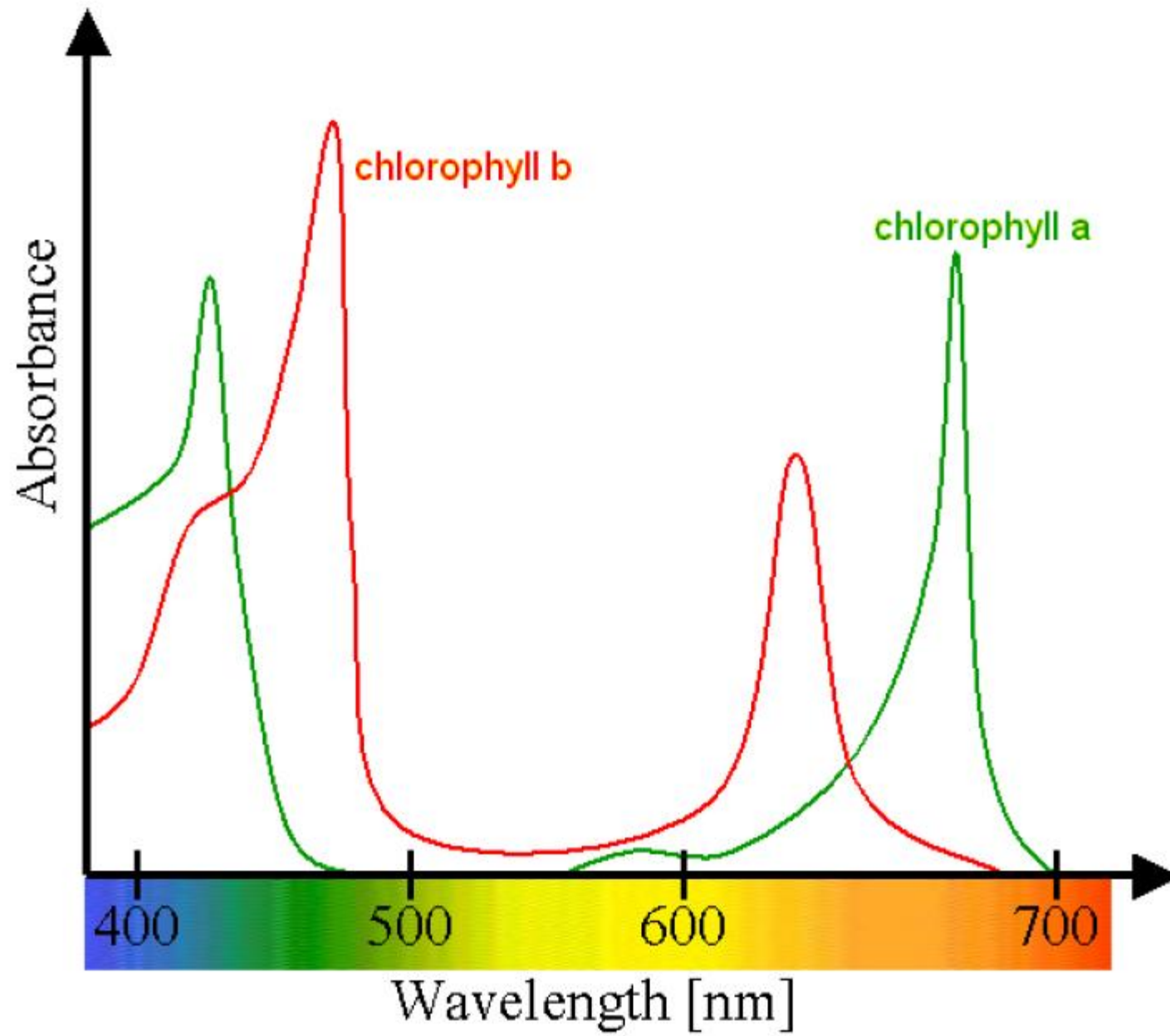
Fig. 3. Structures of primary oxidation products of β -carotene with reactive oxygen species. 1O_2 : $O_2 (^1\Delta_g)$.

Photosystem II



- The antenna chlorophyll transfer their charges to a centralized reaction center.
- There are 2 special P680 consisting of 2 chlorophyll's that are not bound to anything.

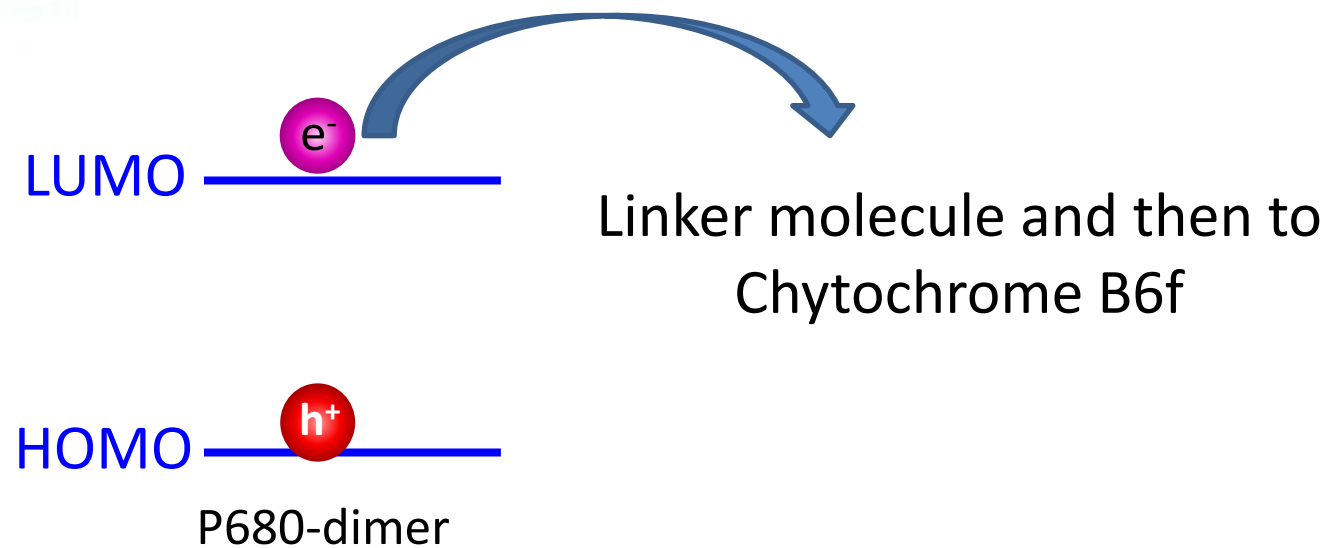
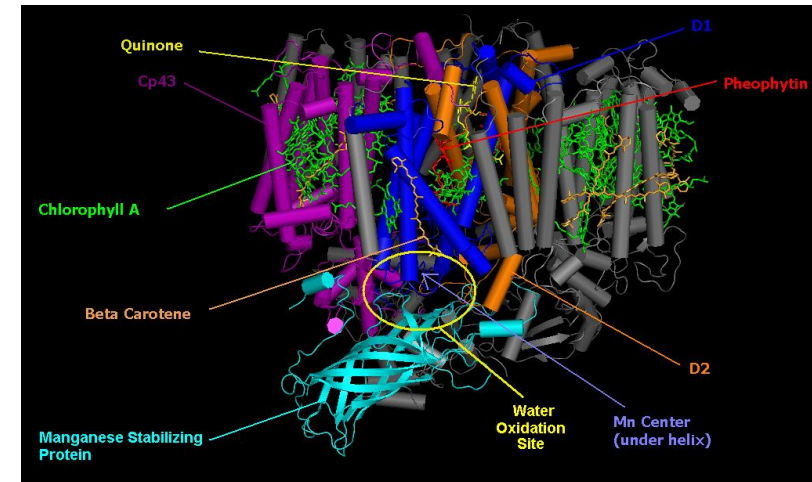
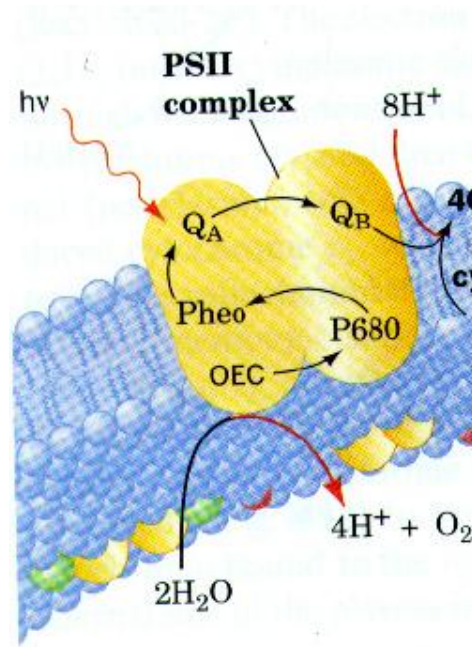




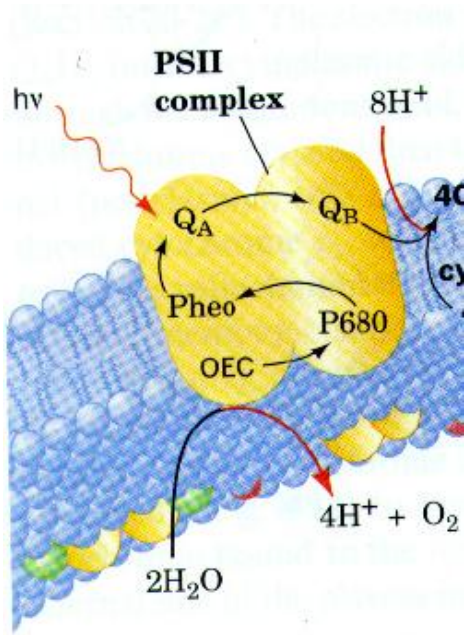
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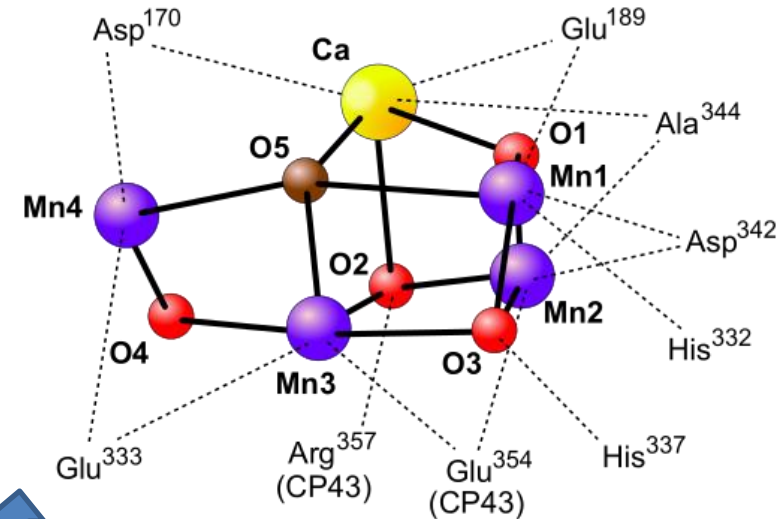
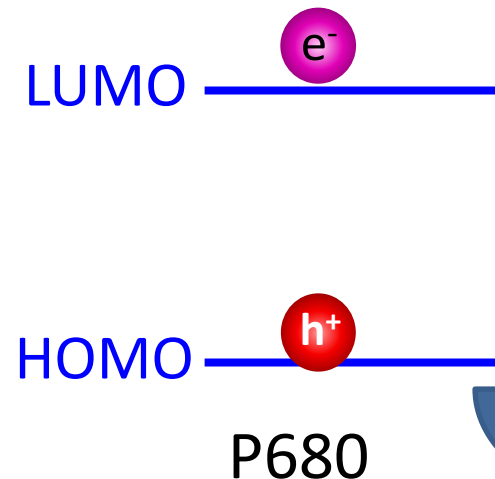
Photosystem II

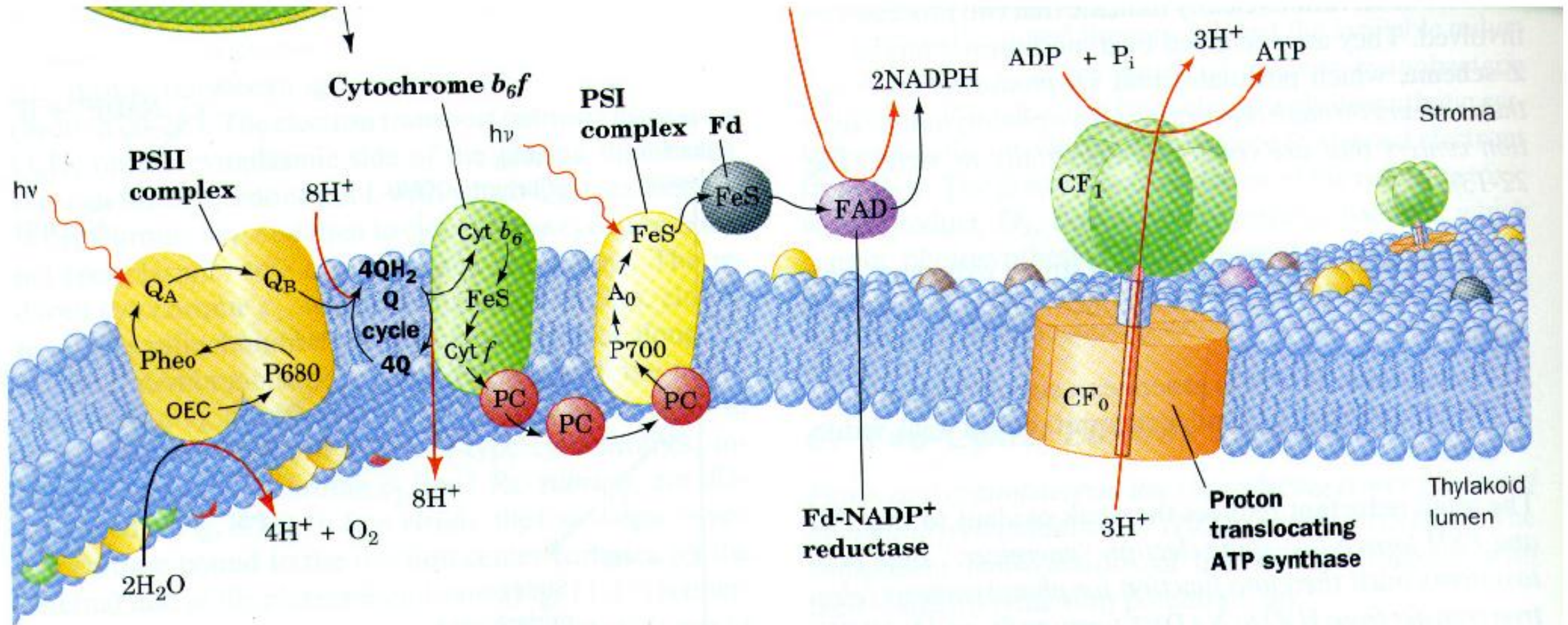


Photosystem II-What about the hole?

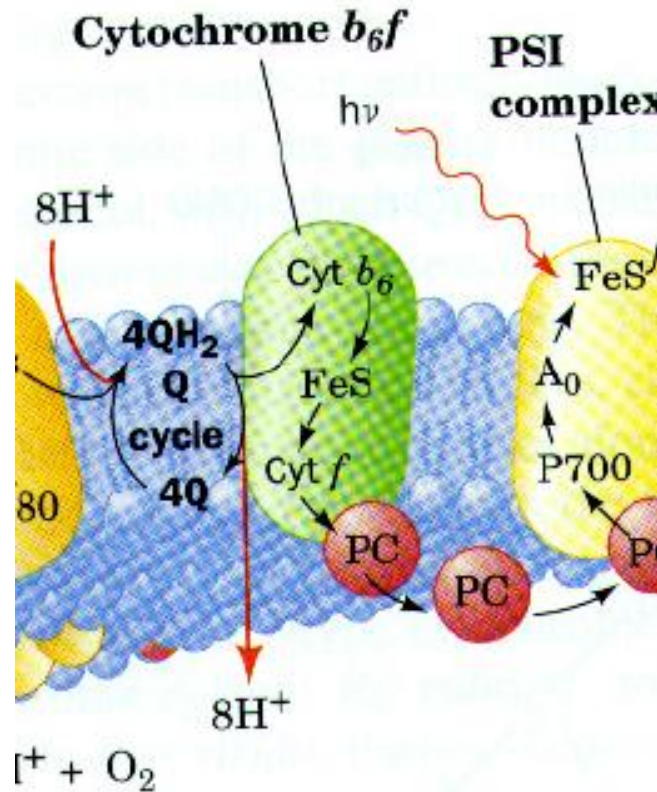


- The hole first transfers to a linker molecule (Tyrosine)
- From Tyrosine, it then goes to the O_2 evolution catalyst



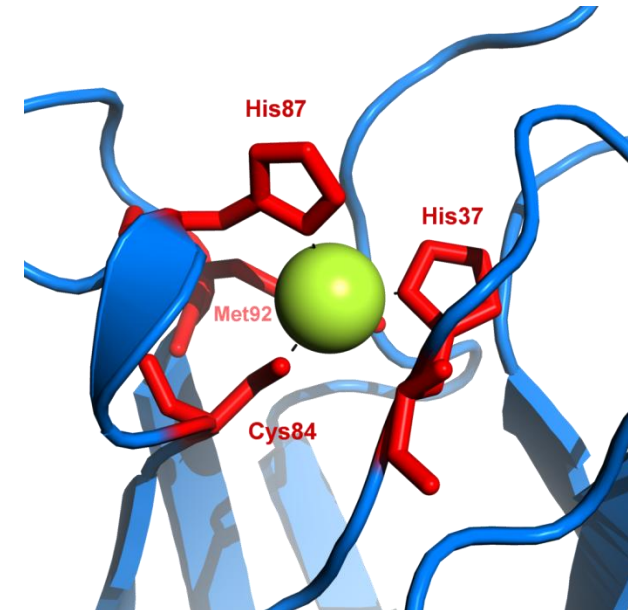


Moving on- Cytochrome b_6f

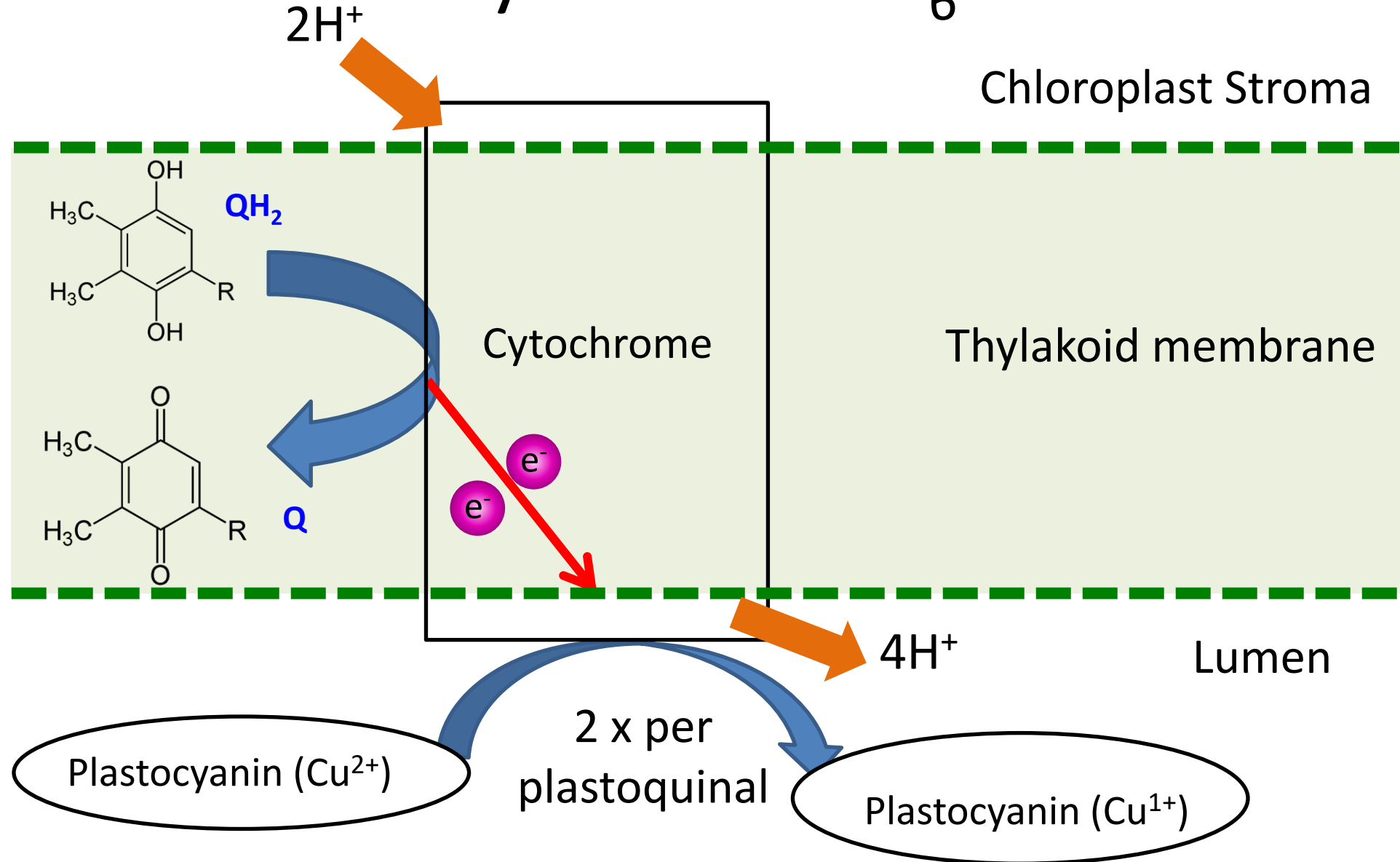


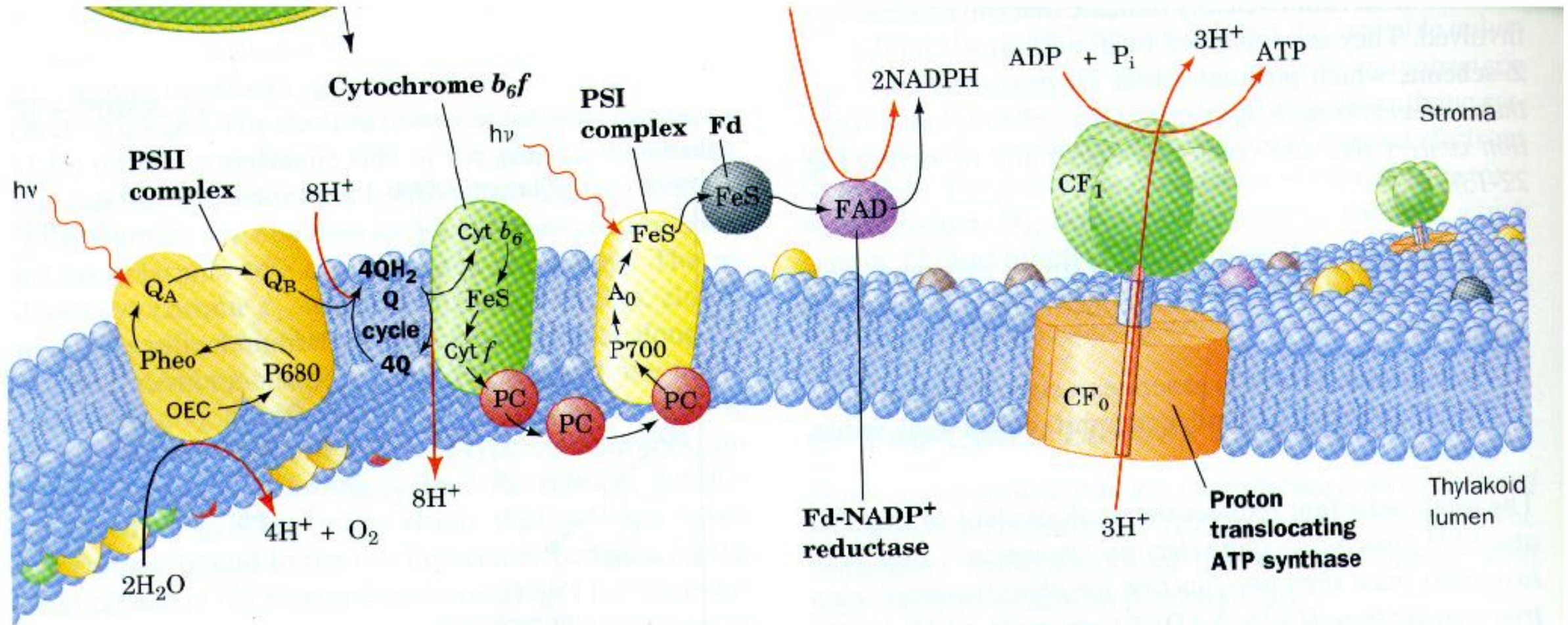
- The Cytochrome b_6f works to pump protons up hill.
- This creates a $[H^+]$ bias that the system will use at a later point.
- Plastocyanin is a huge enzyme that works as an electron transfer molecule

- To transfer electrons a Cu in plastocyanin converts between $2+$ and $1+$.



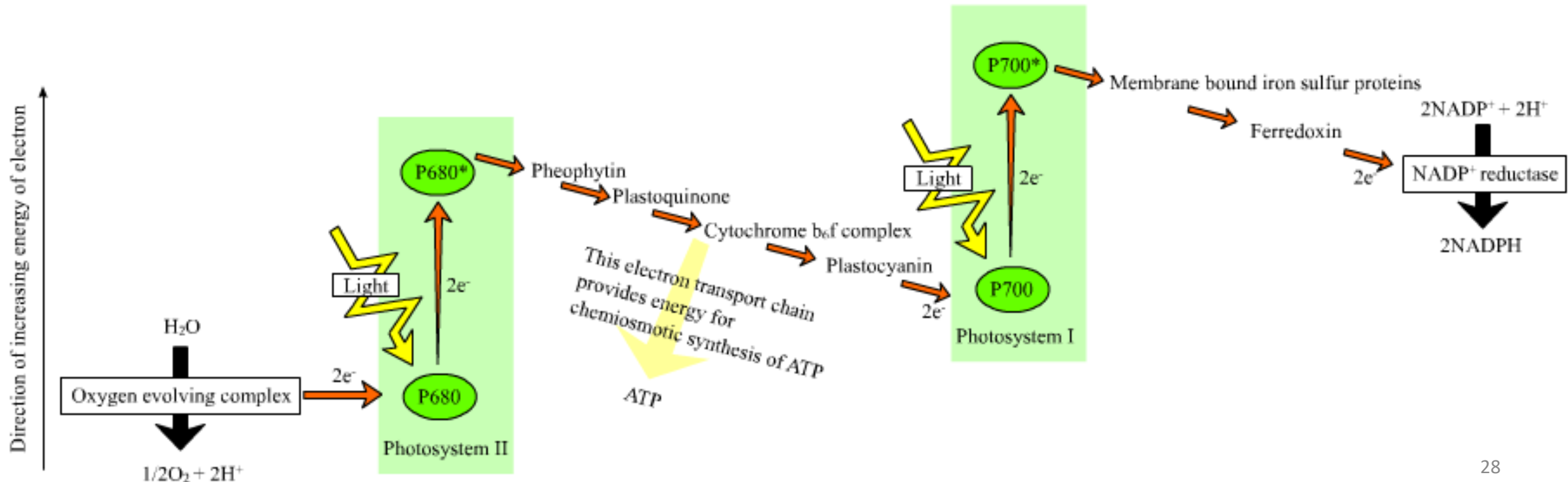
Cytochrome b_6f





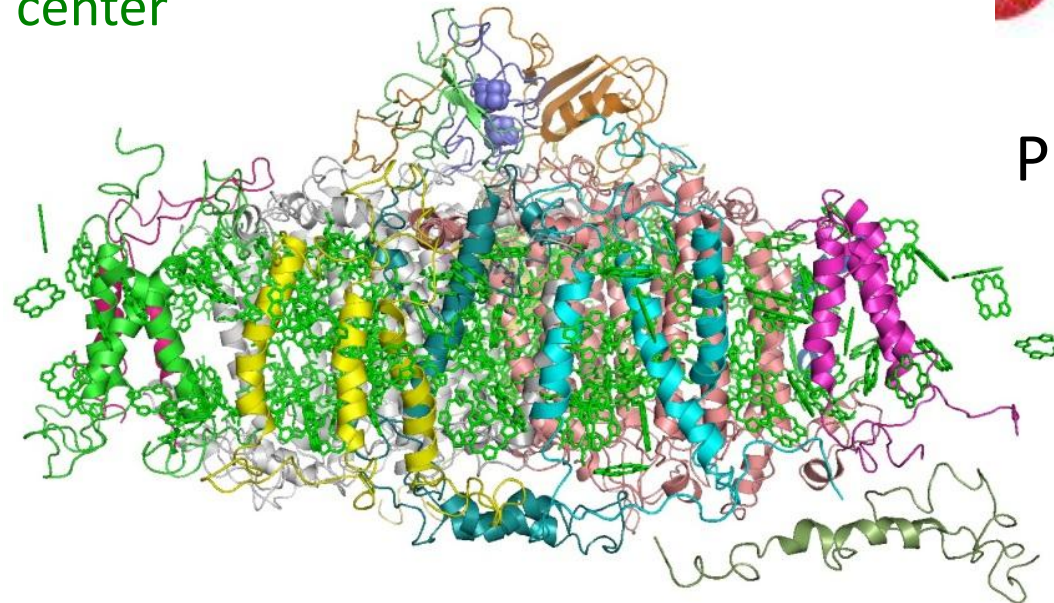
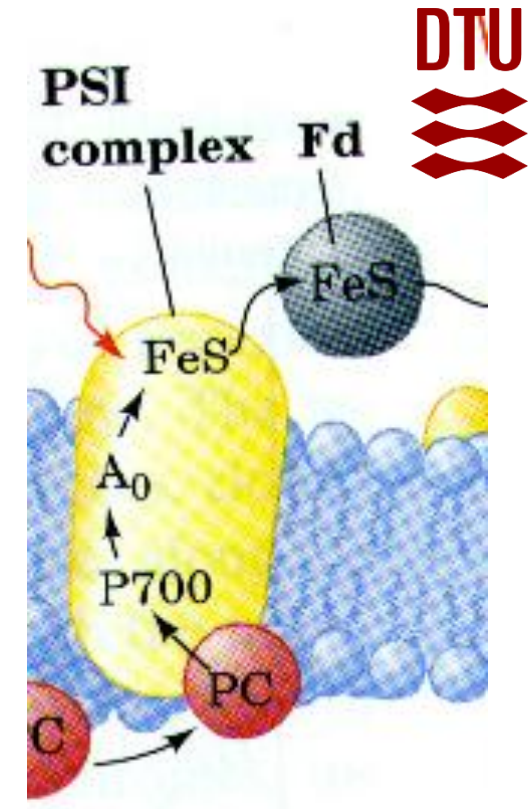
Energetics

- Each photoabsorption gave us energy.
- The fast reaction path prevents almost any direct e^- - h^+ recombination.
- Each reaction step is a slight drop in energy.



Photosystem I

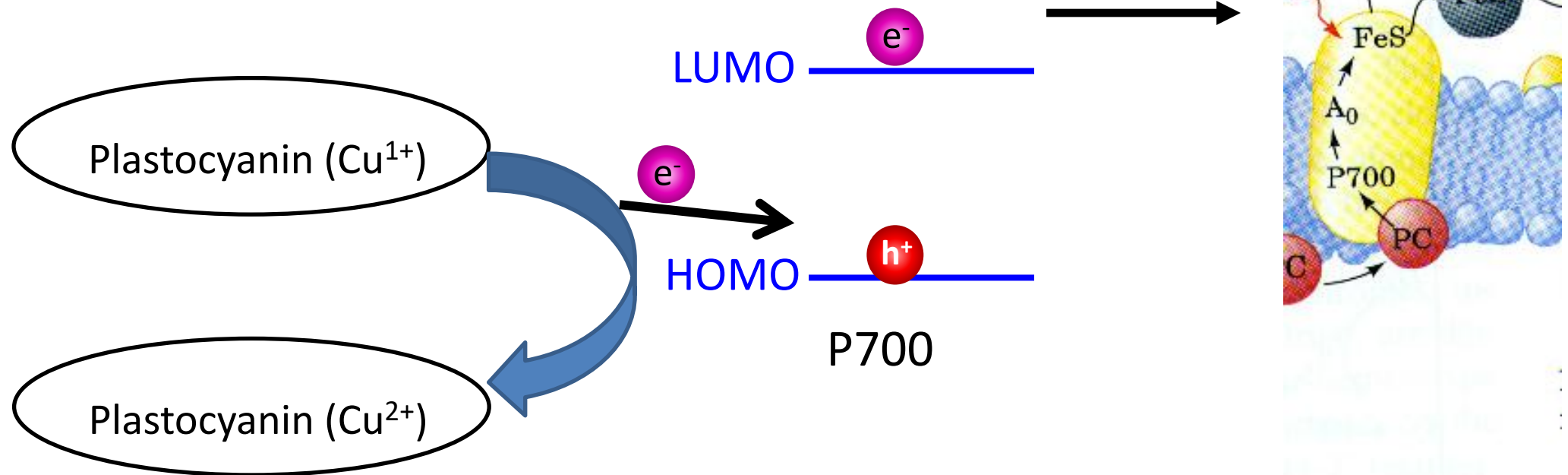
- This is called #1 because it was the first photosystem produced by cells.
- Photosystem I contains
 - 110 cofactors (random helper molecules)
 - 154 Chlorophyll
 - 13 more Chlorophyll's in reaction center
 - 22 beta-carotene
 - 4 different types of lipids



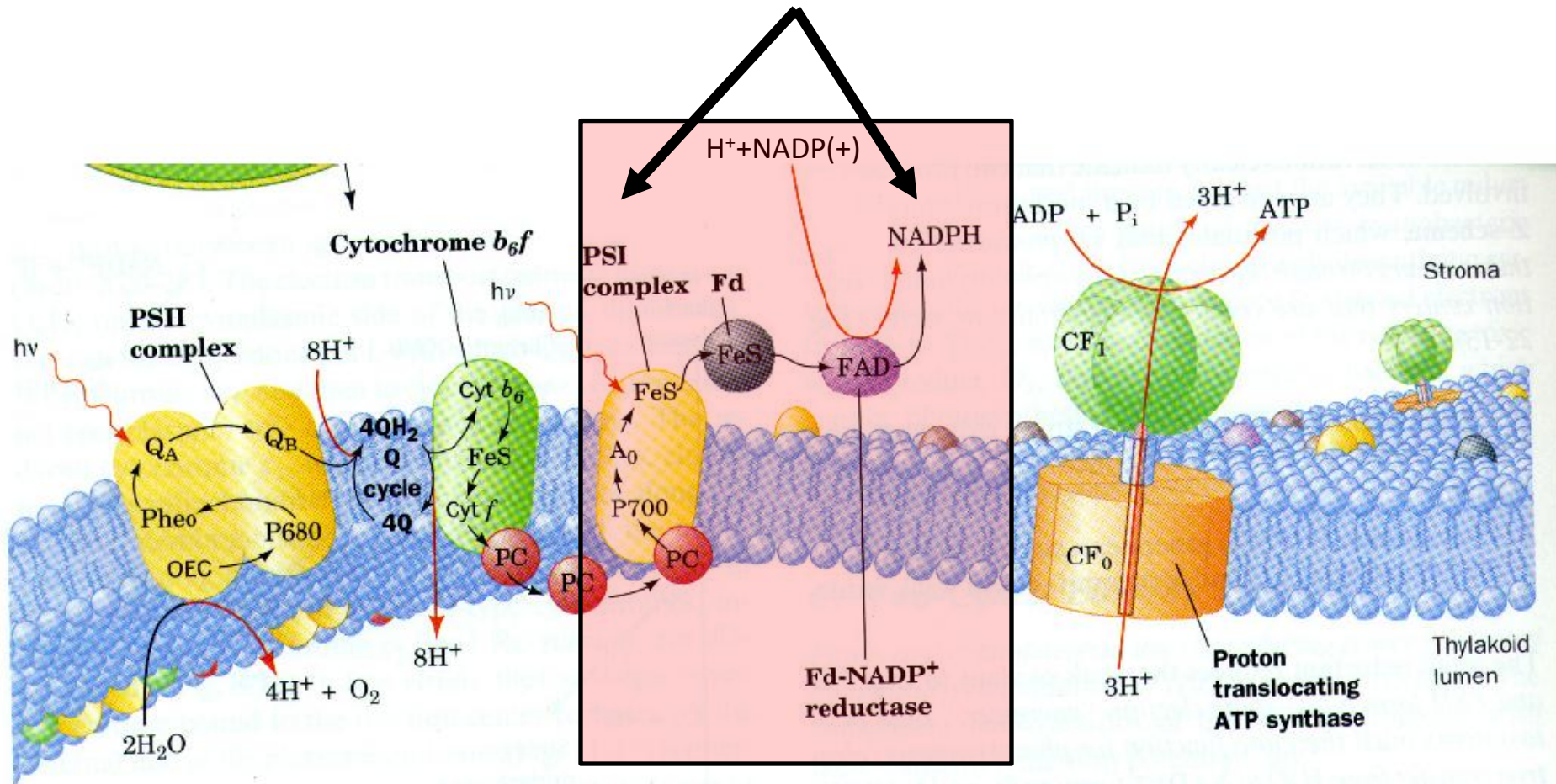
Photosystem I

Plastocyanin-Photosystem I

- The plastocyanin transfers electrons directly to the P700 chlorophyll.
- In other words this scavenges the photogenerated hole.



Photosystem 1 produces NADPH



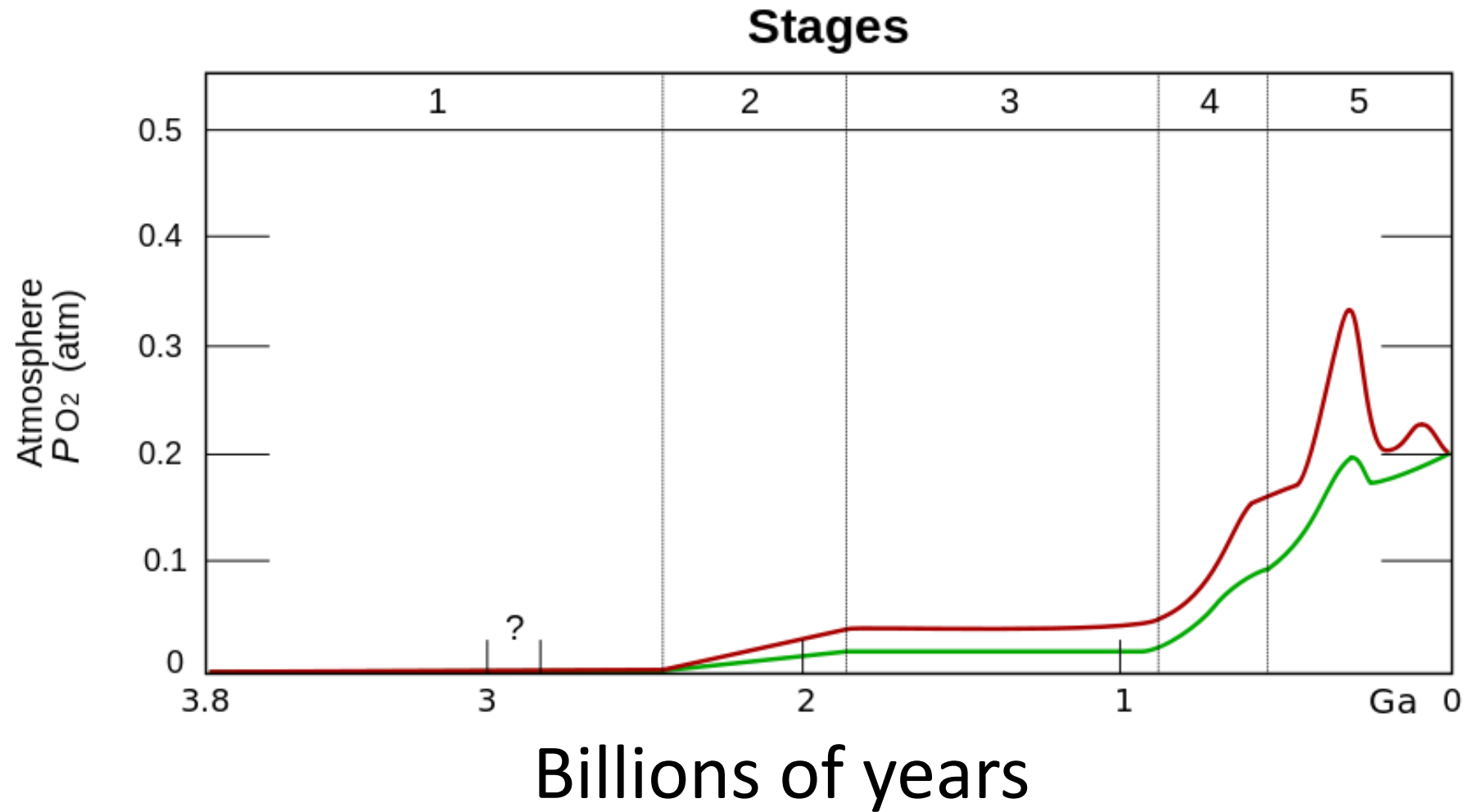
- After going through catalysts and linker molecules, we produce NADPH

History

- Originally the Earth had many reducing gases in the atmosphere so Photosystem I could easily flourish.
 - These early photosystems did not absorb at 680 nm, but rather around 870 nm. Propose a reason why.
- Earth also had a high CO₂ concentration early on as well.
- This allowed for cyano bacteria (with both PSI and PSII) to form and basically take over the world.

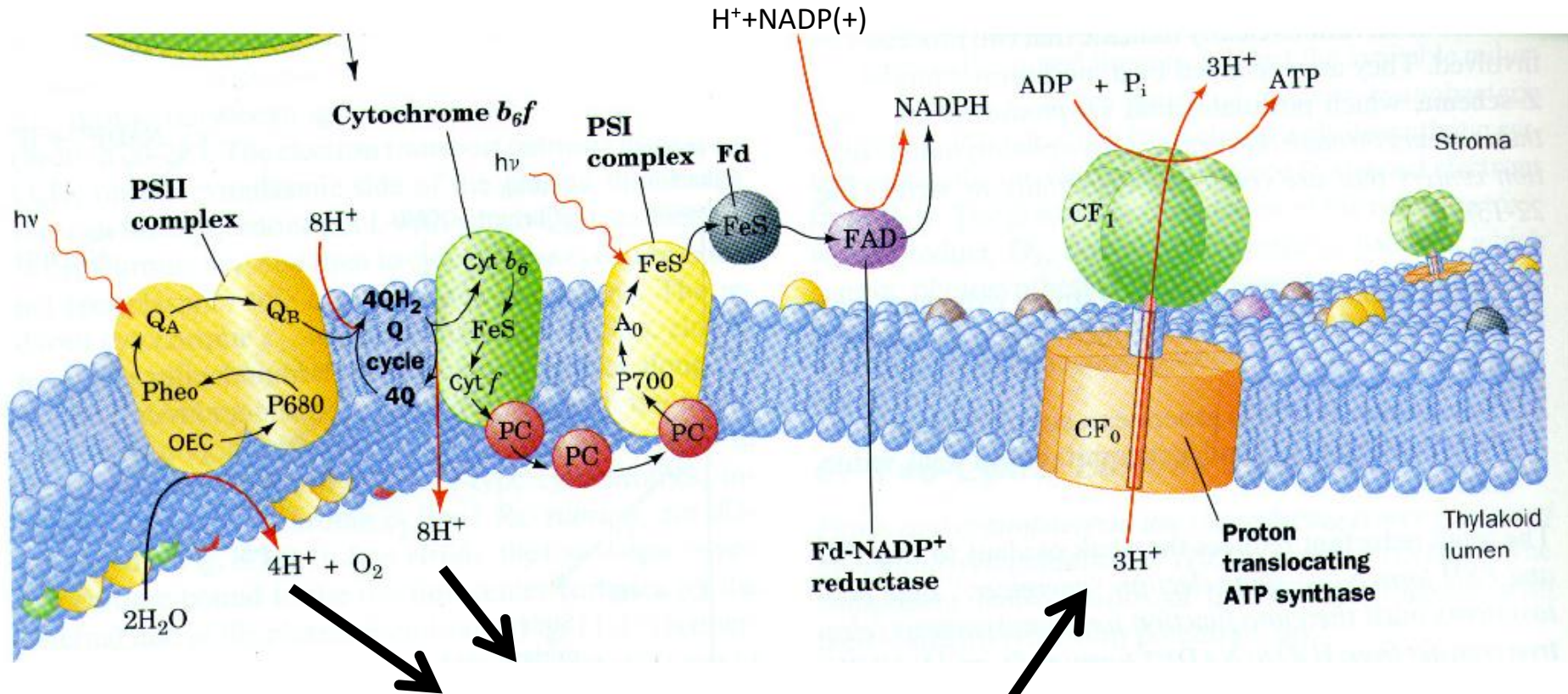
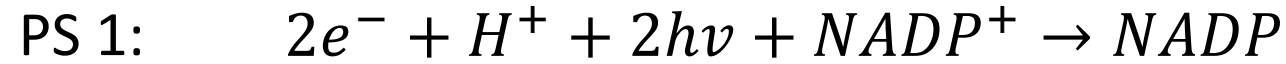
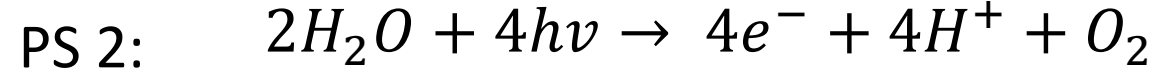


- Early on the earth's atmosphere was composed of CO_2 and reducing agents such as H_2 and H_2S .



Break

Serious Build-up of Protons

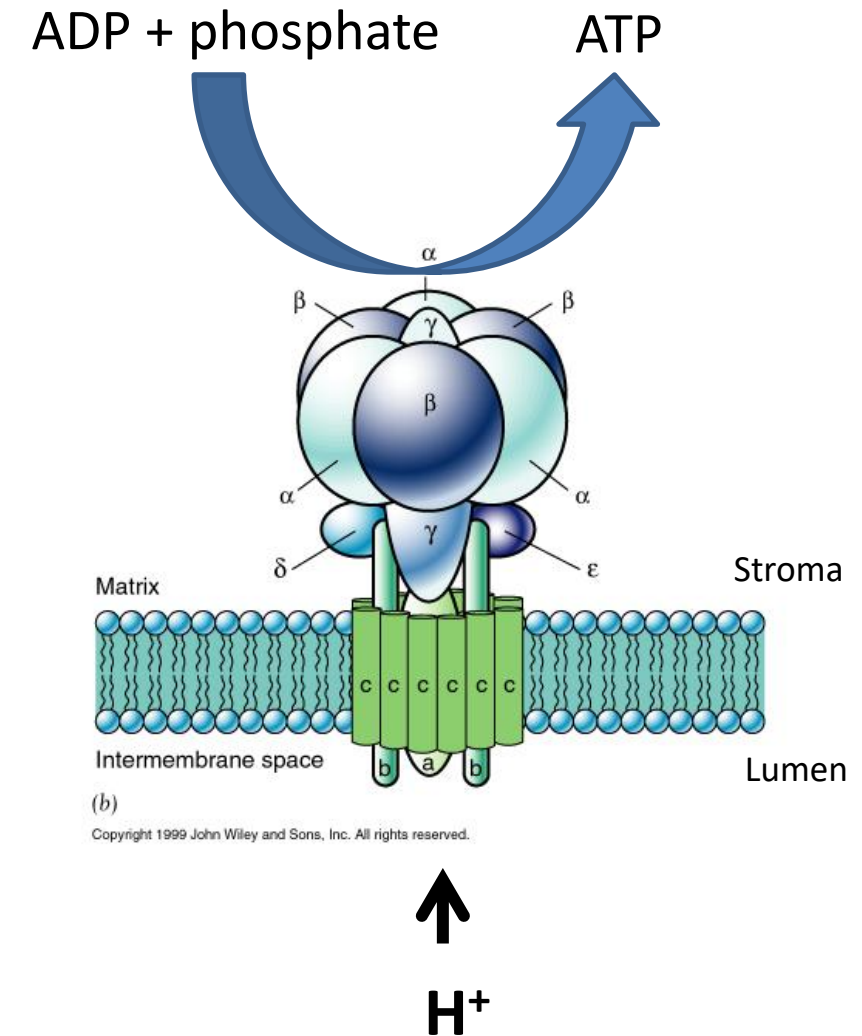


12 protons being pumped in

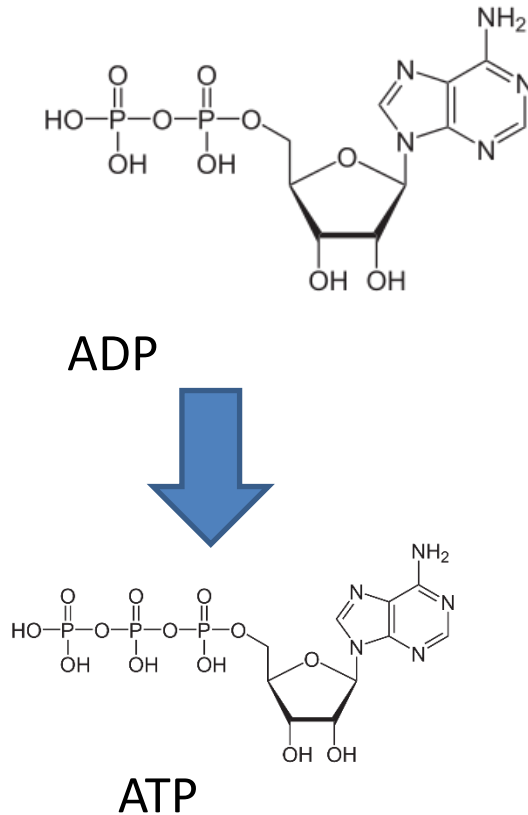
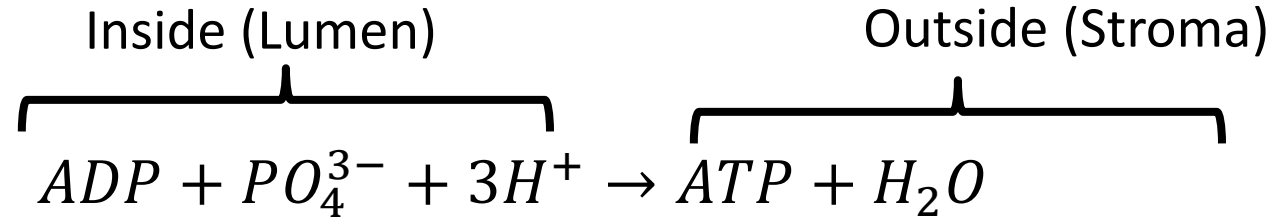


ATP-Synthase

- When the protons go through ATP synthase, it basically rotates the molecule.
- In theory it takes 9 H^+ to form a complete rotation, and this produces 3 ATP molecules.
- In reality it is 4 H^+ going through the ATP. 1 H^+ is necessary for charge balancing



ATP



Gibbs Free Energy

- For this reaction $\Delta G_{Eq} = 30.5 \text{ kJ/mol}$.

$$\Delta G = RT \ln \left(\frac{[Products]}{[Reactants]} \right)_{Lumen \text{ pH}} - RT \ln \left(\frac{[Products]}{[Reactants]} \right)_{Stroma \text{ pH}}$$

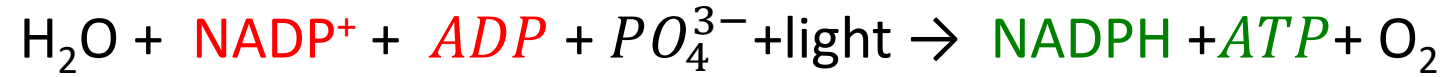
$$\Delta G = RT \ln \left(\frac{[Reactants]_{Lumen \text{ pH}}}{[Reactants]_{Stroma \text{ pH}}} \right)$$

$$\Delta G = 2.3RT * -\log \left(\frac{[H^+]_{Lumen \text{ pH}}}{[H^+]_{Stroma \text{ pH}}} \right)$$

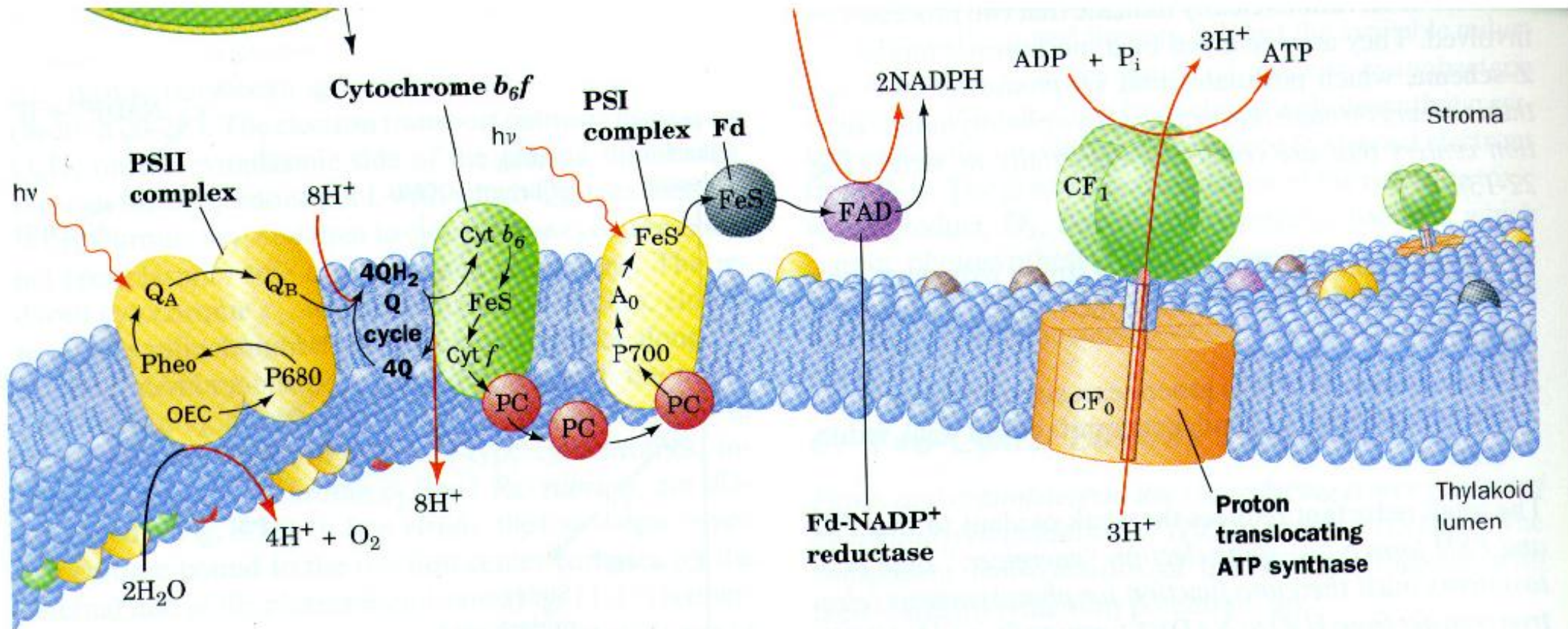
$$\Delta G = 2.3RT * \Delta pH$$

← pH variations provides ΔG driving force₃₇

Overall Reaction



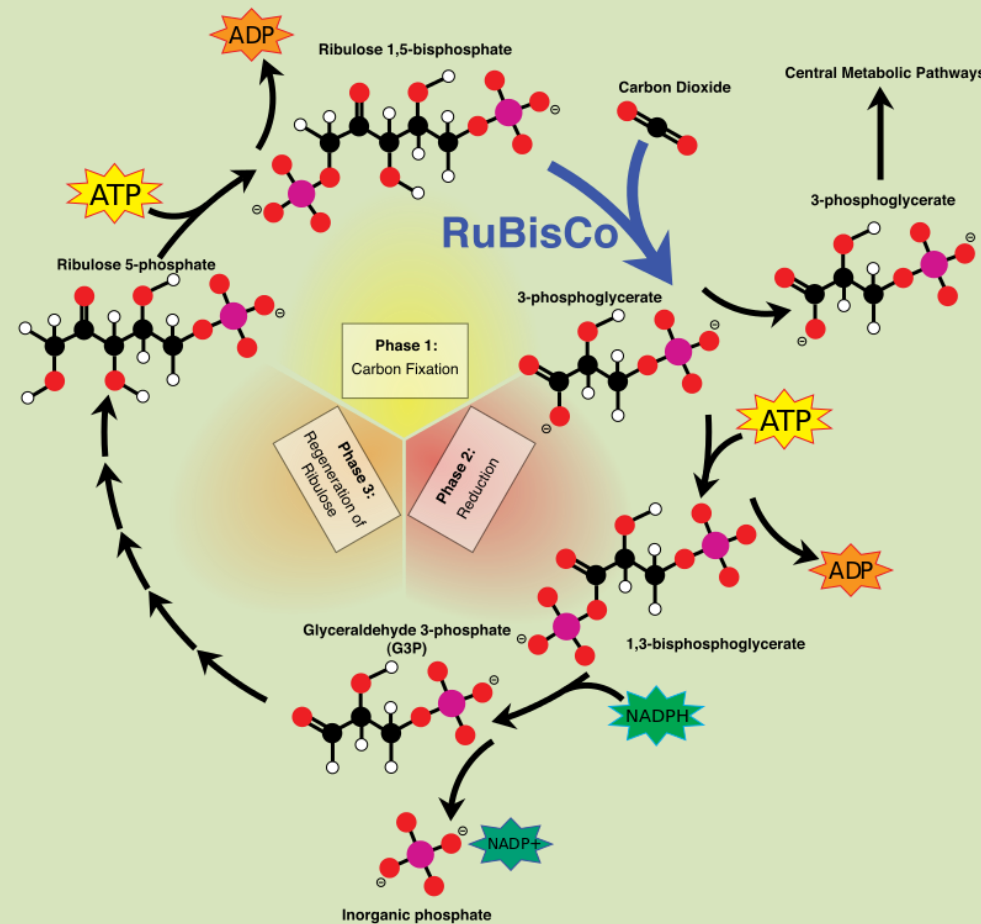
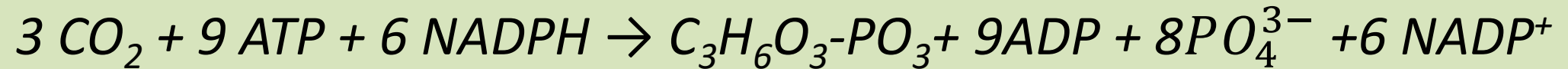
(Unbalanced Equation)



Non-Photosynthesis Reactions (Calvin Cycle)

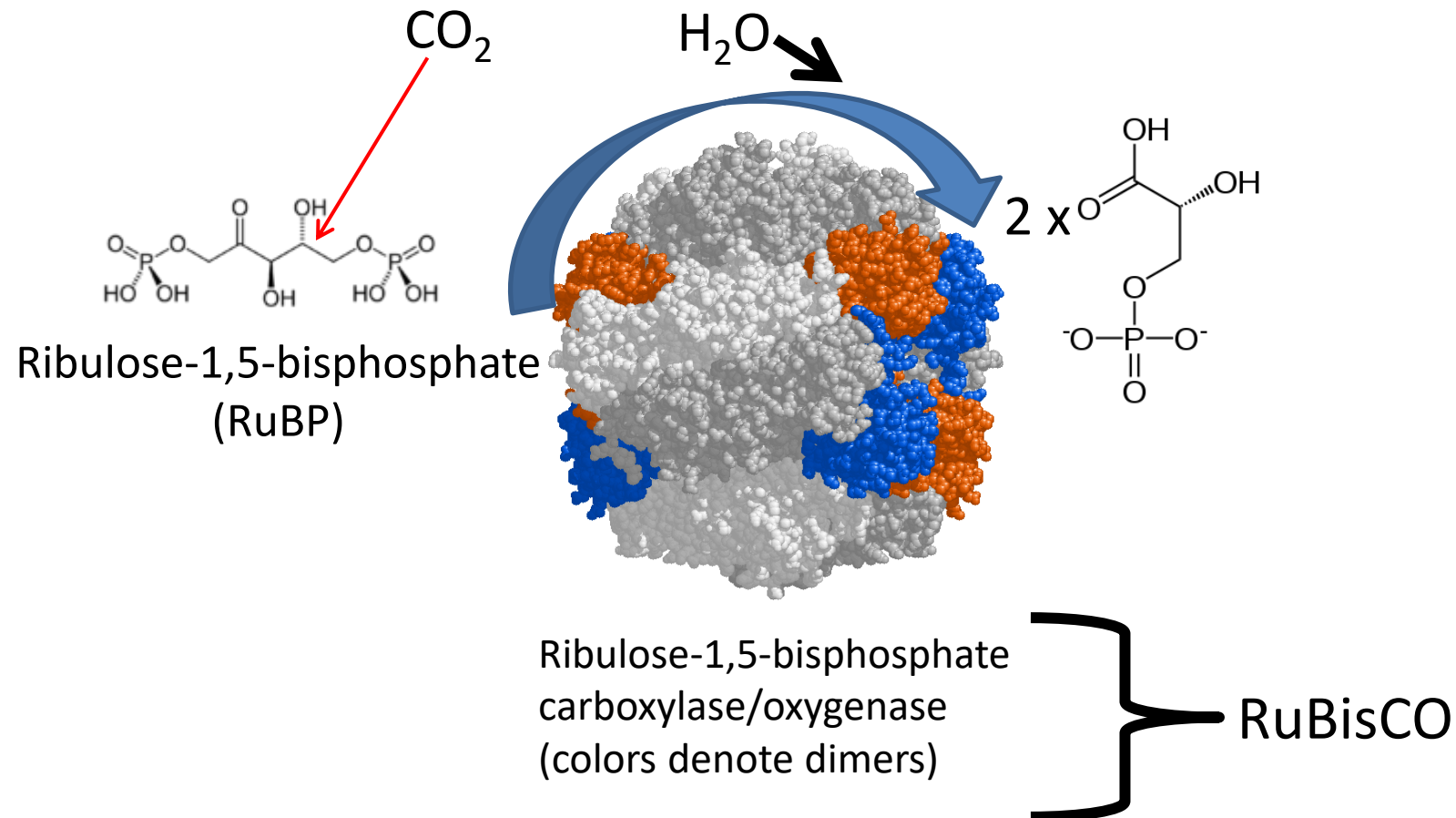
Calvin Cycle

- The Calvin cycle converts CO_2 to hydrocarbons with ATP and NADPH.



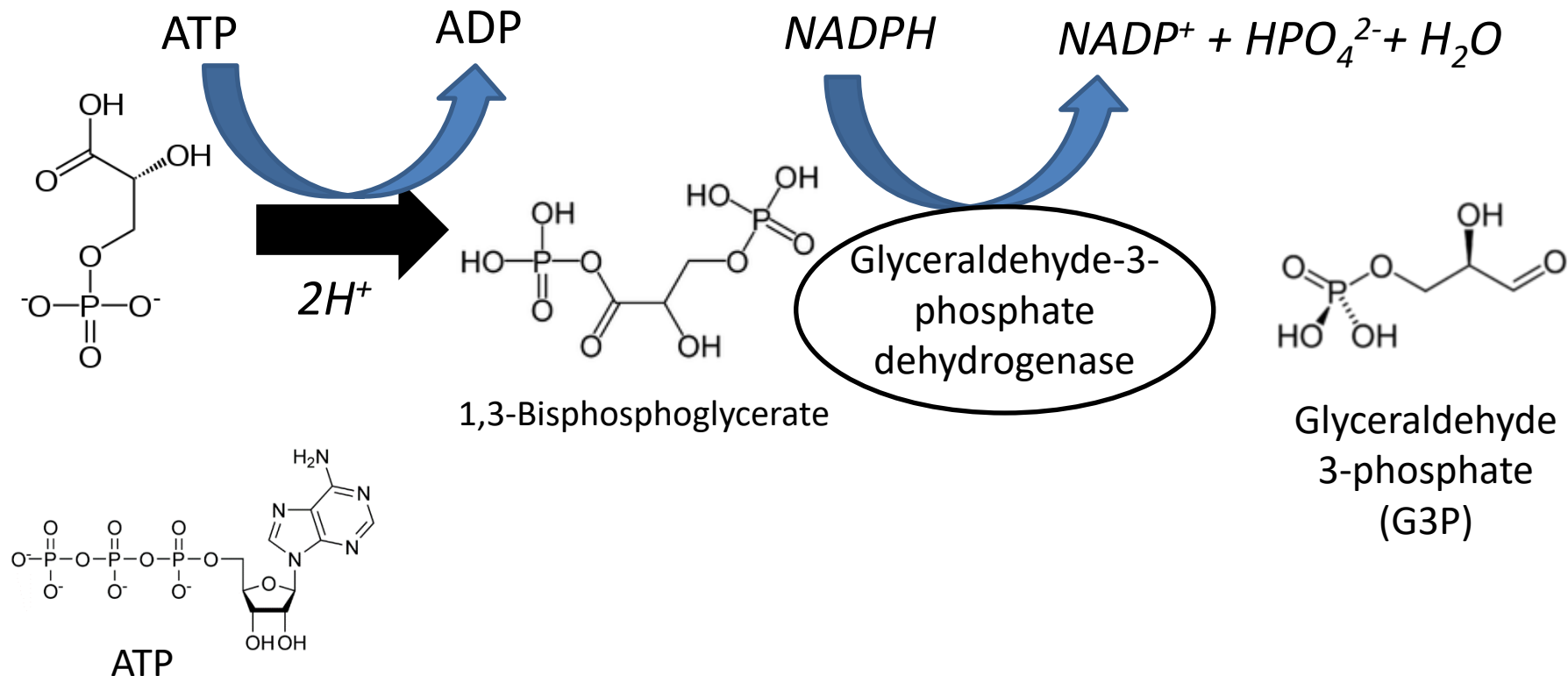
CO₂ adsorption

- The CO₂ basically splits a RuBP into 2 molecules.
- $\Delta G = -35$ kJ/mol.



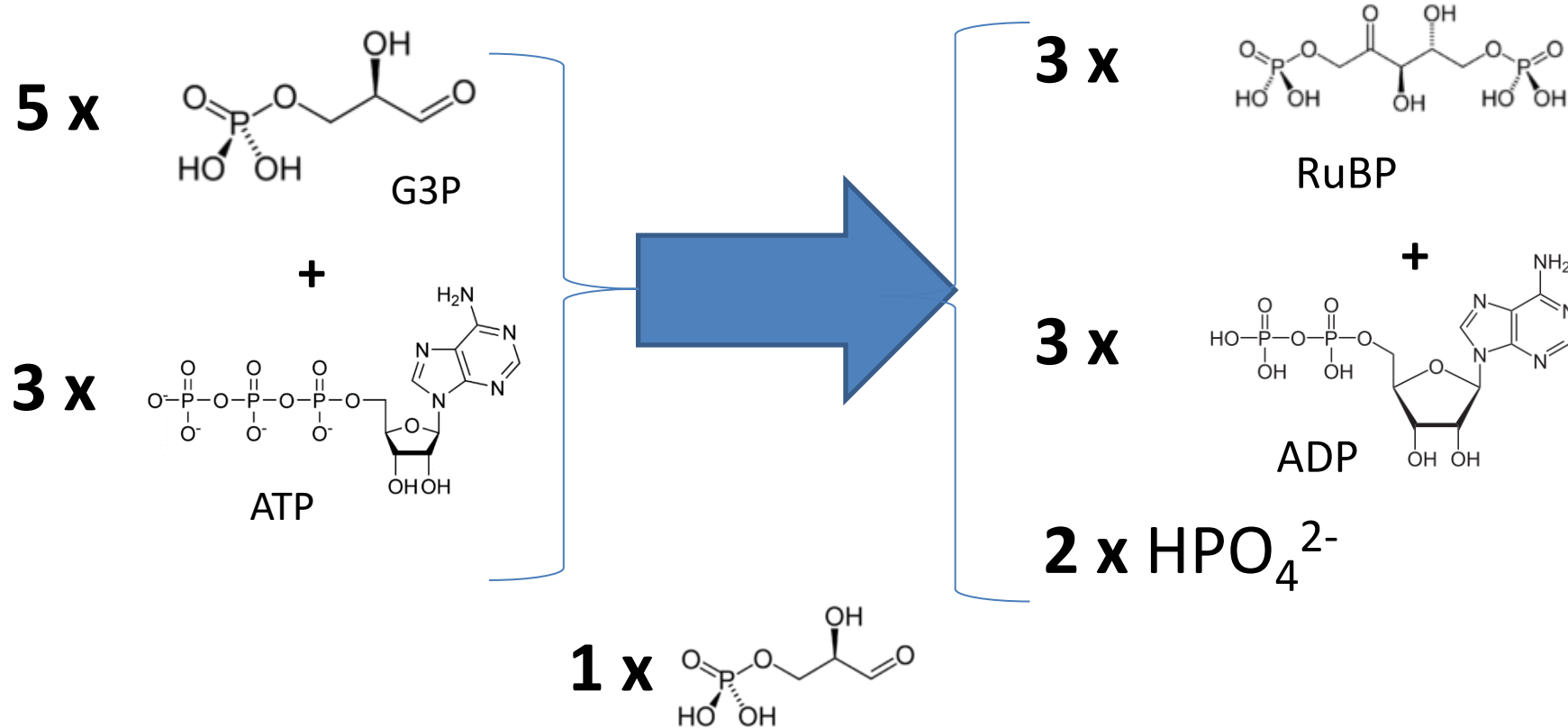
Getting to G3P (i.e. 1/2 a glucose)

- ATP efficiently attaches phosphonate group.
- NADPH replaces the phosphate group with an aldehyde
- Basically, a lot of work to transform a carboxy group to an aldehyde

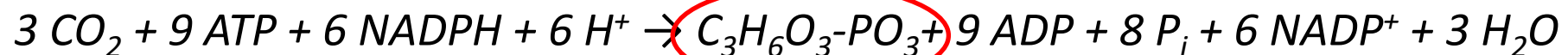


Regeneration of RuBP simplified

- The reaction below is for 3 absorbed CO_2 molecules.



Overall Reaction



↘ This is what we gain (for 24 photons)

G3P- Where to go from here?

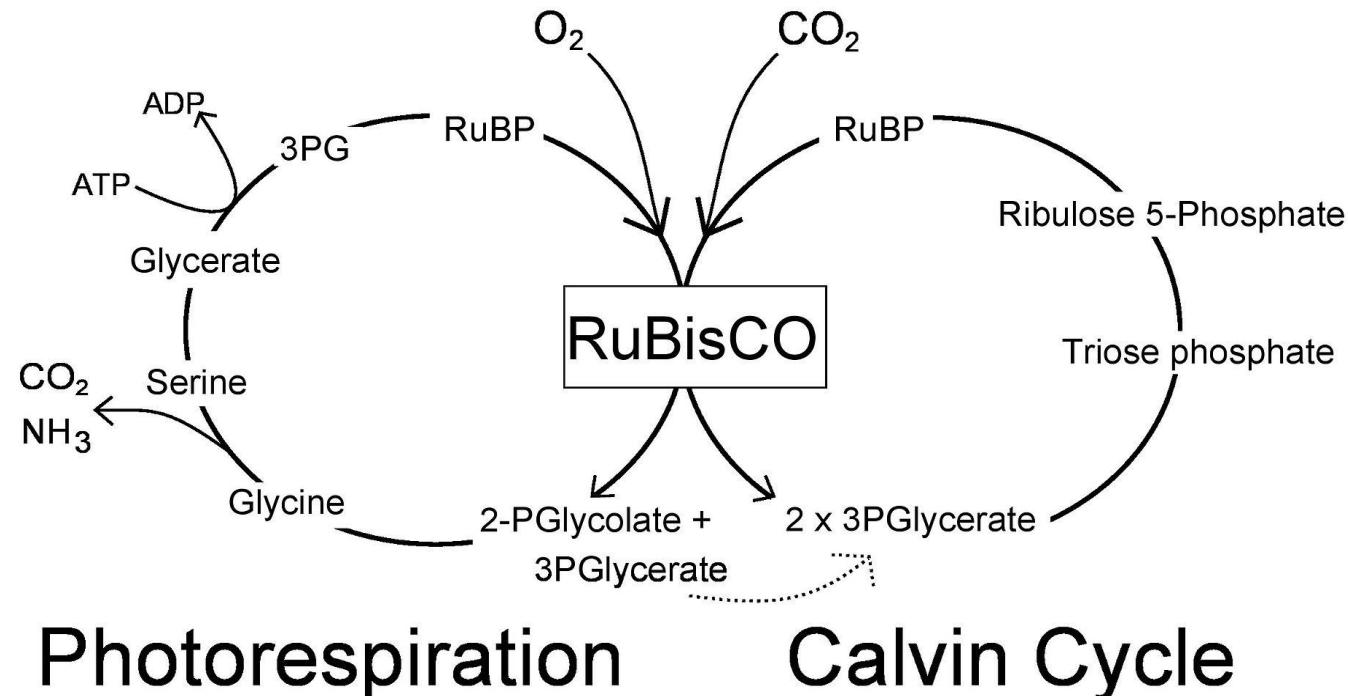
- The molecule G3P ($C_3H_6O_3-PO_3$) normally does 1 of 2 things:
 - Stays in the chloroplast and forms starchs (polymers)
 - Goes to a Cytosol enzyme to become glucose, sucrose, fructose etc.
- How this G3P is used is highly dependent upon the plant.
 - For our sake we want this to provide as much useable energy as possible
- At this point Engineering starts taking over from Biology (i.e we are looking to maximize Biomass production)

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Photorespiration- O_2 causing trouble

- Photorespiration is simply O_2 reacting with RuBP- CO_2 molecule while in the RuBisCO enzyme.
- This process happens about 40% of the time, thus really hurting efficiency.

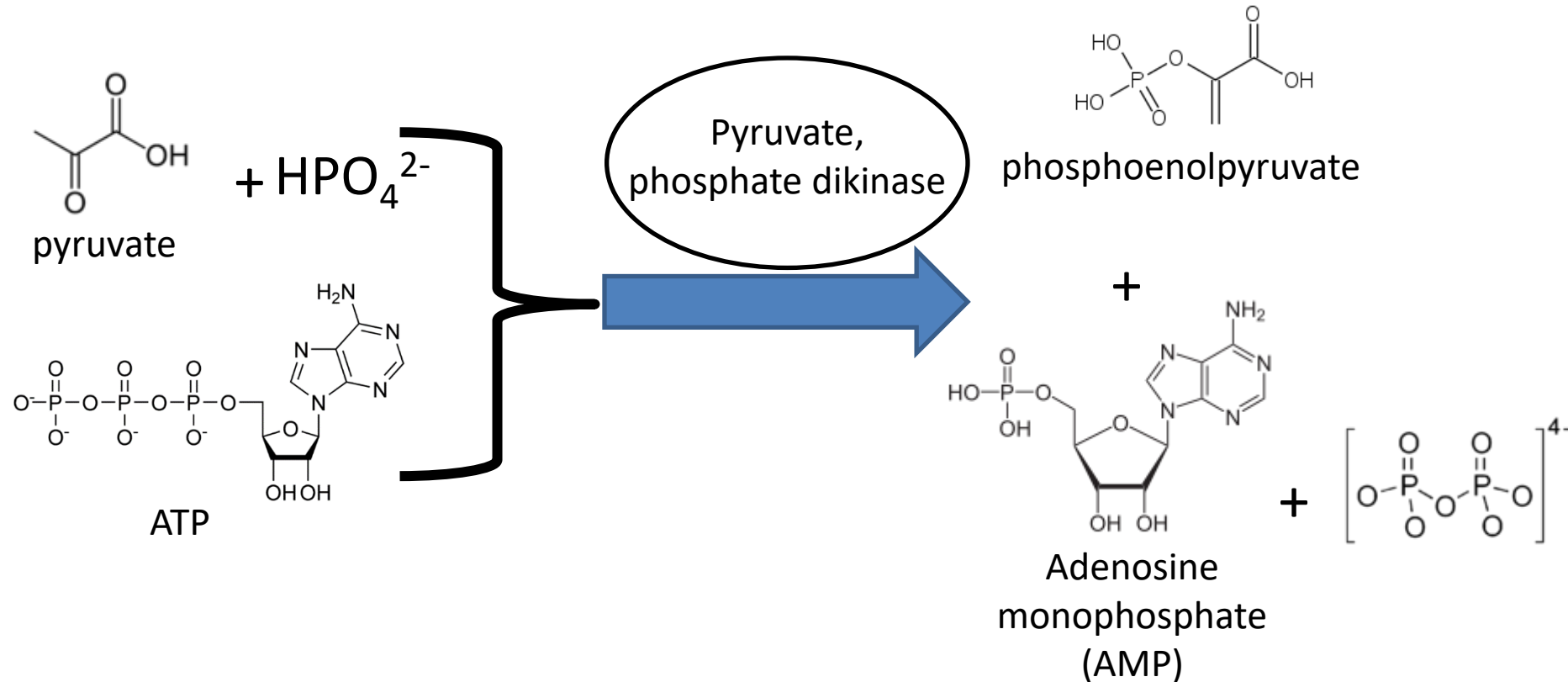


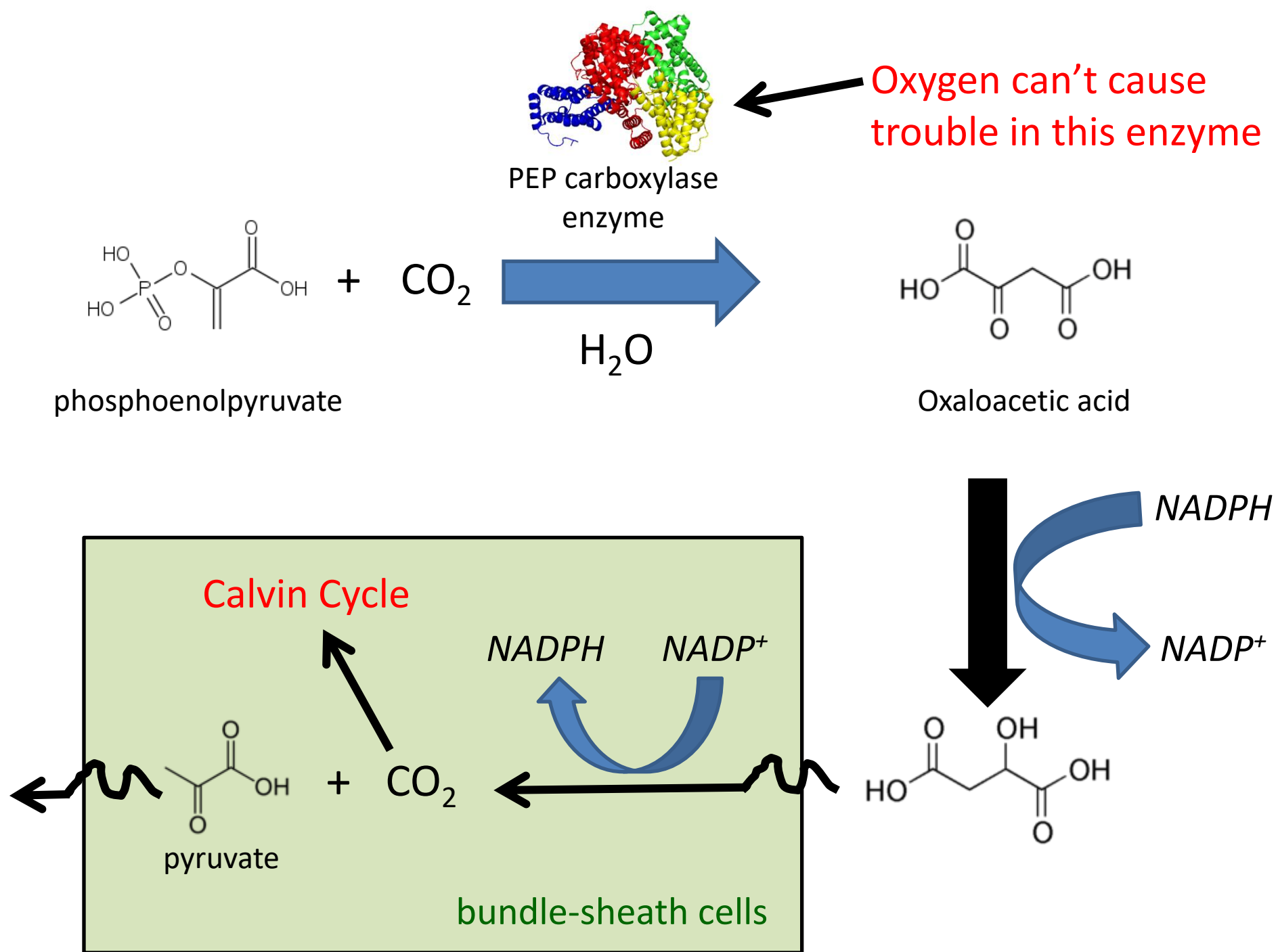
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C₄ Photosynthesis

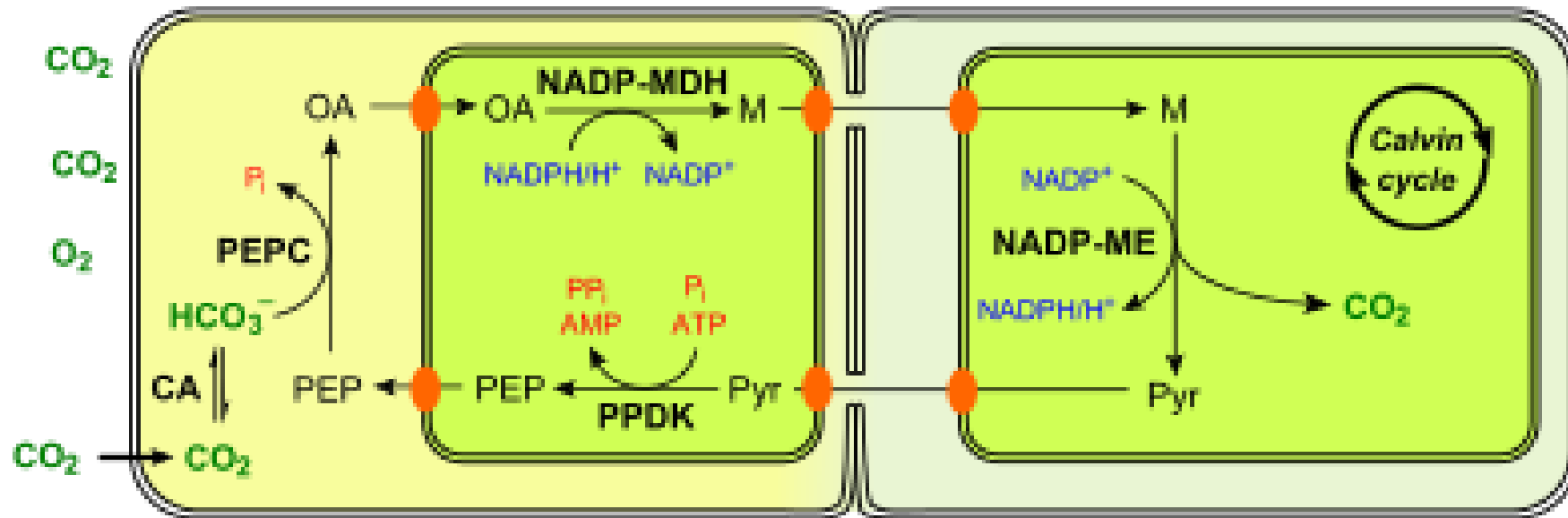
- C₄ is an evolutionary new mechanism that uses a 4 carbon chain instead of a 3 carbon chain.
- Only 3% of all plants use this mechanism.



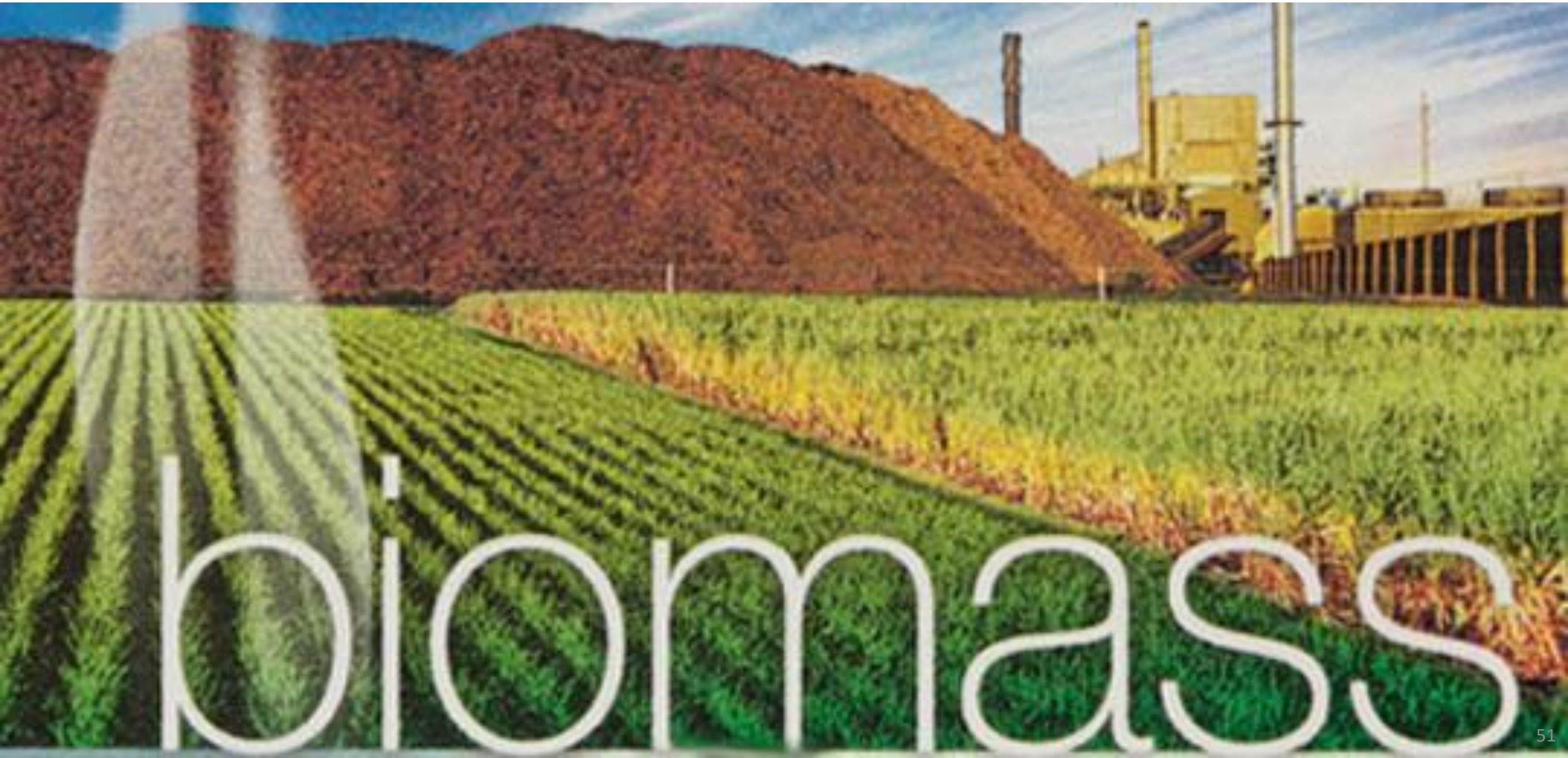


C₄ Photosynthesis

- To fix 1 CO₂ molecule
 - For C₃ you need 3 ATP and 2 NADPH
 - For C₄ you need 5 ATP and 3 NADPH
- C₄ does not get effected by O₂
- C₄ can 'upconcentrate' CO₂



Biomass –Use of Photosynthesis

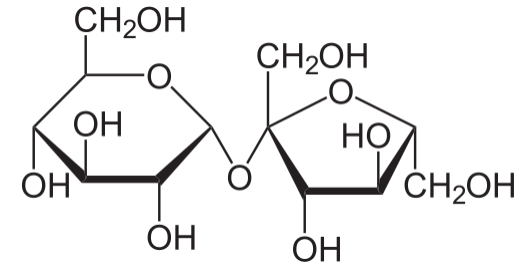


Land usage & Food issues

- The realistic efficiencies of 1-3% means we need much more land than for solar cells with 20% efficiency. However photosynthesis is basically free.
- Food production is a very sensitive issue since everybody needs this.
- There are two major groupings of biomass
 - 1st generations- biomass that is made from food crops
 - 2nd generation- Celluostic or woody biomass (i.e. non-food crop)

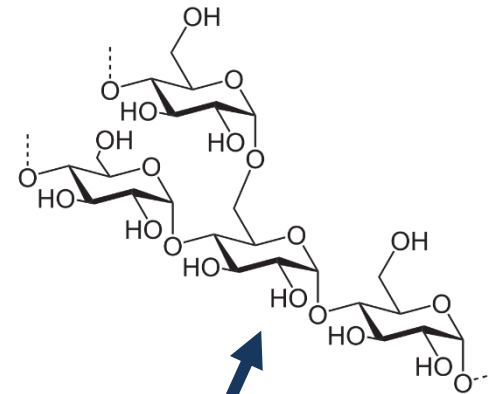
1st generation biomass

- Our bodies can easily break down these materials, thus they are easy to work with from an energy/chemical standpoint.



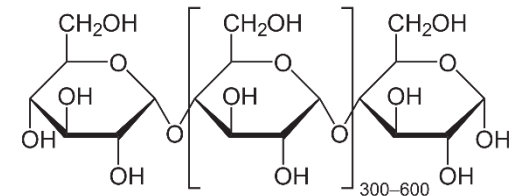
Sucrose

- Sugarcane (sucrose)
 - Mostly Brazil
 - C4 photosynthesis
 - Quite efficient



Starch:

~75 %

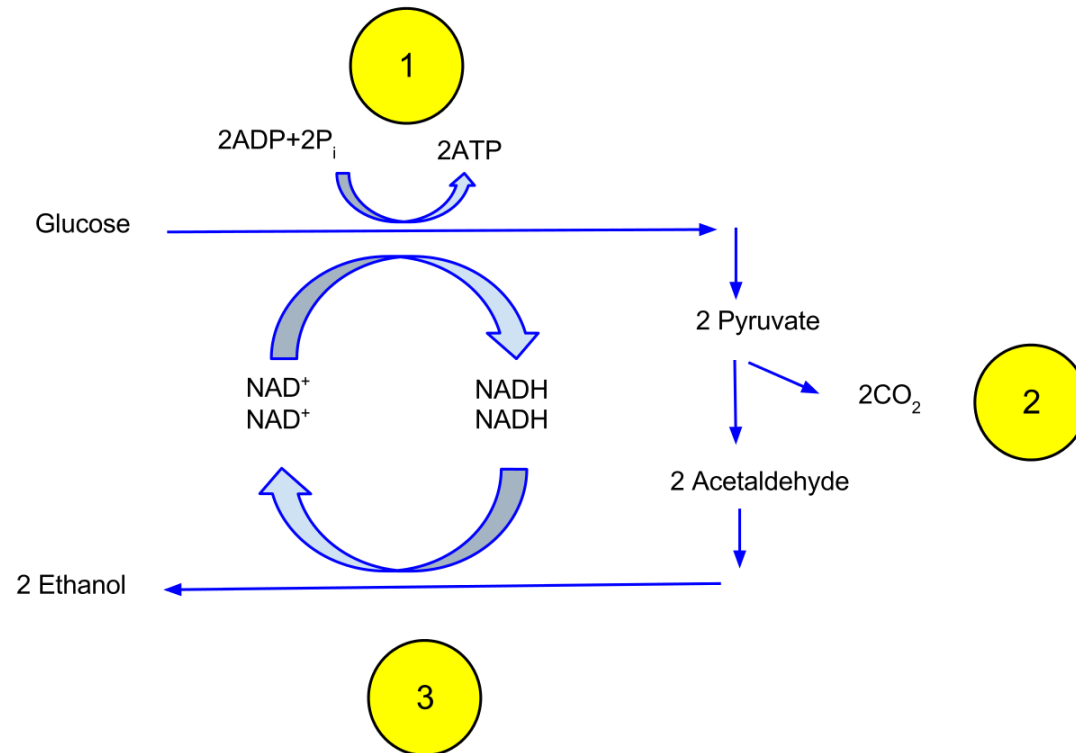


~25%

- Corn (starch)
 - Mostly US
 - C3 photosynthesis
 - Politically appealing (Democrats: renewables , Republican: help farmers)

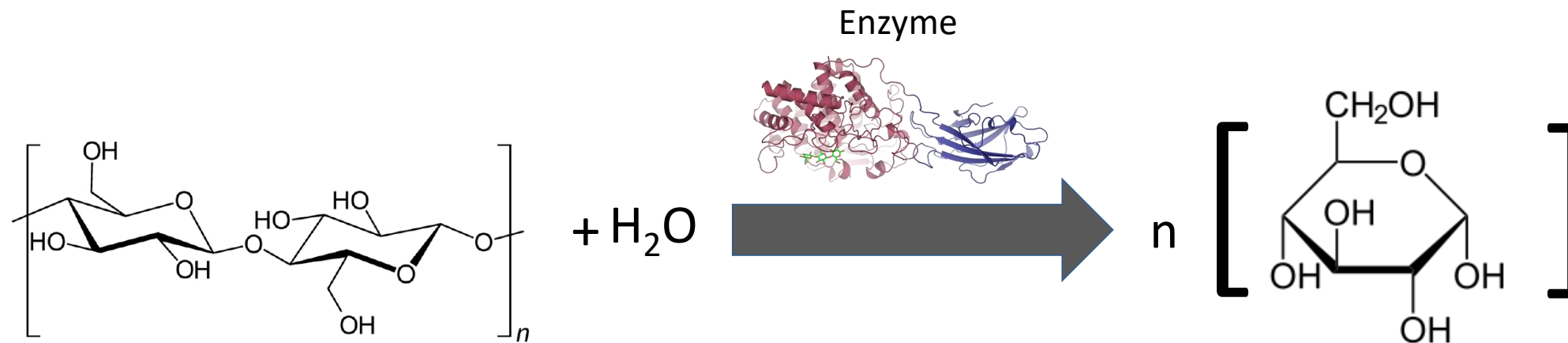
Ethanol Fermentation

- Breaking simple sugars down into glucose allows us to ferment them via the process below.
- Ethanol production uses many of the same entities as used in photosynthesis.
- There is a **1:1 ratio of ethanol:CO₂** when converting glucose.

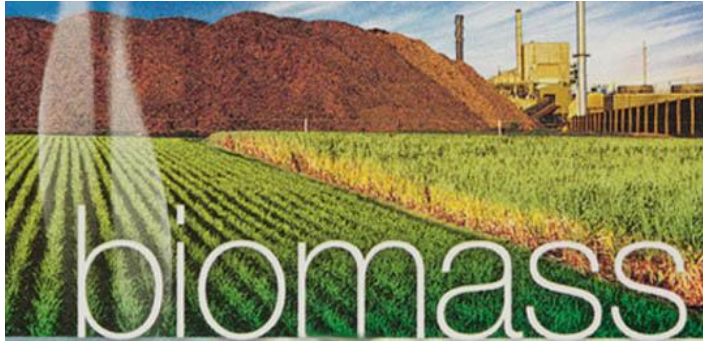


2nd generation biomass - Cellulose

- Basically glucose molecules together attached with an ether bond.
- 90% of cotton and 50% of wood.
- Hard to break down
- Hydrogen binding makes this more difficult to break down than you would expect.

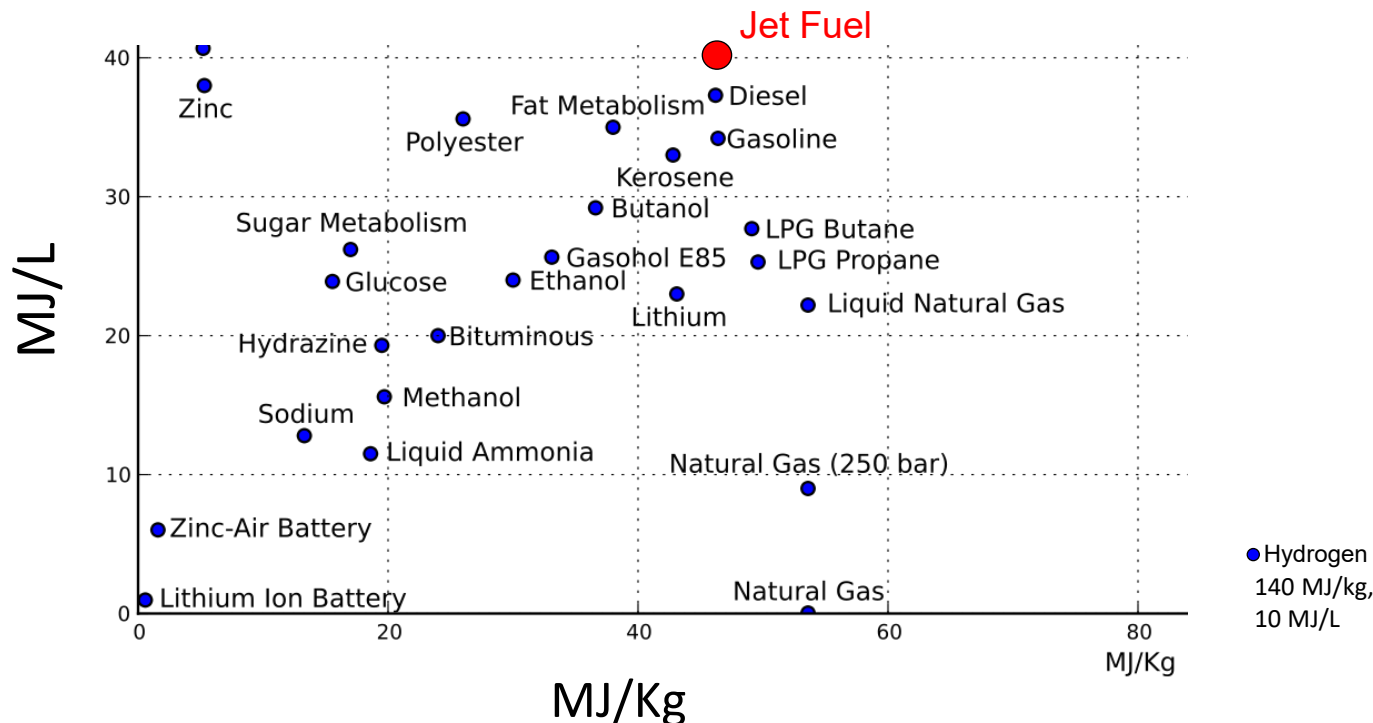


Chemical Conversions





Liquid Fuels - Jet fuel

- At takeoff, 25-45% of the initial weight of the plane is fuel.
- Energy density is everything for airplanes (i.e. no batteries, H₂ needs 4x volume)
- They get anywhere from 32-42 km/L per airplane seat.
- 2.8% of CO₂ emissions are from aviation.



Liquid Fuels - Shipping

- Shipping consists of [2%](#) of global CO₂ emissions.
 - Ships use 'Bunker Fuel', which is the nasty oil remains that no other industry wants. (Emission regulations are less in the sea)
 - Mærsk is the biggest company in Denmark, and the 2nd biggest shipping company in the world (~15% market share)
 - 3 Approaches:
 - Biofuels
 - Ammonia
 - Methanol
- [Center for zero carbon shipping](#)
- 
- 

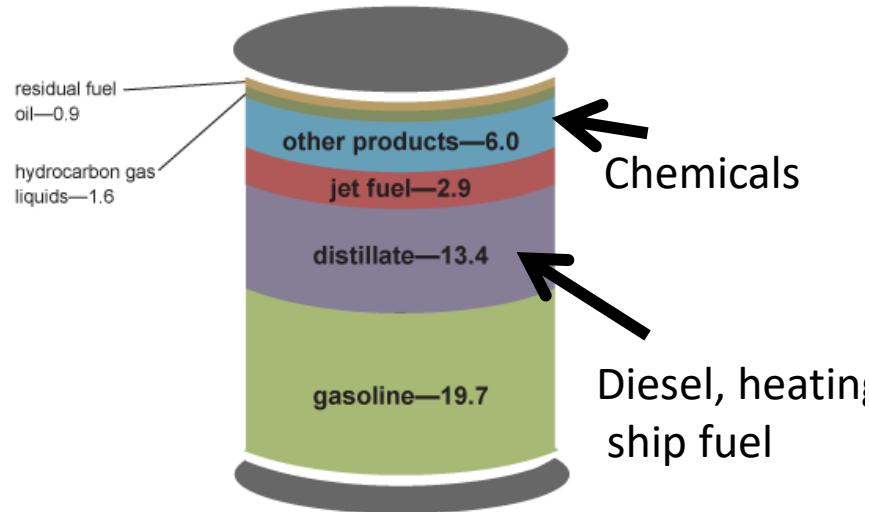
Center for zero carbon shipping



Chemicals

- Chemicals contribute directly to 5% of our energy use
- Indirectly chemicals need to be heated for catalytic conversion to the right molecules

Oil Breakdown

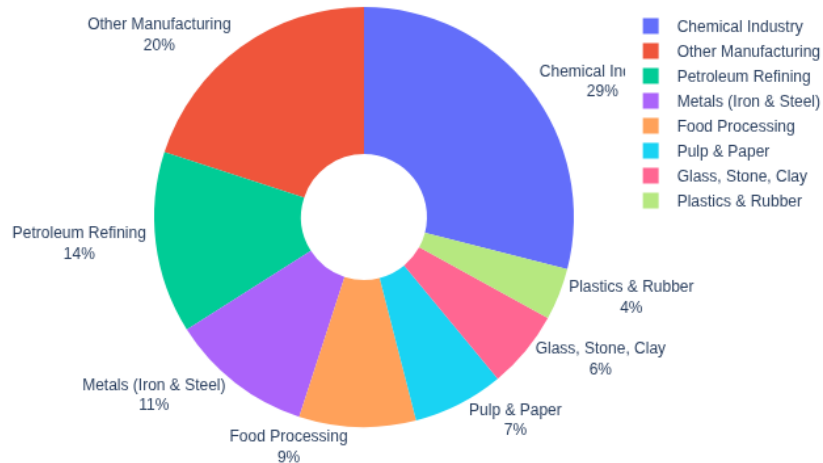


Note: A 42-gallon (U.S.) barrel of crude oil yields about 45 gallons of petroleum products because of refinery processing gain. The sum of the product amounts in the image may not equal 45 because of independent rounding.

Source: U.S. Energy Information Administration, *Petroleum Supply Monthly*, February 2021, preliminary data

Natural Gas Breakdown

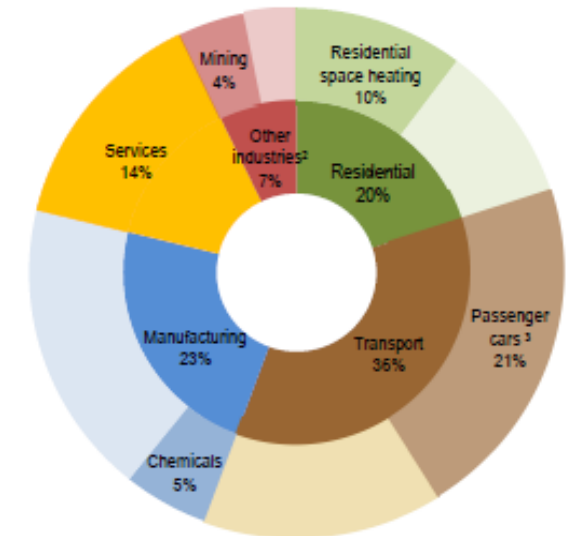
Global Industrial Natural Gas Use by Sub-sector



Based on IEA data from 2023

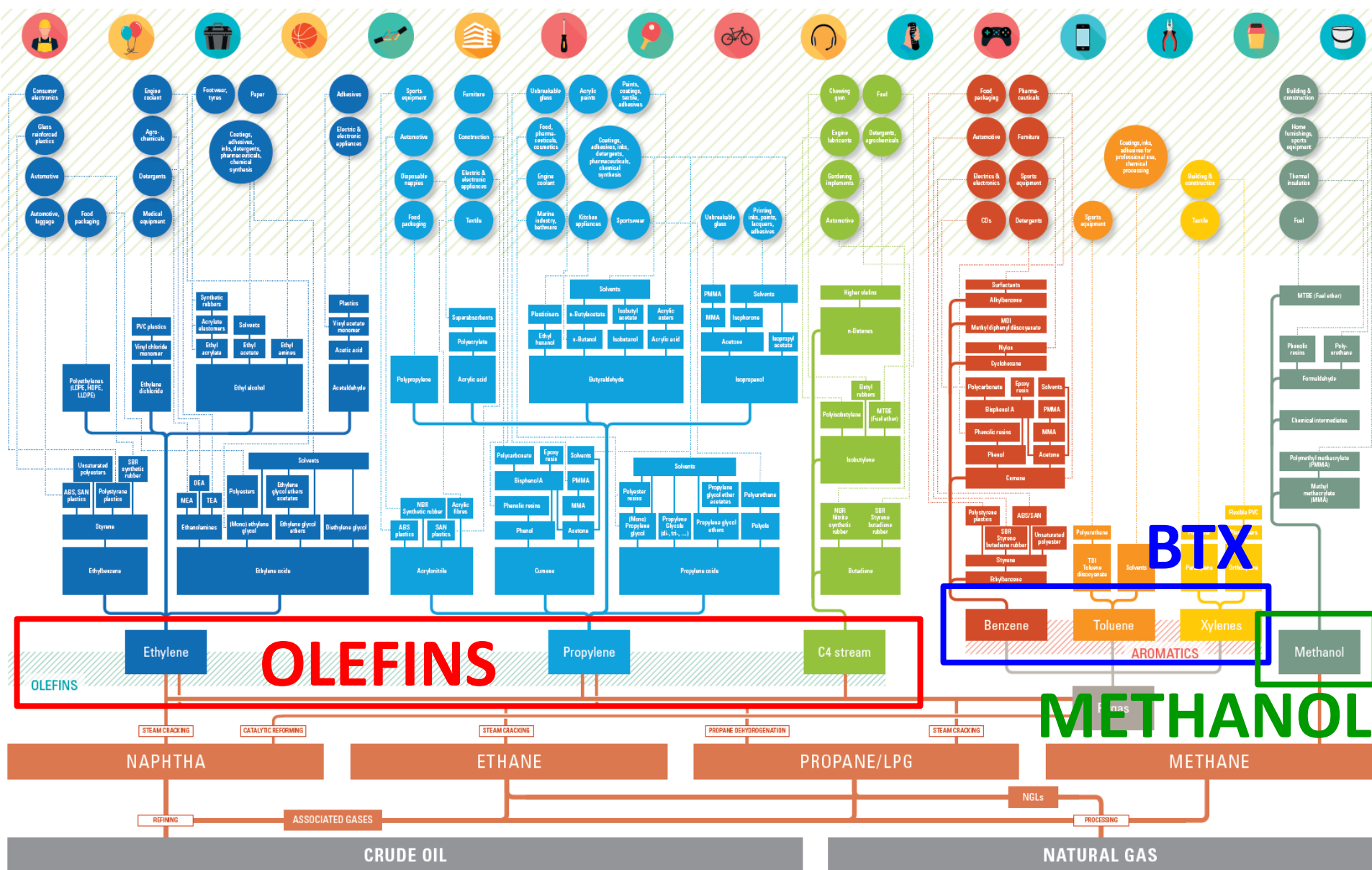
Figure made via Copilot

Overall Energy Breakdown



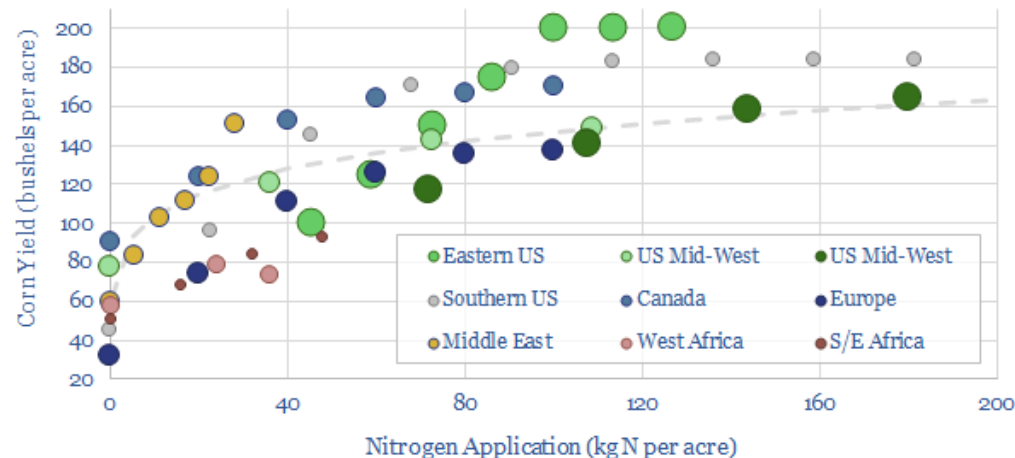
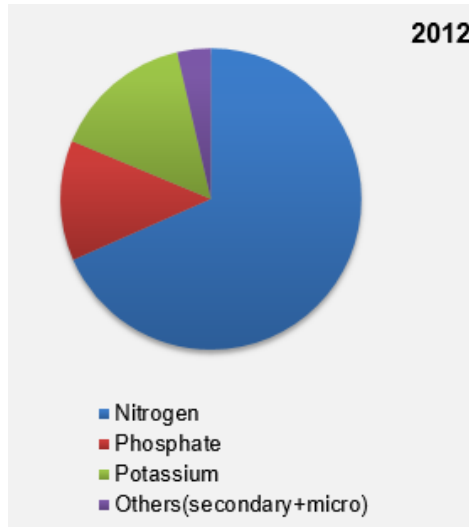
Based on IEA report from 2020

The petrochemical tree

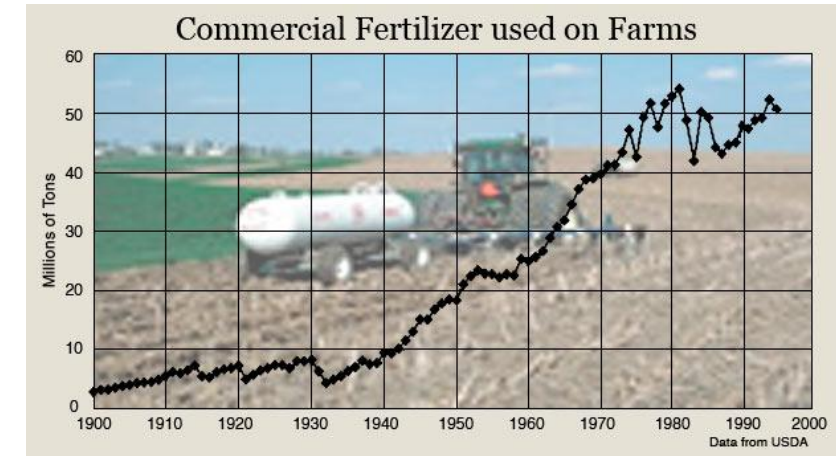


Fertilizers

- The majority of fertilizers are NH_3 or NH_3 -based (e.g., urea).
- This is essential for food production
- NH_3 production is based on fossil fuels.
- ~1.5 % of world's energy goes to NH_3 production.¹



Thunder Said Energy



Based of USDA data

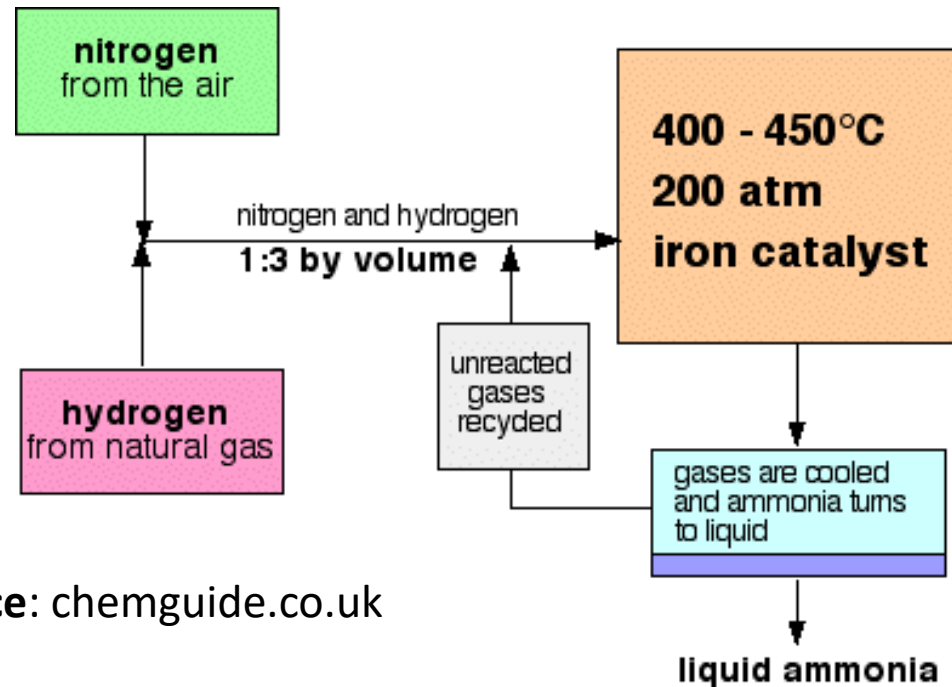
Haber-Bosch process

- Ammonia production is made almost exclusively through the Haber-Bosch process.
- It is also responsible for ca. 55% of worldwide hydrogen demand.



- The reaction is thermodynamically favored, but kinetically hindered.
- N_2 has a triple bond which is very hard to break.
- This conversion is typically conducted at a pressure of 150–250 bar and a temperature of 400–500 °C.
- **Increased pressure shift equilibrium to products due to Le Chatelier's principle.**

Haber-Bosch process



Source: chemguide.co.uk

- The industrial catalyst for the process is based on **Fe₃O₄**, with Al₂O₃, CaO and K₂O as modifiers (increased activity and stability).
- Ru is actually better catalyst, but it is much more expensive, so it is not used industrially.

Haber-Bosch process

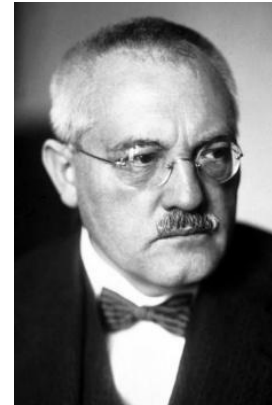
- In 1909, **Haber** synthesized NH_3 using an osmium catalyst , thereafter **Alwin Mittasch** found iron oxide to be almost as good (after 20 000 experiments!)
- **Carl Bosch**'s work in engineering and reactor design made it possible to operate industrially at the high pressures needed (1913).
- **Gerhard Ertl** earned the Nobel Prize for his surface science studies on elucidating the reaction mechanism of ammonia synthesis (2007).



Clara Immerwahr
First woman to earn a
chemistry PhD in DE



Fritz Haber
Nobel Prize in
Chemistry 1918



Carl Bosch
Nobel Prize in
Chemistry 1931



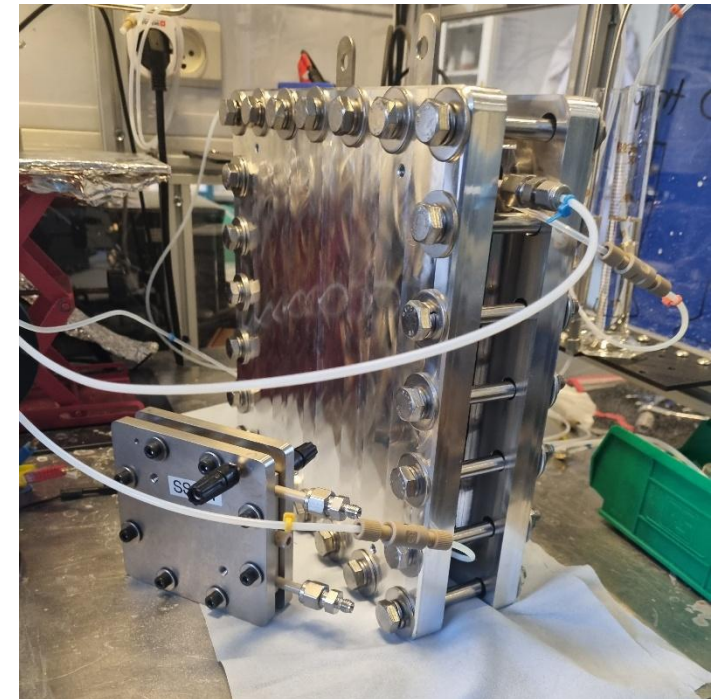
Gerhard Ertl
Nobel Prize in
Chemistry 2007

Nitrovolt

- A DTU startup is doing electrochemical ammonia production.

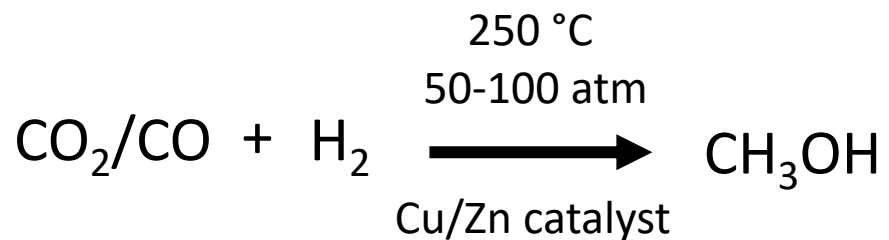
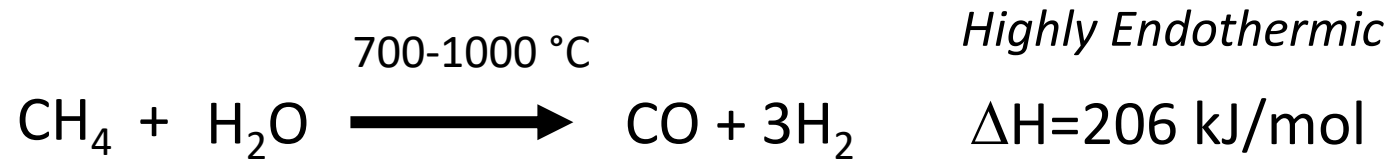


- The nitrogen first reacts with Li metal and then protons attach to the nitrogen to form ammonia.
- Their market is for places that need ammonia produced locally.
- They are not economically competitive with Haber-Bosch process



Methanol

- We use about 80 Mton of Methanol
- Currently methanol is derived completely from natural gas
- Methanol is a leading candidate for sustainable shipping fuel



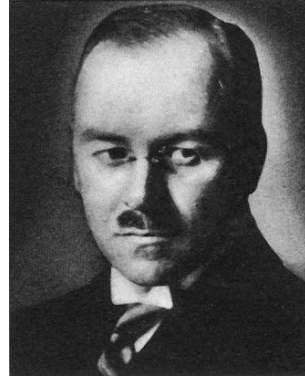
[Methanol Institute](http://MethanolInstitute.com)

Fischer-Tropsch Reaction

- This process was discovered in 1925, and used extensively in WW2 since Germany had coal, but no oil.
- Product distributions tend to favor longer chain carbons- Good for diesel & aviation fuels.
- The process is inefficient and struggles to produce small and mid-sized molecules.



Franz Fischer

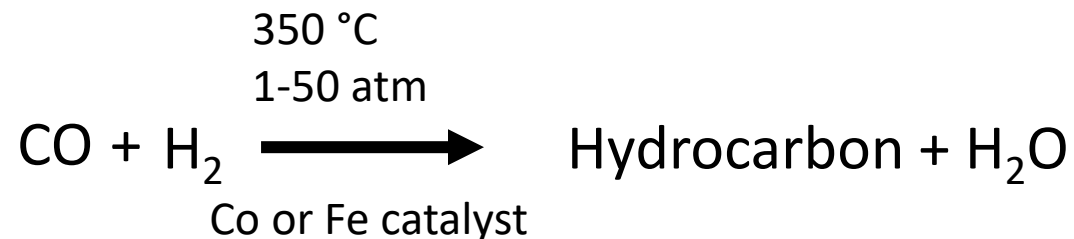


Hans Tropsch

*Reverse Water-Gas
Shift Reaction*



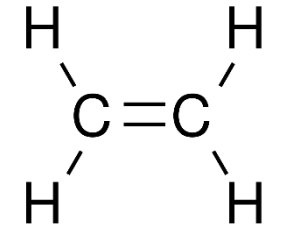
*Fischer-Tropsch
Reaction*



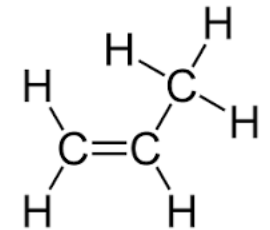
Highly Exothermic
 $\Delta H = -165\text{ kJ/mol}$

Steam Cracking

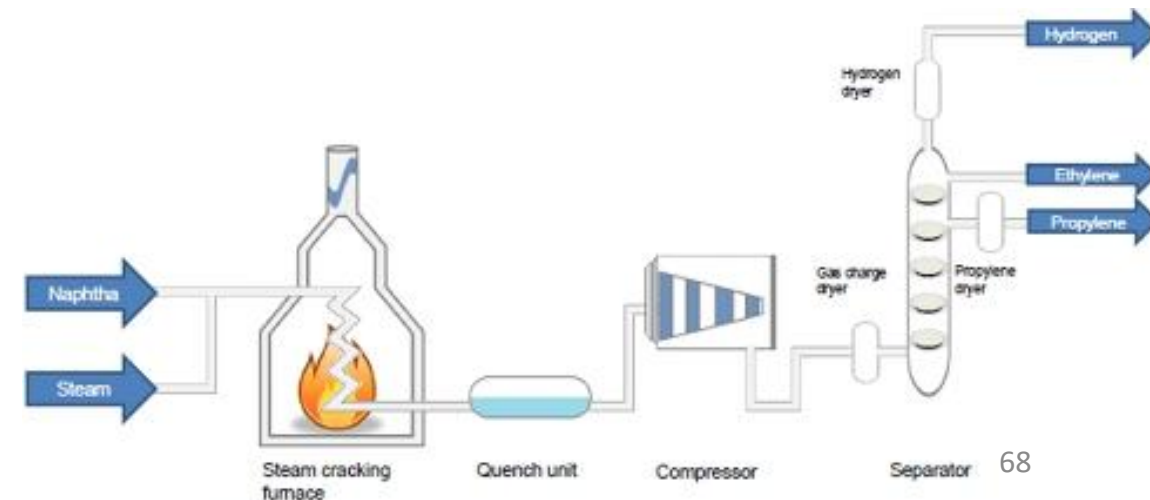
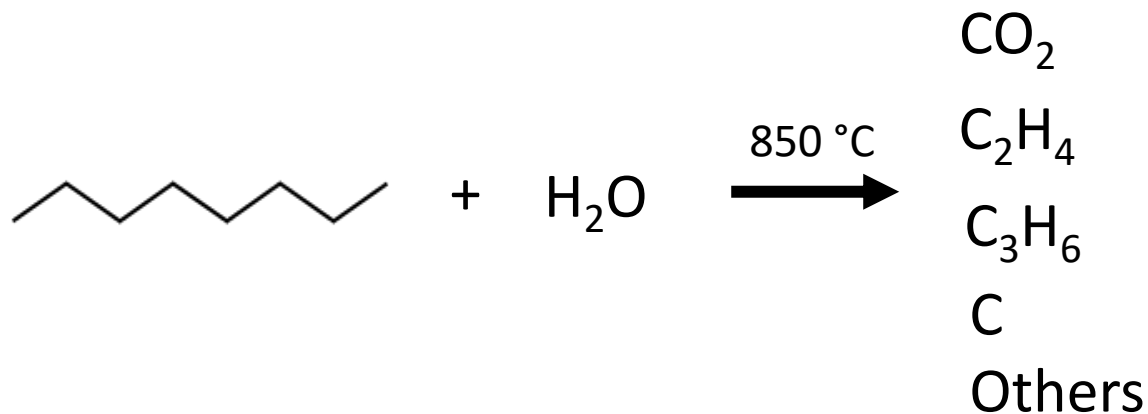
- The main method to make ethylene and propylene is through steam cracking of hydrocarbons
- This process is inefficient producing 1.0-1.6 kg CO₂/kg ethylene.
- We use about 180 Mton of ethylene, as poly-ethylene is the #1 plastic in the world.



Ethylene



Propylene



Summary

- Aviation needs liquid fuels (C10-C14 hydrocarbons), and shipping probably, but maybe methanol or ammonia would work.
- The chemical industry takes big molecules, breaks them into little molecules, and then builds back up to get the molecules we want.
- From CO₂ & H₂ Fischer-Tropsch reaction can basically get us back to oil products, albeit at some energy loss.
- From starting with only 8-9 molecules, we can get all the chemicals we need
- Ammonia and plastics are the two biggest chemicals.

Lecture - Learning Objectives

At the end of this lecture you should be able to:

- Understand the entire photosynthesis process and efficiency losses from light absorption to sugar production.
- Understand the Calvin Cycle.
- Know the major building block chemicals on which most of the chemistry industry is built on.
- Understand the basic materials in biomass
- Understand the primary chemical processes in converting biomass into useful chemicals and fuels.

Exercises

- What is the minimum pH gradient across the Thylakoid membrane assuming no catalytic losses in the ATP Synthase .
- If we spend ~ 48 photons (of wavelength 620 nm) to get one molecule of glucose, what is our thermodynamic conversion efficiency. What would our efficiency be for just the 620 nm light (Basically if we assume the sun just produces 620nm light)?