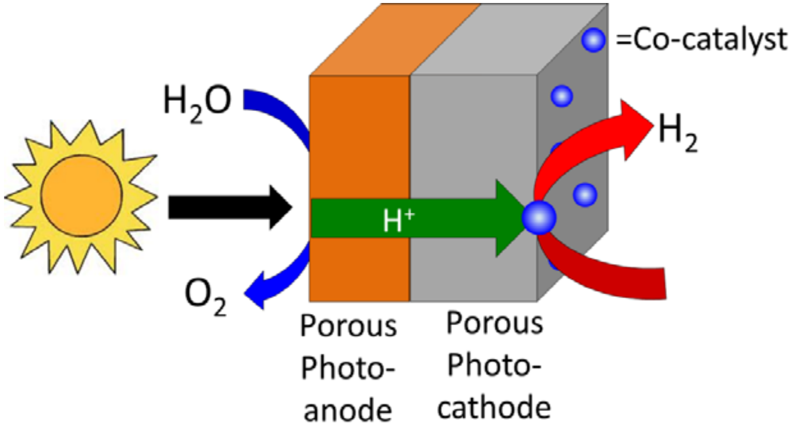
Photoelectrolysis & Photosynthesis



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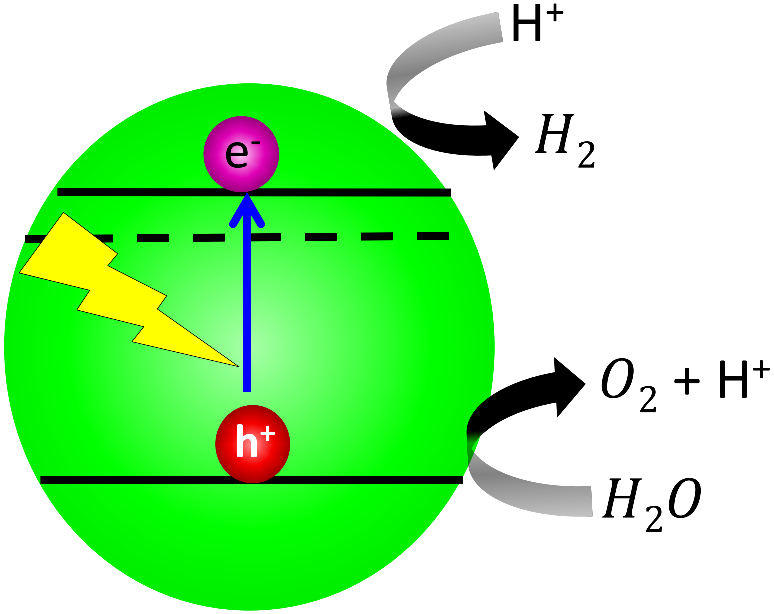
Lecture - Learning Objectives

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

- Explain the basic’s concepts relating to photoelectrochemistry.
- Understand the entire photosynthesis process from light absorption to sugar production.
- Understand why photosynthesis is as efficient/inefficient as it is.
- Understand the Calvin Cycle.

Photocatalytic water splitting

- This approach uses the sun's photons to take water and produce H_2 and O_2.
- Sometimes this is called the artificial leaf even though this produces H_2 not sugars. (A marketing major slipped into this field.)
- This effect was discovered in 1972 by Honda and Fujishima.
- They used a TiO_2 photocatalyst and also applied an electrochemical bias.
- There efficiency was much less than 1%.

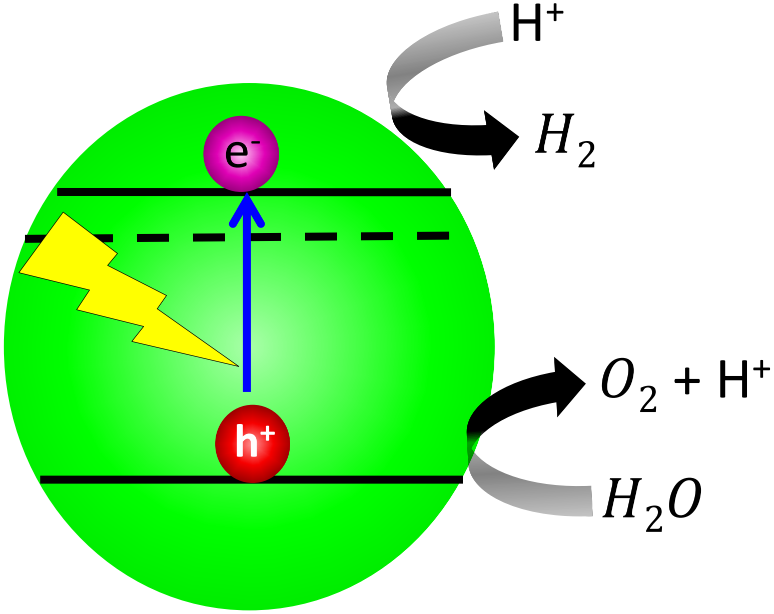


Photocatalytic water splitting

- In photovoltaics we care about power (P = iV).
  - The optimal semiconductor is a compromise between photocurrent and photovoltage.
- In electrolysis:
  - We need at least 1.23 eV + overpotential, but too much is just a waste.

- Taking into consideration,
  - Your knowledge of the solar spectrum
  - Your photovoltaic knowledge
  - Your electrolysis knowledge

What should be the band gap of an efficient photocatalytic water splitting material? What efficiency will that be?

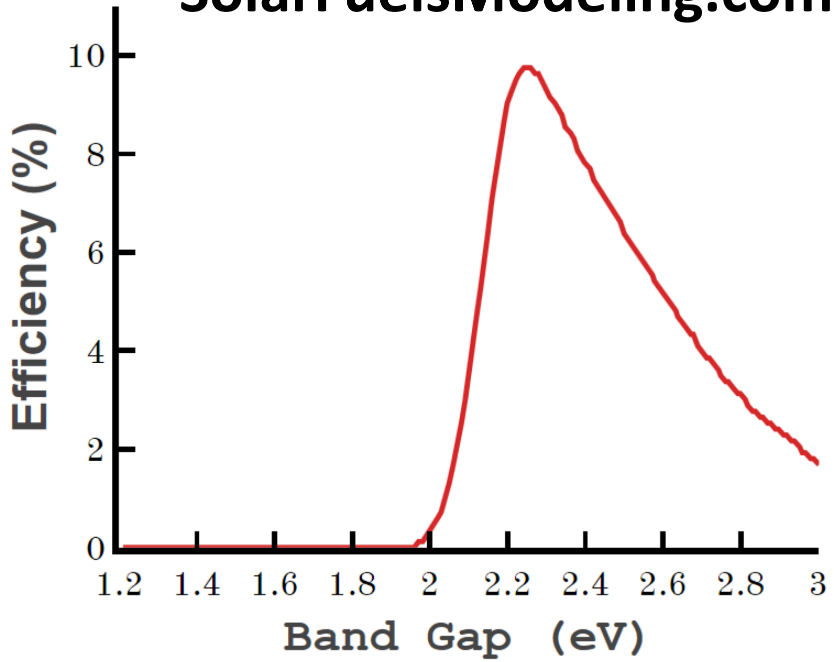


Overall water splitting

- From today we realized we need 1.23 eV plus:
  - 300 mV for anode (scaling relationship)
  - 50 mV for cathode
  - In this situation ionic and ohmic conductivity should not be an issue
- From photovoltaics the photovoltage is the band gap minus:
  - 300 mV due to thermodynamics
  - ~100 mV to get a decent current

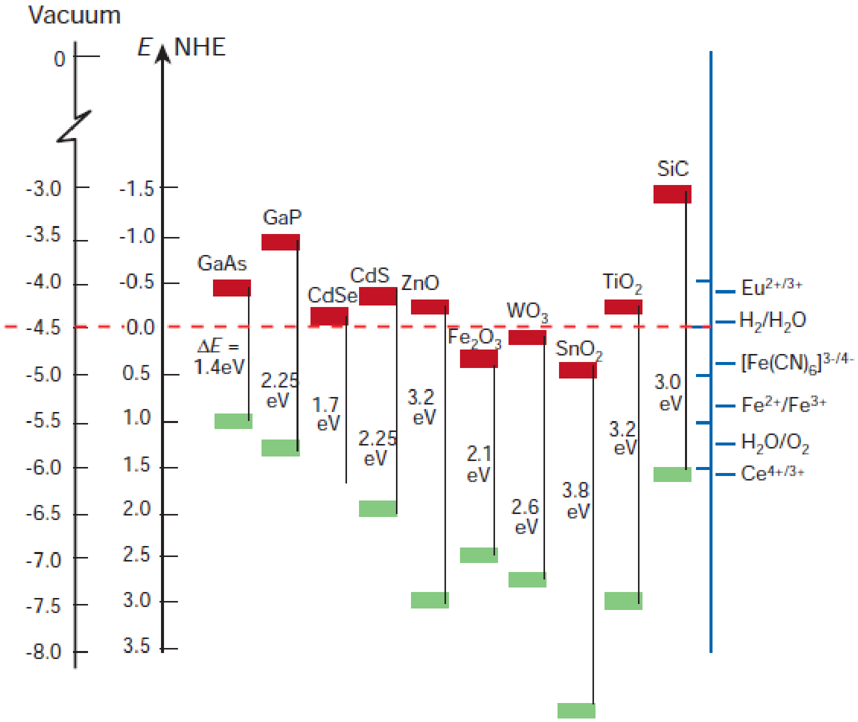
- Thus we need a bandgap of 2.0 eV if we optimize everything.
- In reality we are looking at 2.2-2.3 eV.

SolarFuelsModeling.com



Energy alignments

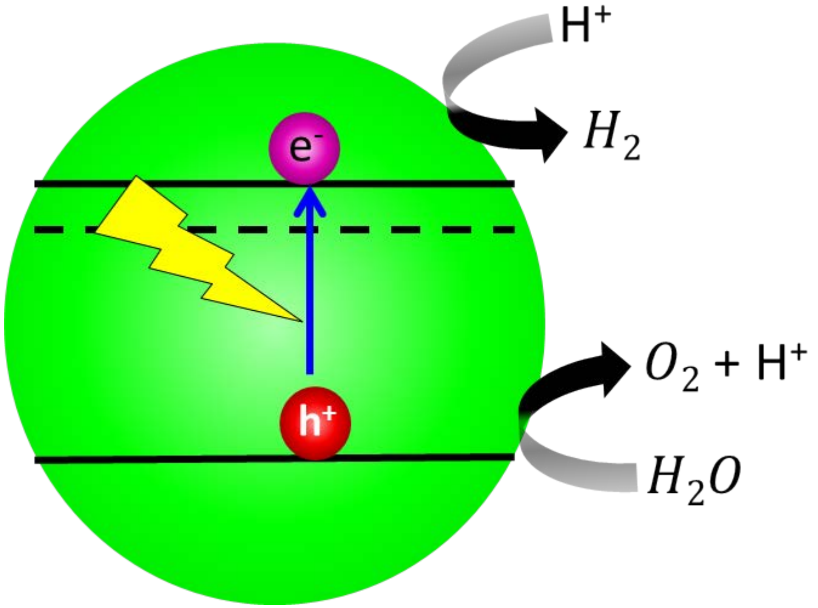
- When water comes into contact with a semiconductor, the surface dipole interaction sets the semiconductor potential relative to H^+/H_2.
- Thus each semiconductor will have it's valence and conduction band at various locations.
- For water splitting:
  - The conduction band needs to be higher than the H^+/H_2 potential.
  - The valence band needs to be lower than the H_2O/O_2 potential.



Gratzel, 2001, Nature

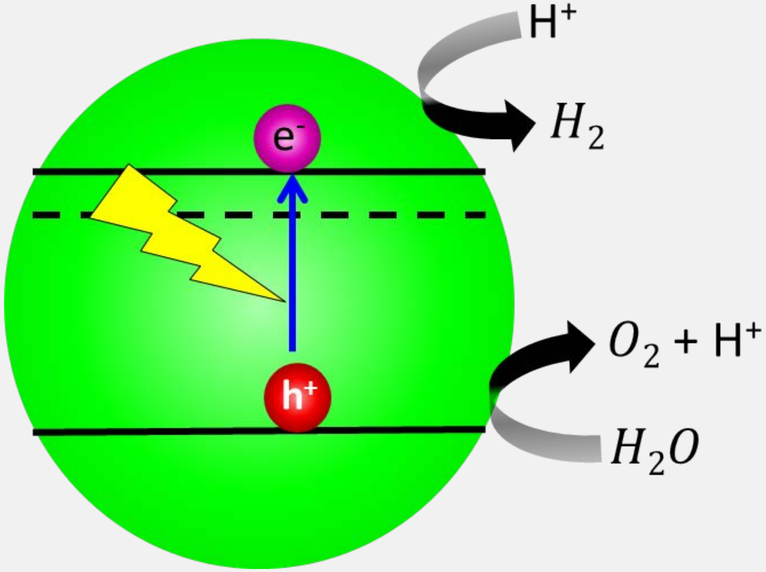
Water splitting by particles

- This is inherently a cheap method because you can use nanoparticles dispersed in water rather than aligned films.
- Since both H_2 and O_2 happen on the same particle ionic conductivity losses are also minimized.
- With no ionic conductivity issues we can run at neutral pH.
- There is lots of surface area, thus lots of recombination
- There is no band bending to separate charges.
- Recombination of gases can be an issue



Water splitting by particles

- How does the electron and hole get to the surface?
- The particles typically are too small to have band bending.
- Since the particles are so small, diffusion can lead them to the surface. This area hasn't been researched that thoroughly.
- While having lots of surface increases the H_2 and O_2 reaction area, it also increases the h^+-e^- recombination rate.
- Smaller particles (i.e. higher surface area) is a double-edged sword.



Recombination of gases

- We are producing H_2 and O_2 right next to each other.
  - Not exactly a safe combination of gases

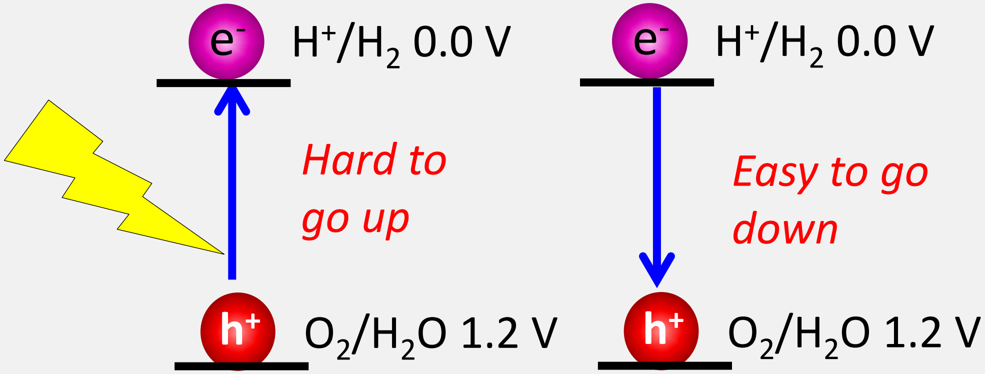
- If this approach is to be scaled, there will be major safety concerns.

- We want catalysts that are very good at producing H_2 and O_2. These catalysts are also good at reacting H_2 and O_2 to water.

- Electrolyzers have a membrane, so this isn't an issue.

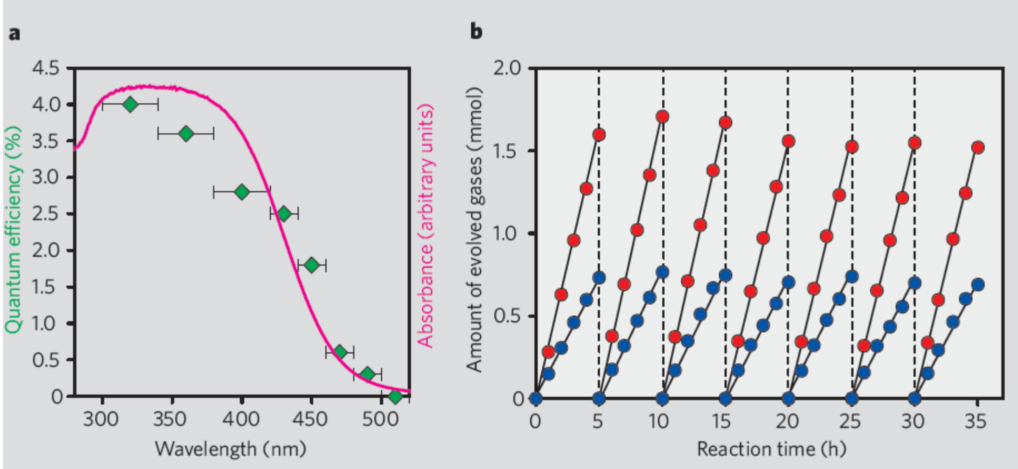
- What we need is a 'diode-catalysts'.

- Does anybody have any ideas?



Actual Results

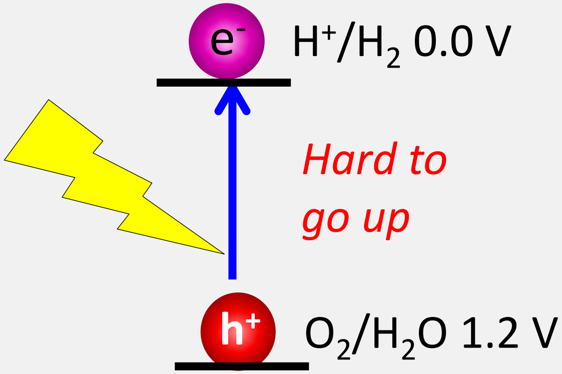
- The world record for water splitting is absolutely horrible.
- The record is around 0.1%. The exact value is very rarely reported
- Typically the efficiency at given wavelengths is reported.
- This is useful from a scientific standpoint
- While inefficient, these are very durable.
- In a lab Domen's group tested a sample for 6 months with negligible degradation.

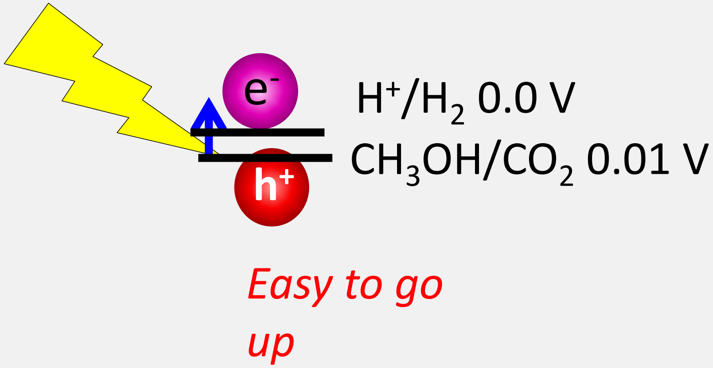


Maeda, Nature, 2006

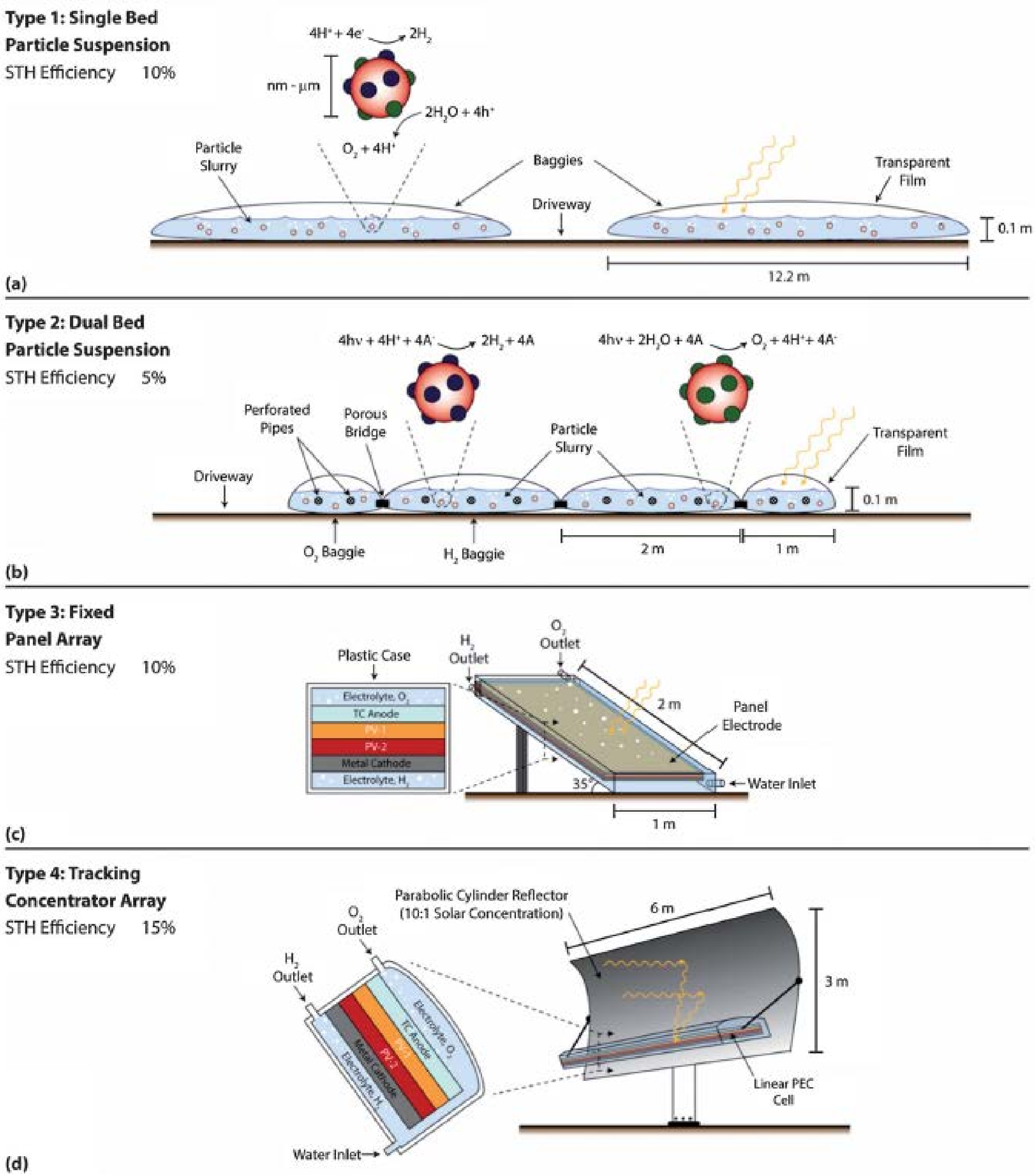
Cheating !

- Water splitting is hard, so people cheat.
- Instead of using water, they use water with methanol (or another organic.)
- While they produce H_2, they produce CO_2 rather than O_2.
- Methanol → H_2 is called ‘reforming’ and the petrochemical industry does it all the time.
- This is probably the greatest fraud in water splitting. *It is not water splitting unless you prove you are producing both H_2 and O_2.*





Are there other approaches ?



Long version (128 pgs.)

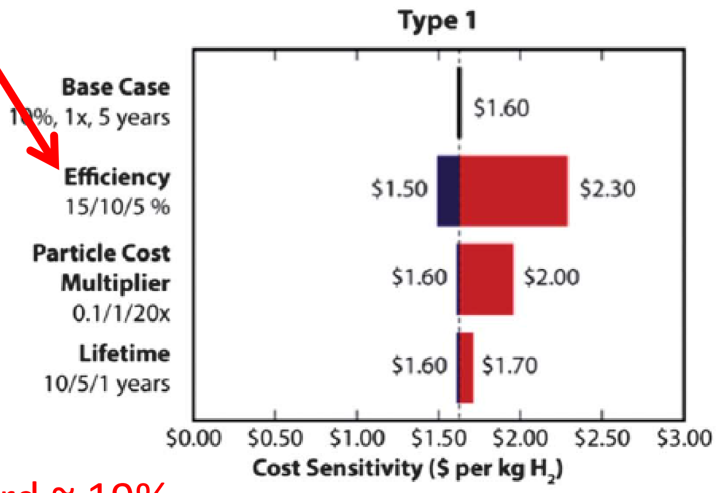
[*Technoeconmic Analysis of Photoelectrochemical Water Splitting*, DOE Contract number, GS-10F-009J]

Short version (17 pgs.)

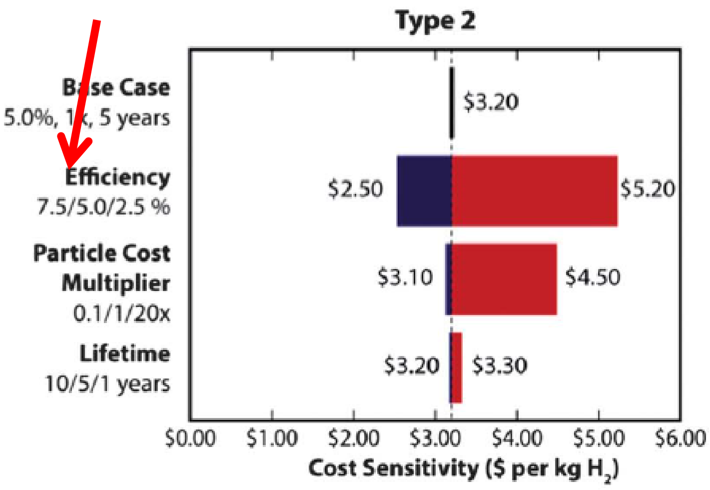
[*Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry*, EES, 2013]

Techno-economic feasibility

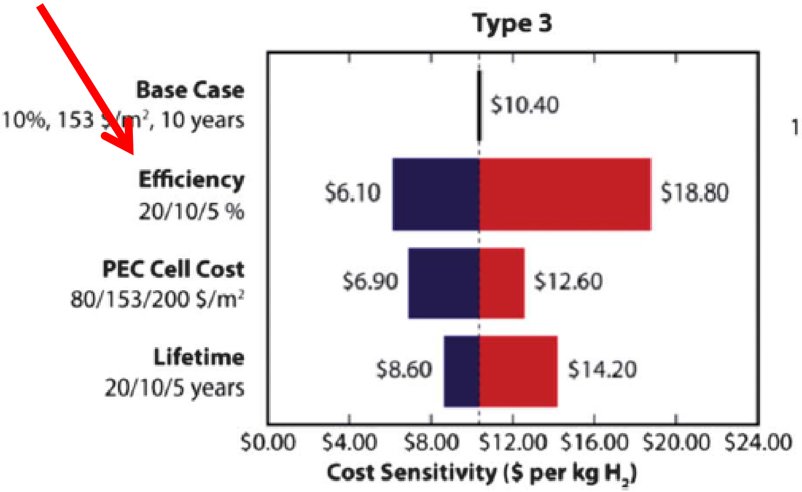
World record ~ 0.1%

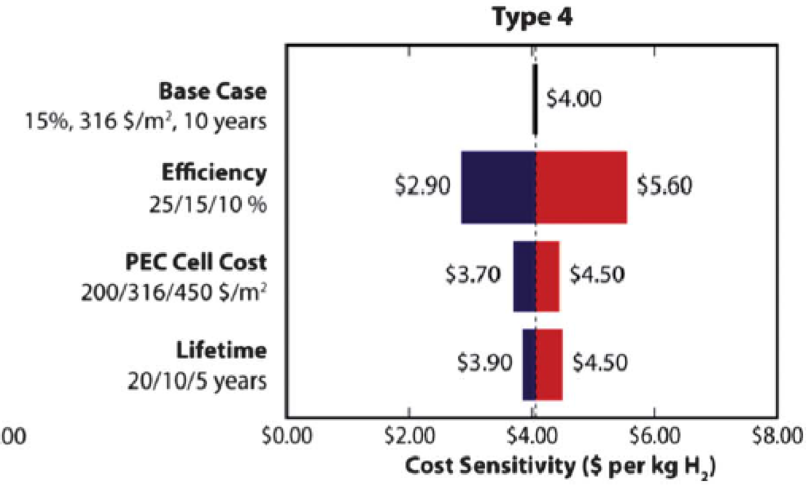


World record ~ 0.2%



World record ~ 19%

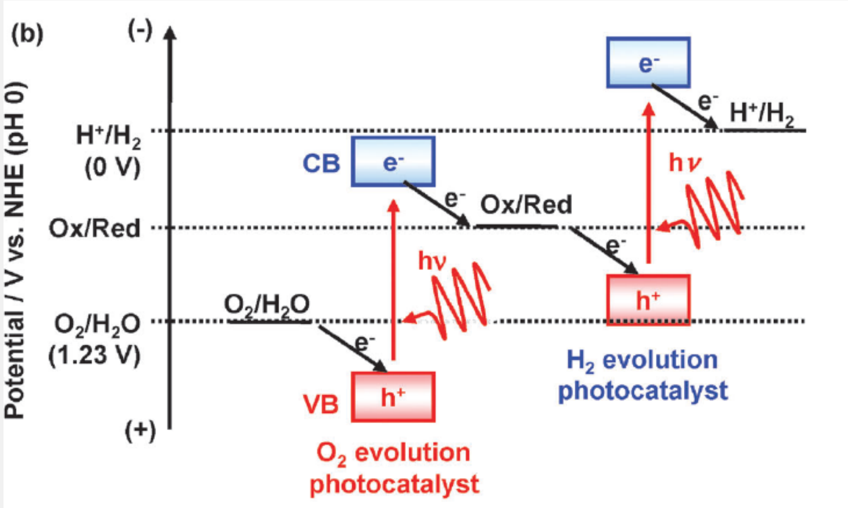


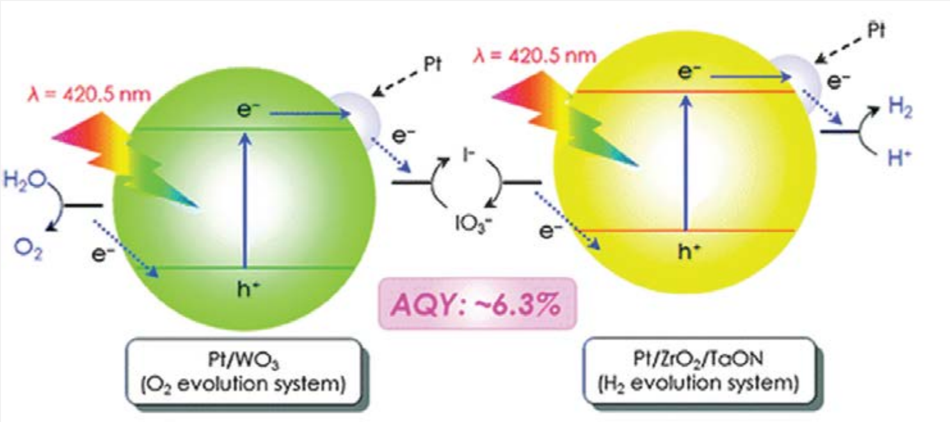


Pinaud et al., 2013 EES

Type 2 approach

- There are a few people working on this approach, but it is under investigated.
- Typically an I/IO_3^- redox couple is used as an intermediate material.
- The fundamental issues with this approach closely mimick that of a Type 1 approach.

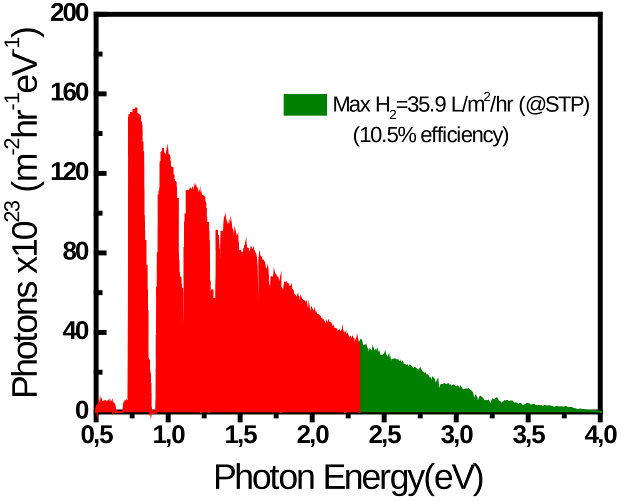




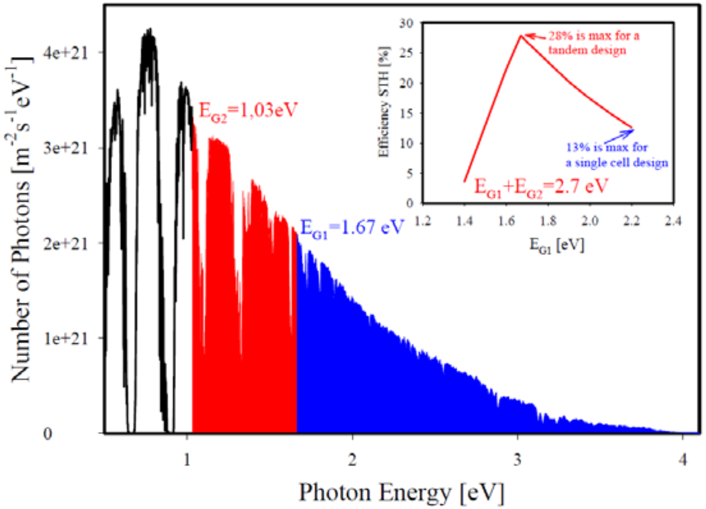
Domen, Chem. Rev., 2014

Type 3 (or 4) approach

- The problem with particles is that the voltage to split water forces a high band gap, which limits the photons we can absorb.
- In a fixed panel approach, you can take advantage of tandem cells.
- How many photoabsorbers do we need.



Particle Approach



Panel approach

Type 3 (or 4) approach

- The graph below is for optimized solar cells.

@ AM1.5

Assume 500 mV loss per semiconductor

# of cells in tandem device	Bandgap #1	Bandgap #2	Bandgap #3	Bandgap #4	Photovoltage (V)	Current (mA/cm^2)
#1	1.3				0.8 V	35.8
#2	1.9	1.0			1.9 V	17.0
#3	2.3	1.4	0.8		3.0 V	8.9
#4	2.6	1.8	1.2	0.8	4.4 V	5.7

Marti et al., Solar Energy Materials and Solar Cells 43 (1996) 203-222

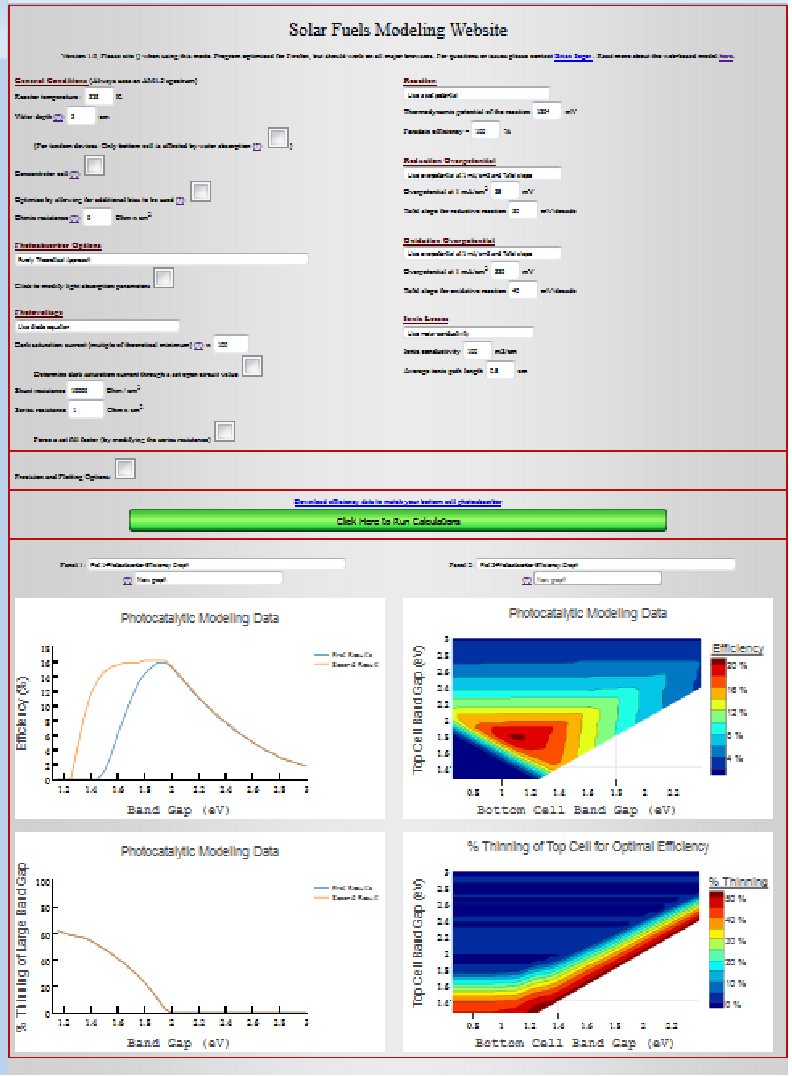
- The optimal band gaps for a photoelectrolysis device.

Device	$V_{operating}$	Band gap #1	Band gap #2
Photoelectrolysis	1.8 V	1.8 eV	1.0 eV

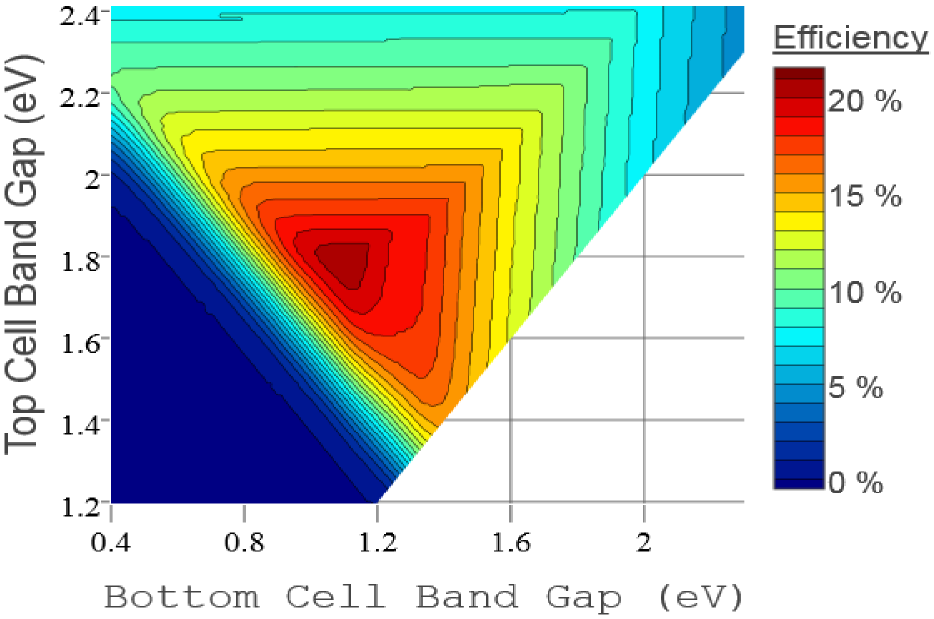
Seger et. al, Solar RRL, 2017

Modeling Efficiencies

- SolarFuelsModeling.com allows you to model device efficiencies



SolarFuelsModeling.com



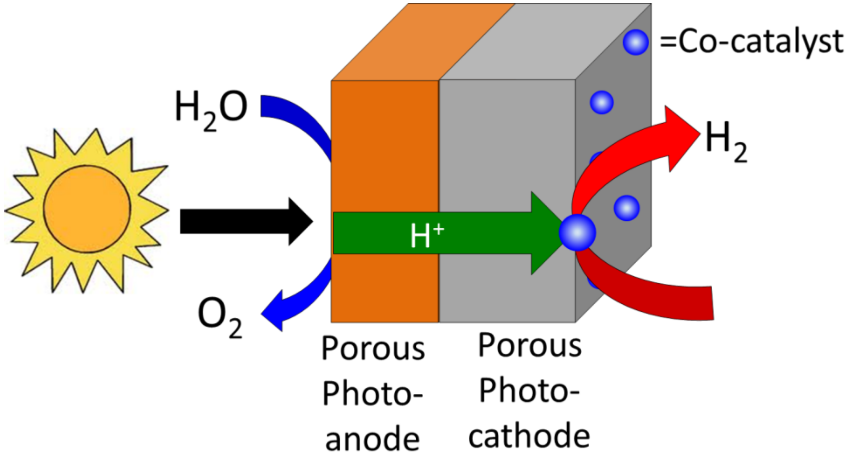
Max Efficiency Point

Efficiency: 20.8%

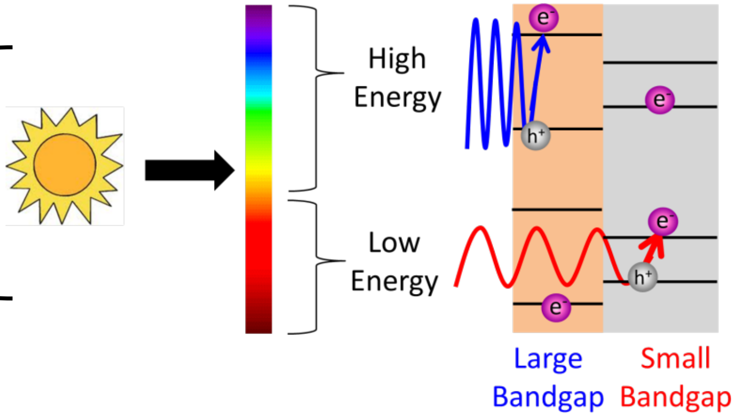
E_{top} : 1.79 eV

E_{bot} : 1.00 eV

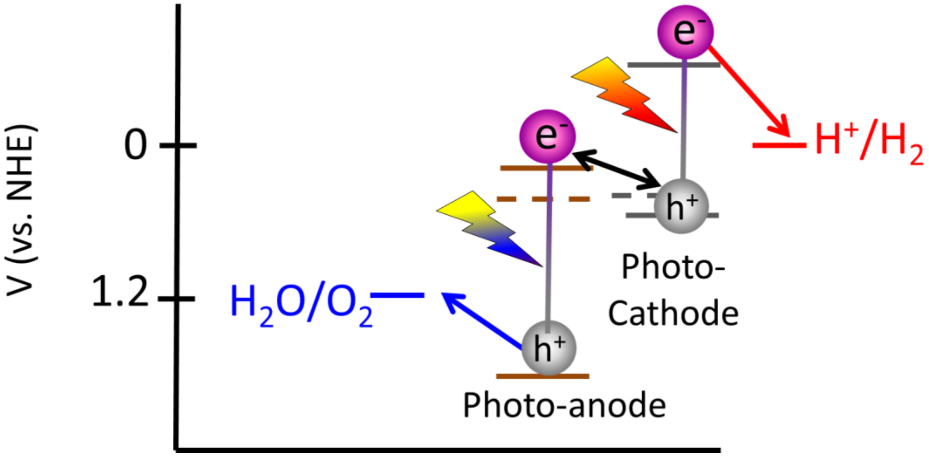
Physical Design



Optical Absorption Properties

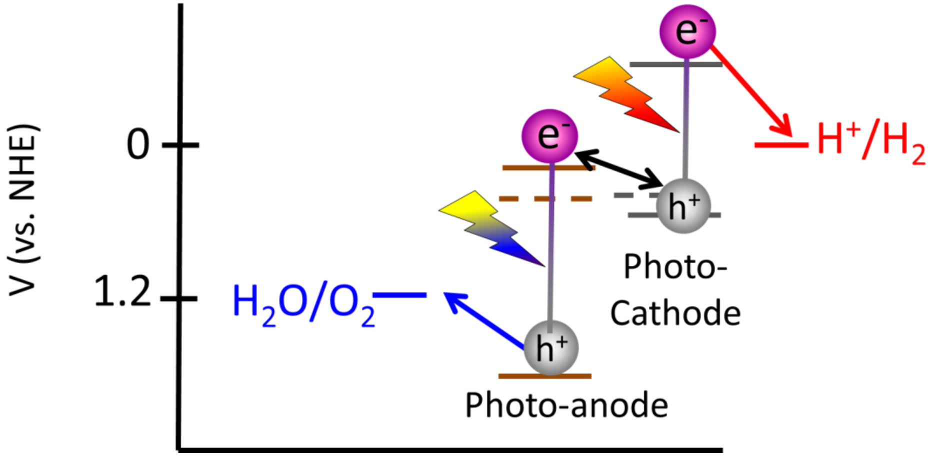


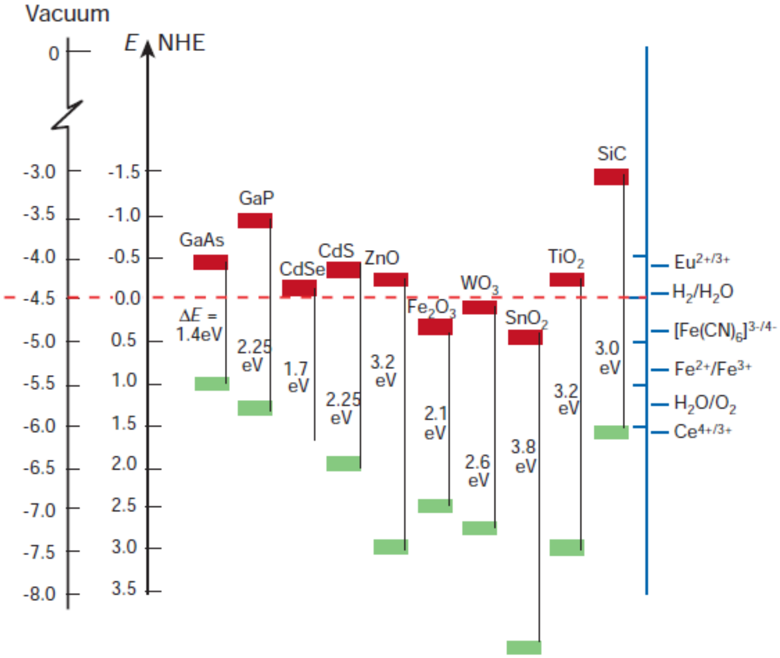
Energetic Properties



Energy alignments

- We need to find 2 materials with:
  - The right band positions
  - Actually good photovoltaic properties (long e^--h^+ lifetimes, high mobility)
  - Stable
  - Earth abundant and non-toxic
  - Right dopant density

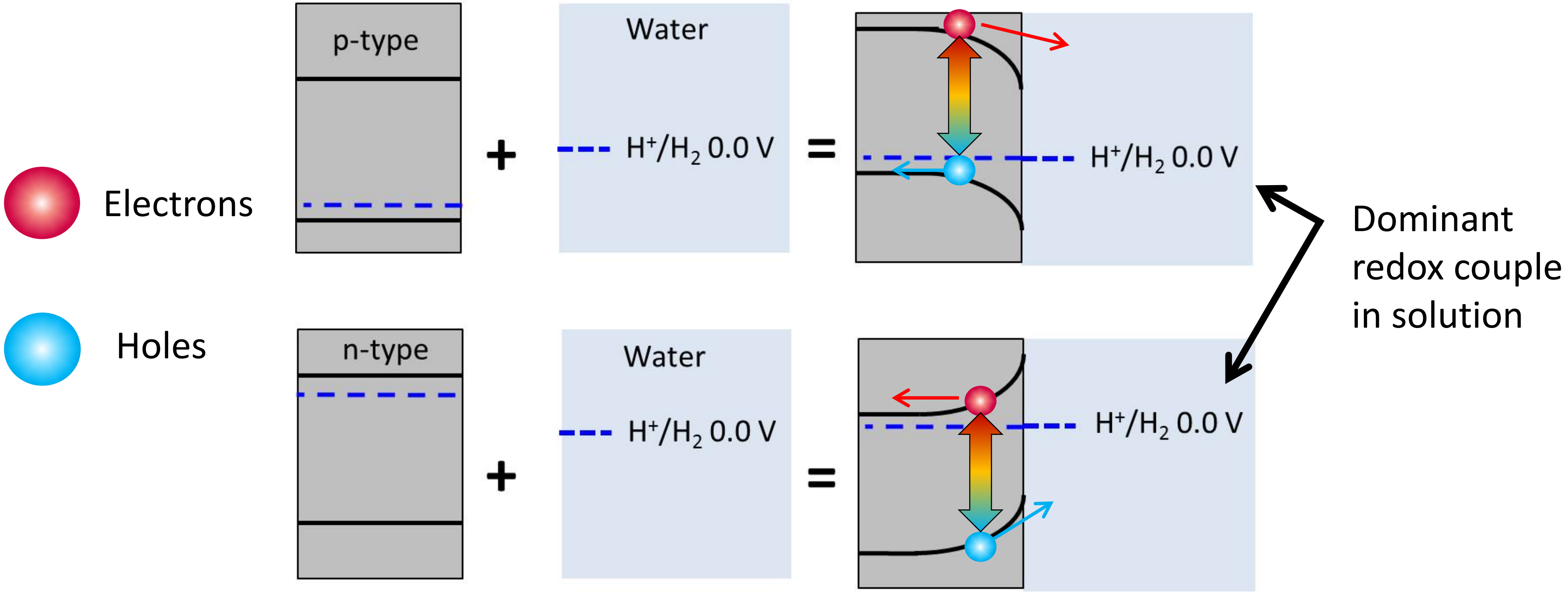




Gratzel, 2001, Nature

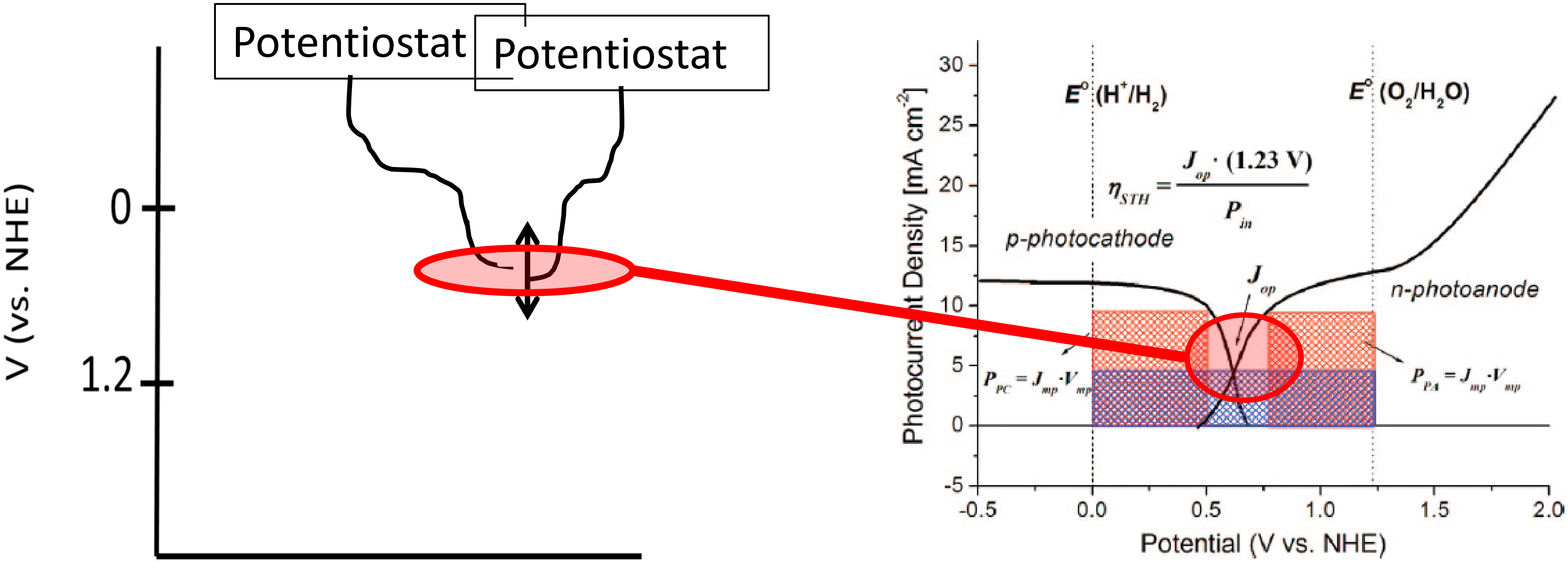
The electrolyte advantage.

- Since the semiconductor is ‘pinned’ at the surface, we can use this to form a quasi p-n junction.
- The electrolyte has much more charge carriers, thus all the band bending will occur in the semiconductor.
- P-type materials will only do reductive reactions (H_2 evolution) and n-type materials will only do oxidative reactions (O_2 evolution).



Energy Levels of Our Processes

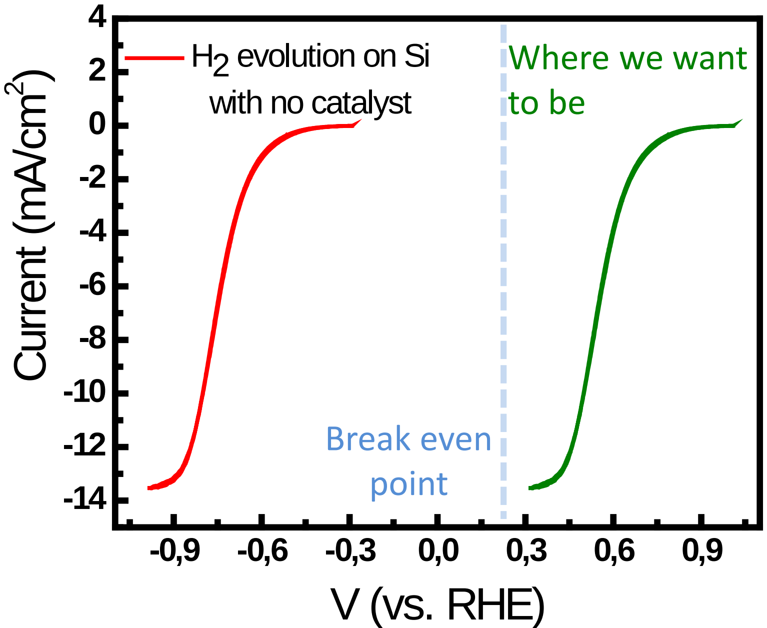
- Using electrochemistry, we can study each ‘half-reaction’ independently.

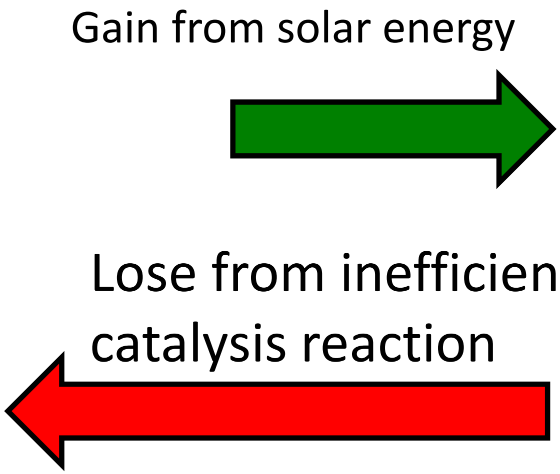


Walter et al. , Chem Review, 2010

Photocathodic H_2 evolution

- The Si photocathodes will give us photovoltage, while inefficient catalysis will lose us voltage.
- H_2 evolution on pure Si is horrible.
- We need to get to 0.0V vs. RHE just for the solar energy to balance the inefficiency of the H_2 reaction.
- Since Si is 1 of 2 photoabsorbers, we only need to get about ½ the 1.23 V (i.e. 0.6 V vs. RHE)

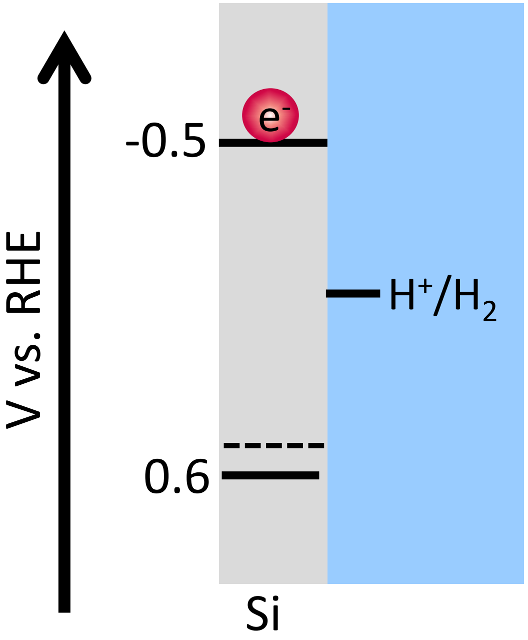



Gain from solar energy

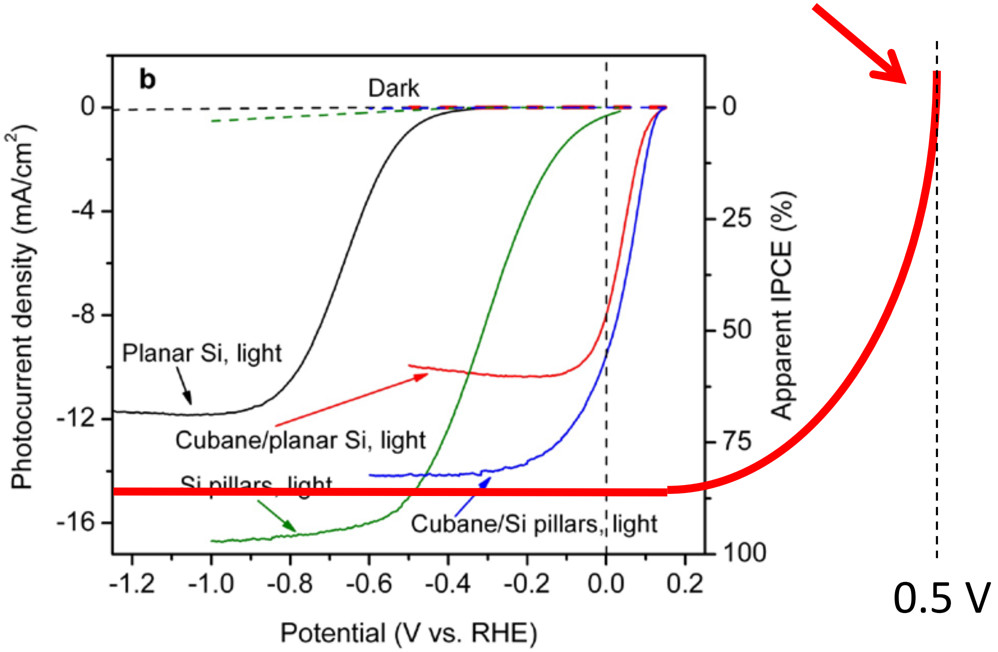
Lose from inefficient catalysis reaction

Si for Photocathode

- We used p-type Si for H_2 evolution with a pretty good MoS_2 catalyst, and got crappy results.
- World class Si can get 700 mV photovoltage and H_2 evolution overpotential costs us about 200 mV with MoS_2.
- Why are we getting bad results?



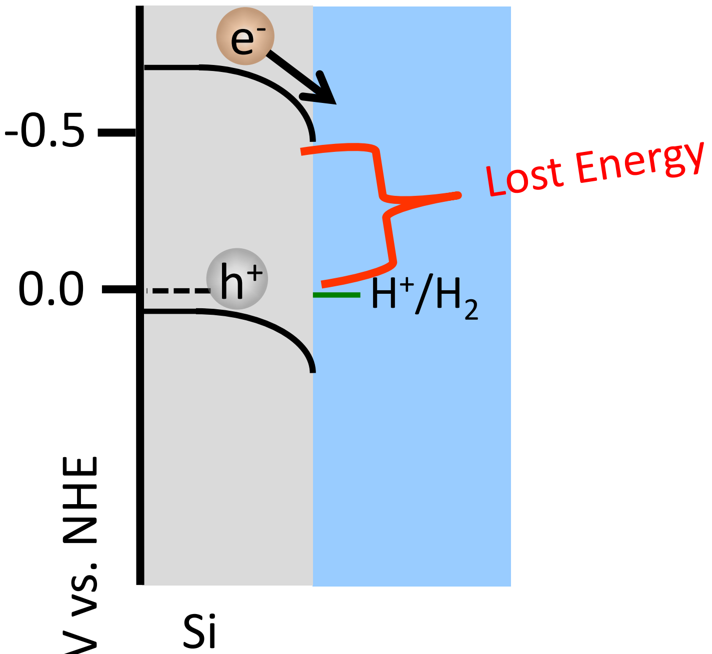
What we want

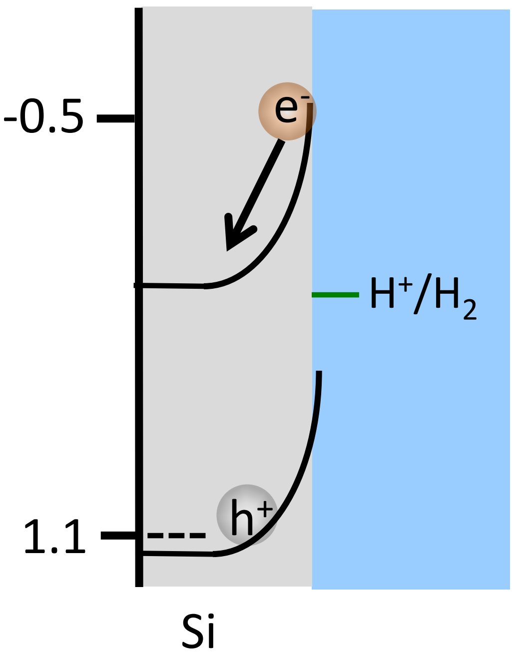


Hou Y. D., *et al.*, *Nature materials*, **10**, 434-438 (2011).

Photochemistry Issues

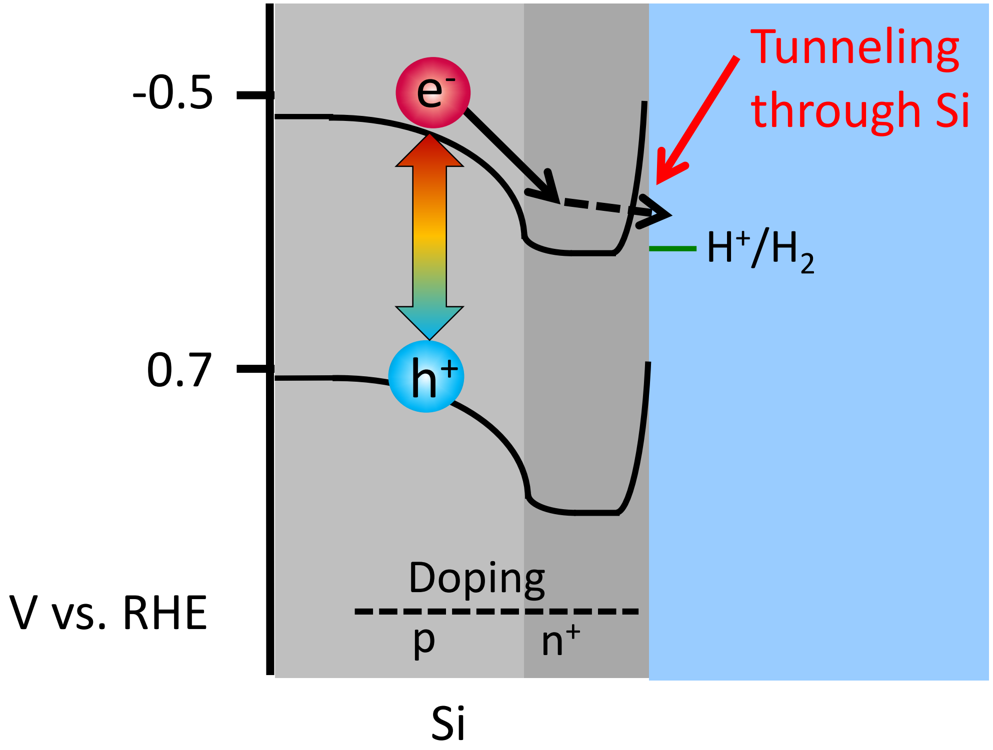
- The highly reductive conduction band is Si actually hurts performance.
  - We have a guaranteed loss of at least 500 mV with Si.
- Band bending issues prevent us from maximizing voltage.
- The 500 mV loss from band bending combines with the 300 mV loss for thermodynamics and 200 mV loss for non-world class optimizations, giving us about 100 mV of real photovoltage.

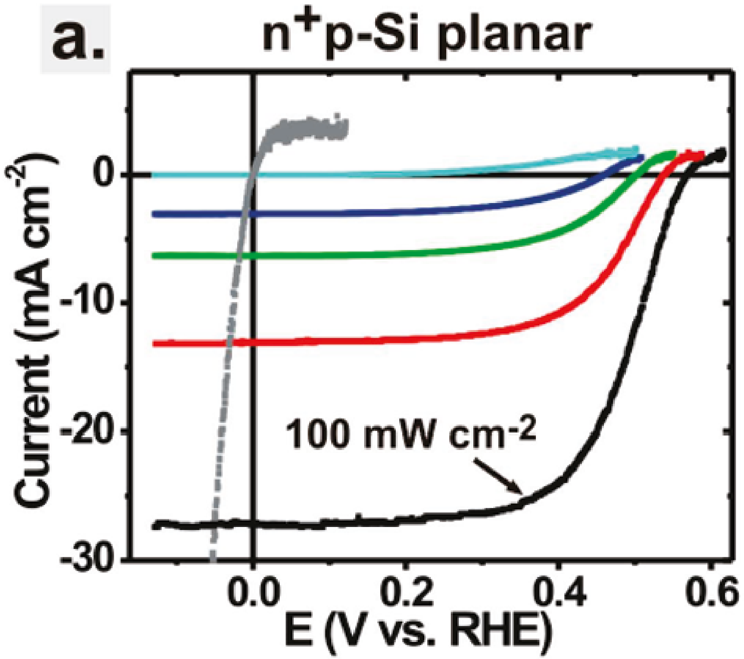




Isolating the Photovoltage

- Adding a high doped n$^+$ layer to the Si does 2 things:
  - Creates optimal band bending independent of electrolyte.
  - Allows tunneling at the semiconductor-electrolyte interface.
- This doping in effect allows the band positions to effectively float.

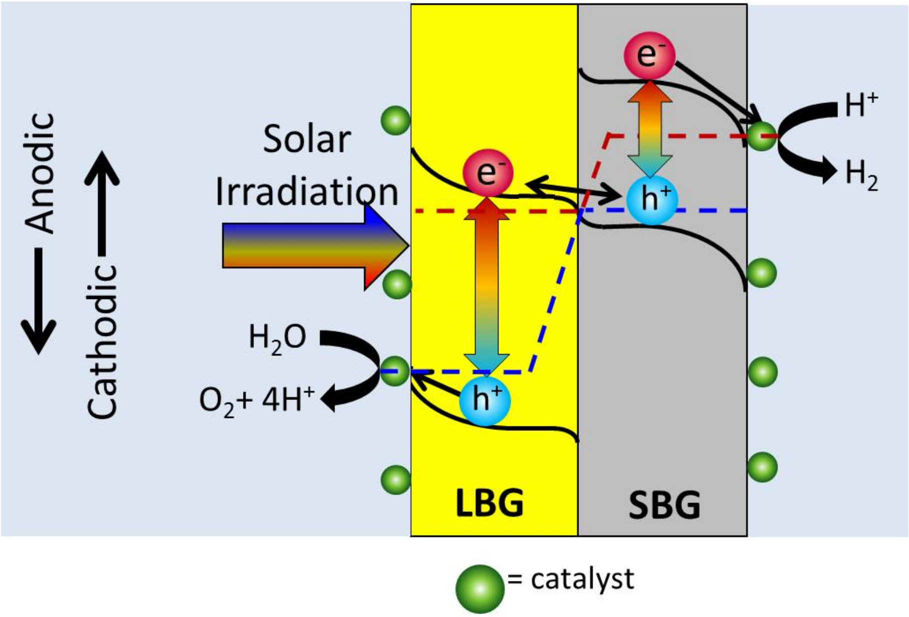




(Boettcher et. al., JACS, 2011)

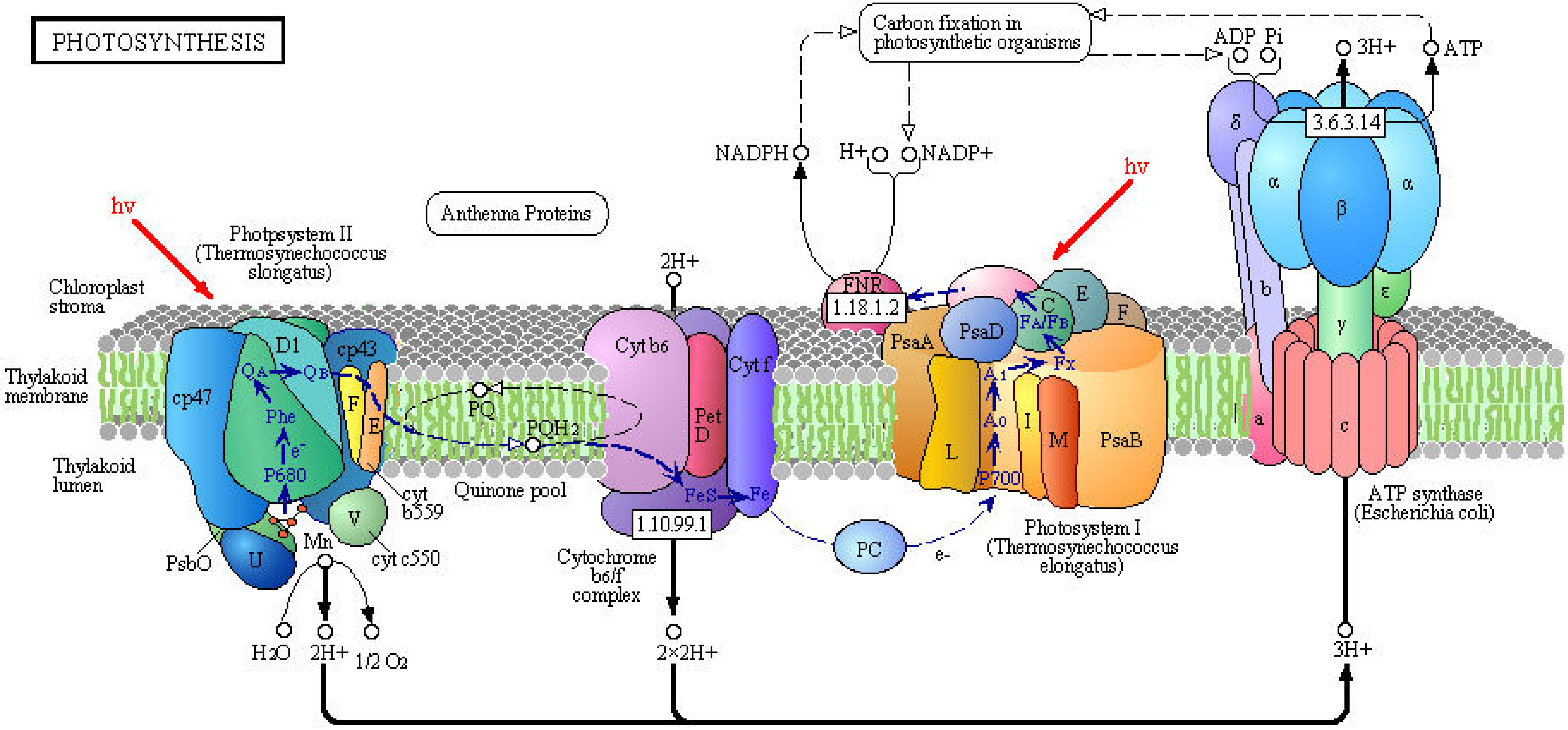
What do we need to complete this device

- We need the following:
  - Large band gap photoabsorber- GaInP, ???
  - Small band gap photo absober- Si
  - Membrane- Nafion in acid, Fumatec in base
  - H_2 evolution catalyst- Pt, MoS_2 in acid, NiMo or Pt in base
  - O_2 evolution catalyst- $NiFeO_x$ in base, unstable IrO_2 and RuO_2 in acid



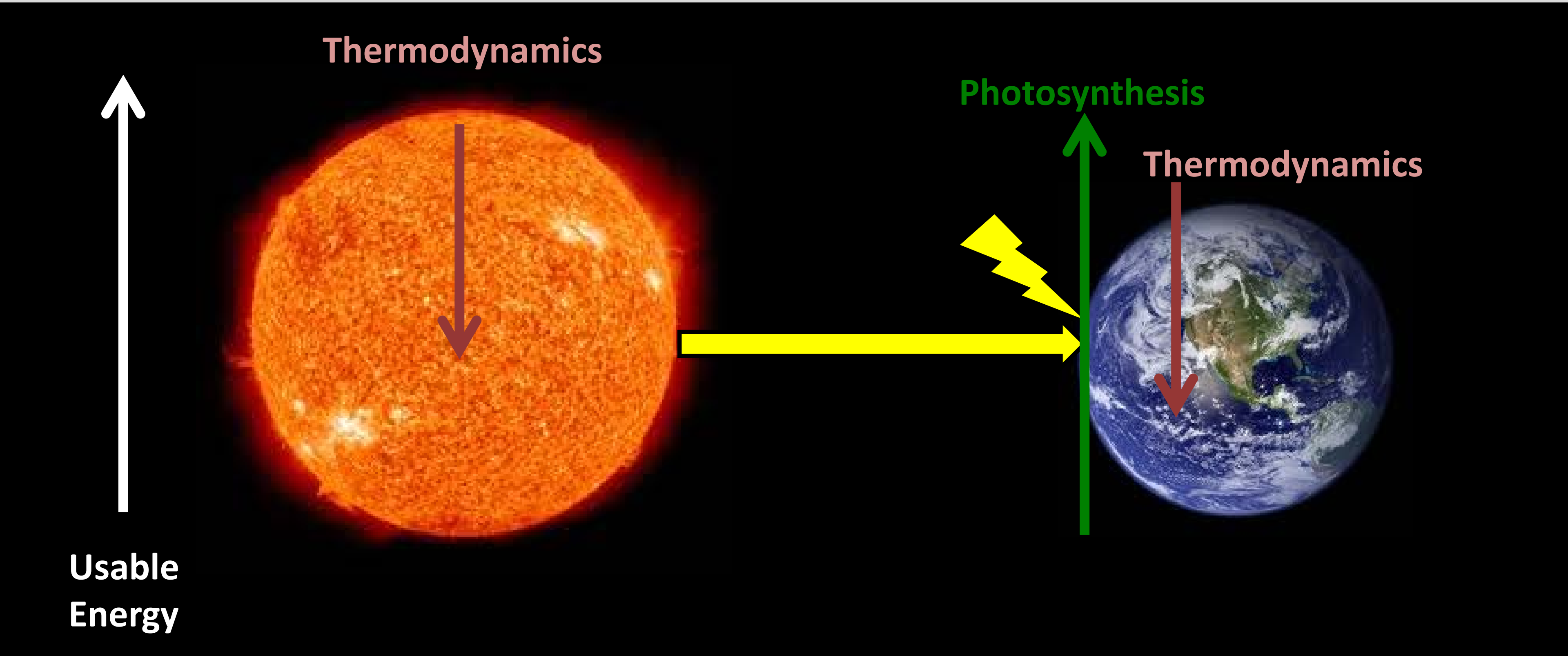
Break

Photosynthesis

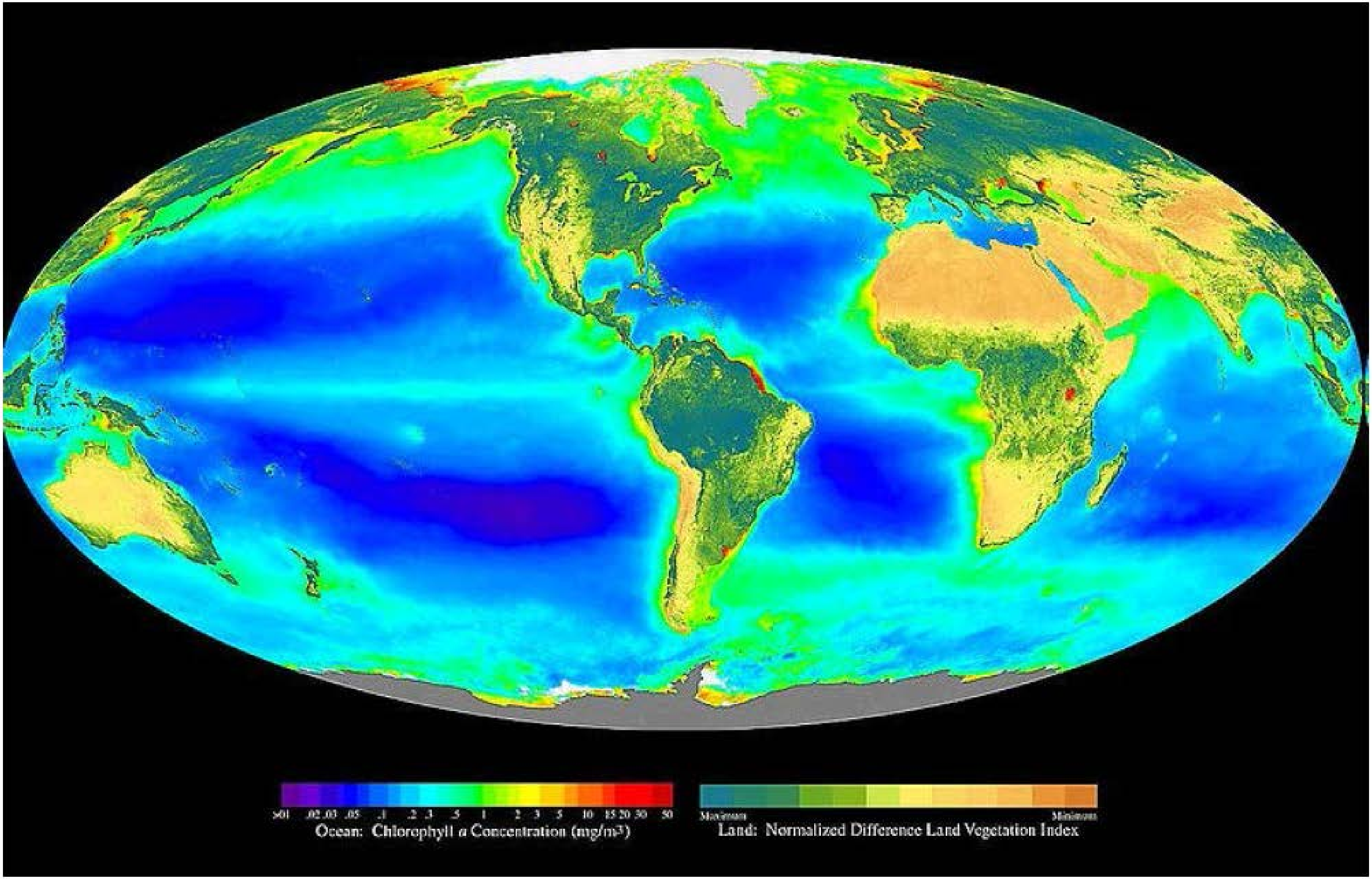


Energy

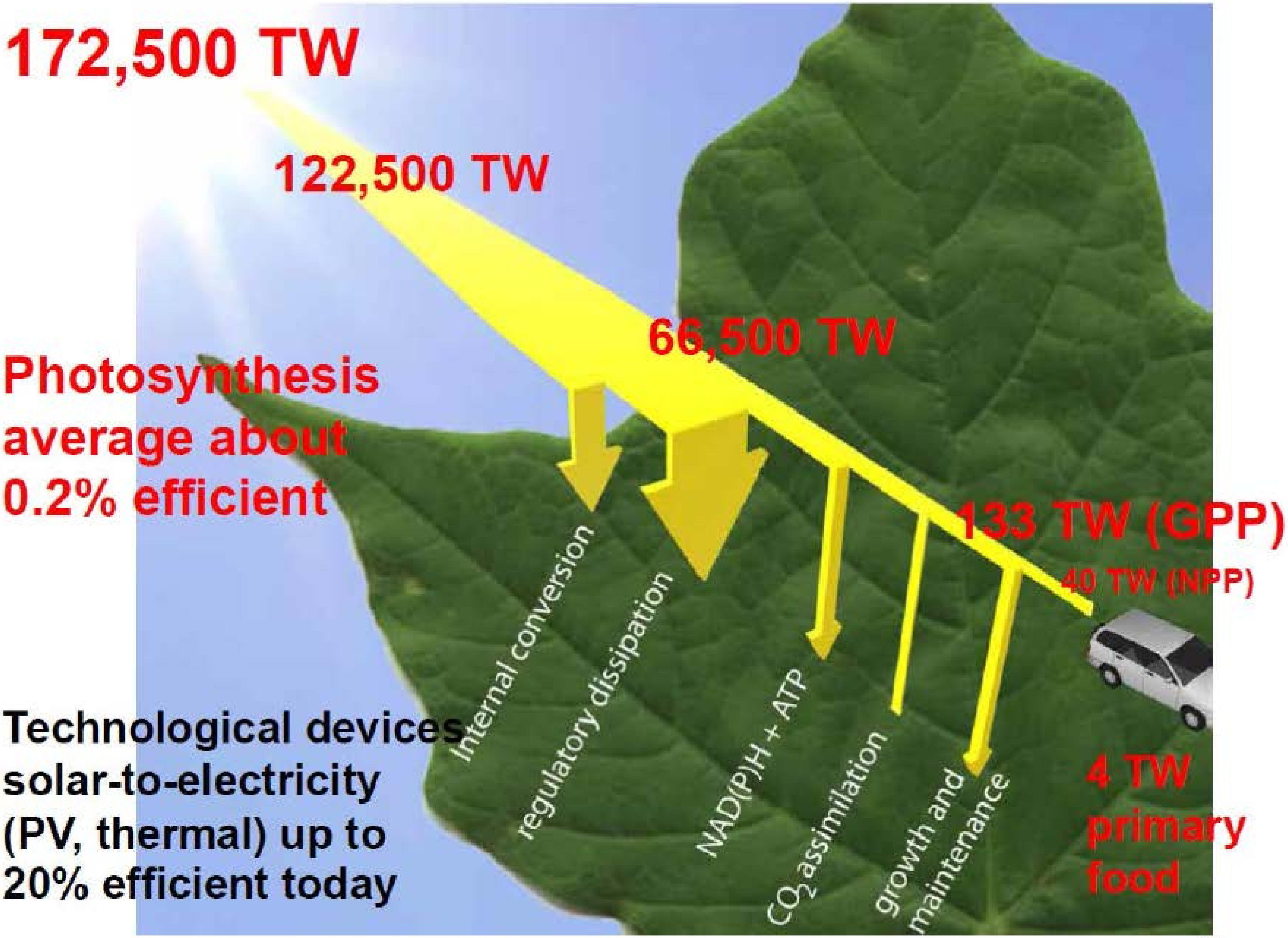
- *Thermodynamics*- You will always go to a lower energy state. If you are really lucky/clever, you can break even.
- *Photosynthesis*- Takes photons and creates high energy states.



Where Photosynthesis is Located



Graphical photosynthesis loss



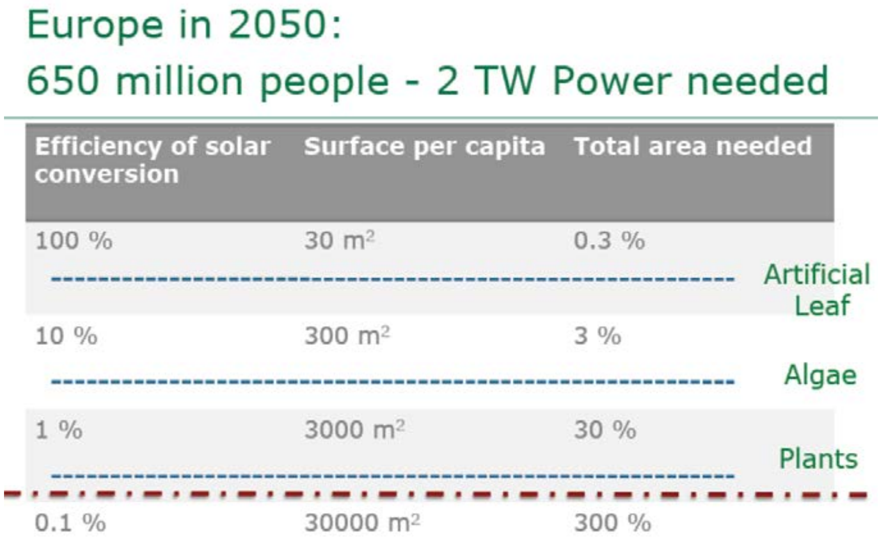
Photosynthesis average about 0.2% efficient

Technological devices solar-to-electricity (PV, thermal) up to 20% efficient today

Adapted from Gust, Kramer, Moore, Moore & Vermaas, MRS Bulletin, 2008

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 46.5% 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

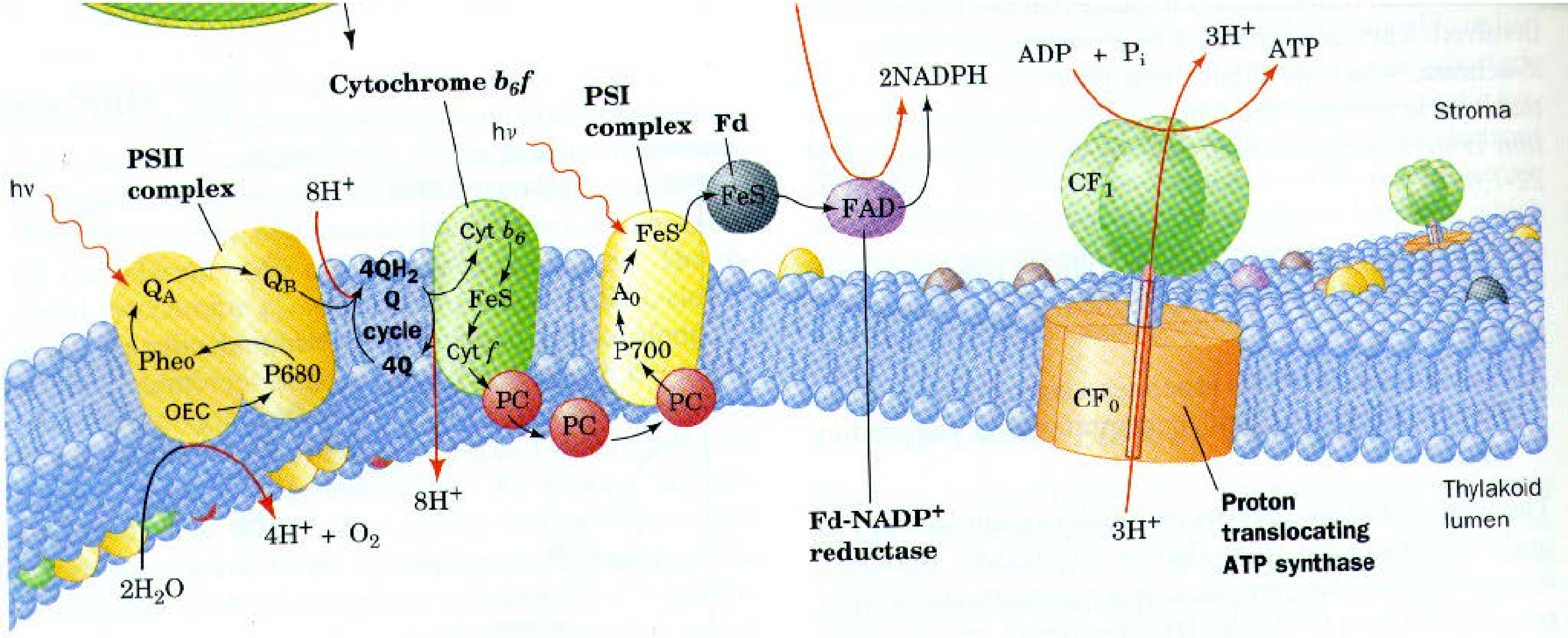
Efficiency of solar conversion	Surface per capita	Total area needed
100 %	30 m²	0.3 %
10 %	300 m²	3 %
1 %	3000 m²	30 %
0.1 %	30000 m²	300 %

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 chlorophyl) → 68% loss in conversion of ATP and NADPH to d-glucose, leaving
- 9% (collected as sugar) → 35–40% 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

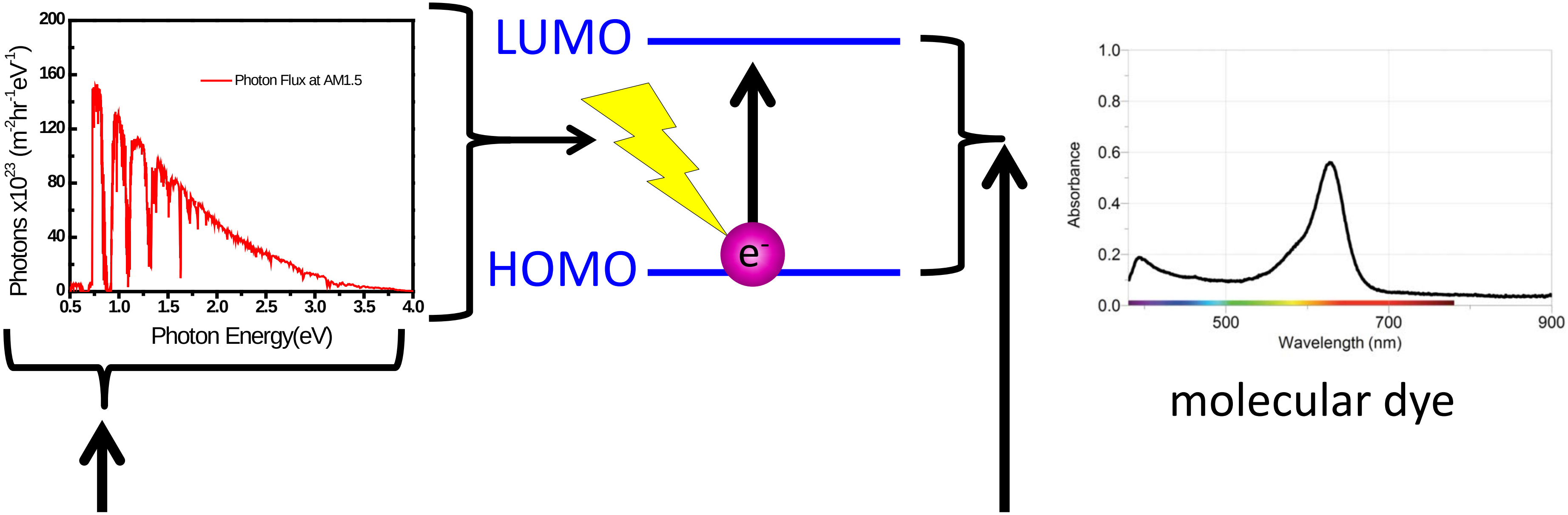


Fundamental Physics

- 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 photocatalysts have distinct energy levels.



molecular dye

This photon energy needs to match this energy gap.

- Molecular photocatalyst only absorb efficiently at one wavelength.

Overall Efficiency

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- 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
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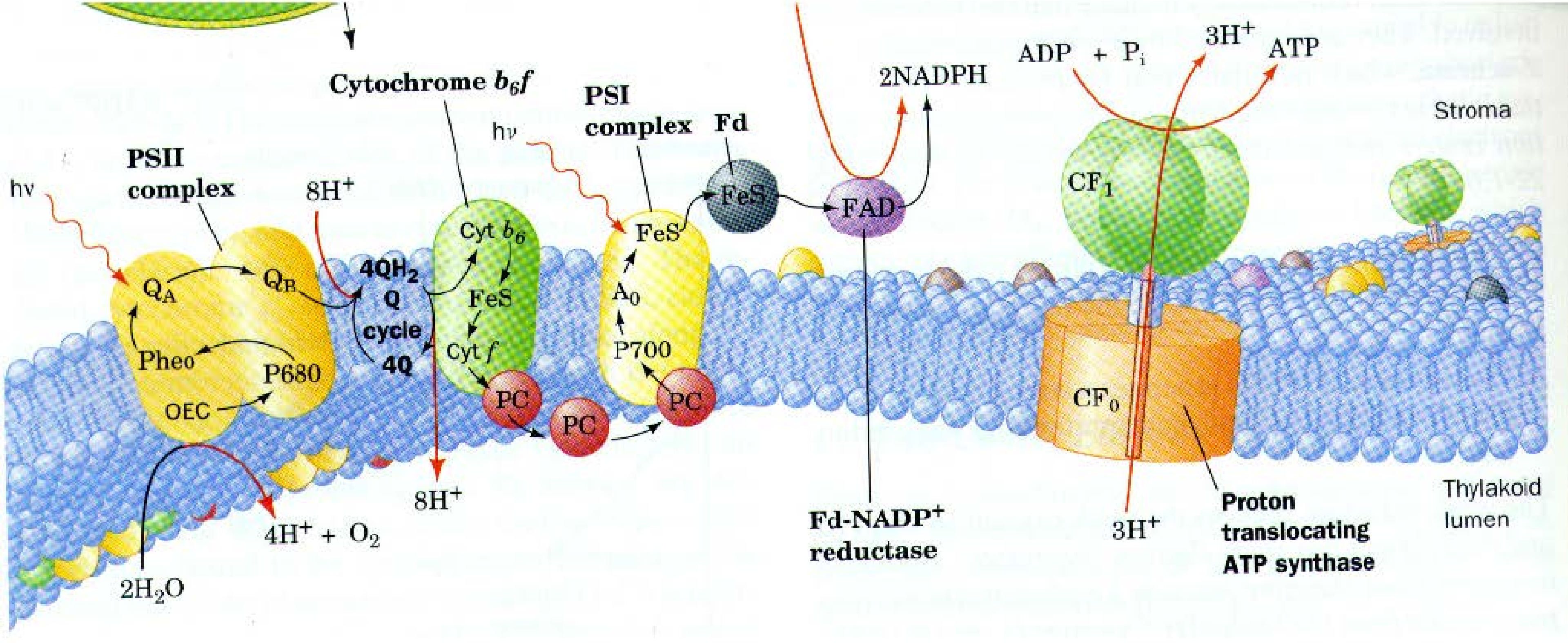
- 5.4% net leaf efficiency

- In reality, the energy conversion efficiency is much less.
- Most photosynthetic processes are 0.1 %, with the most efficient at 1%.

Basics of Photosynthesis

PS 2: $2H_2O + 4h\nu \rightarrow 4e^- + 4H^+ + O_2$

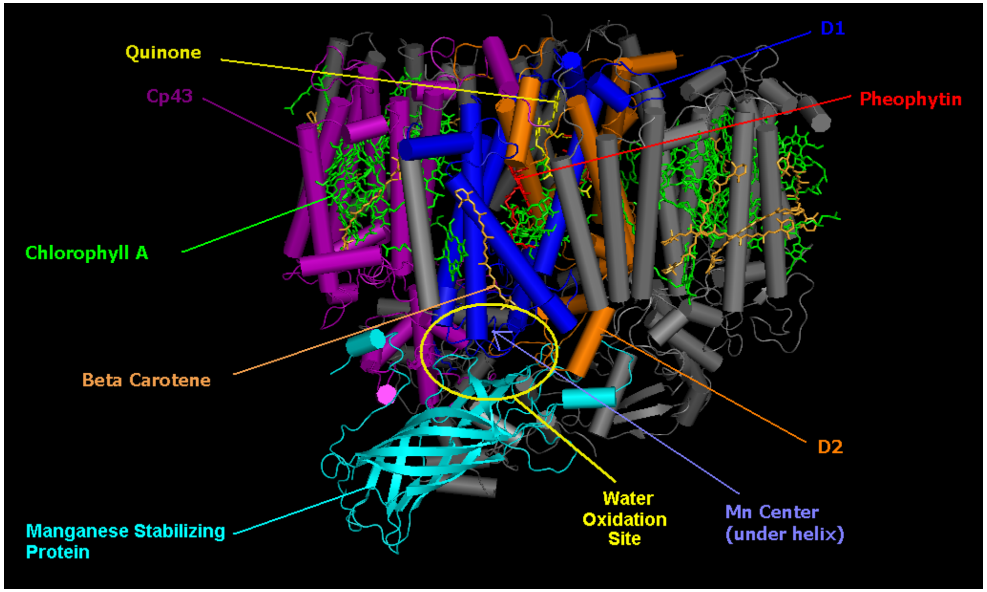
PS 1: $2e^- + H^+ + 2h\nu + \text{NADP}^+ \rightarrow \text{NADPH}$



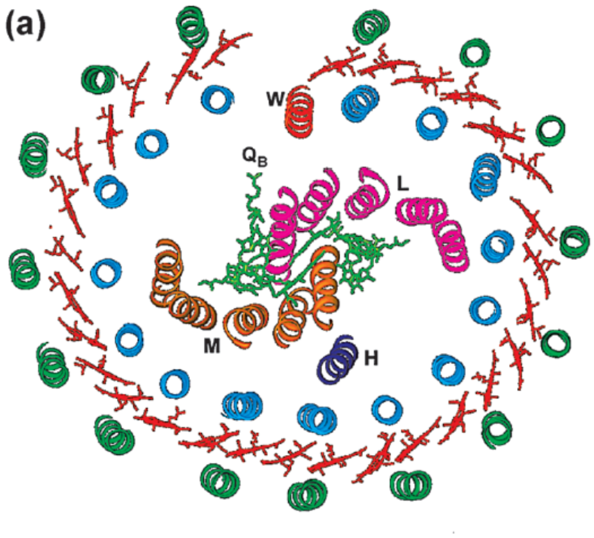
Photosystem II

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

- Many linked chlorophylls



Photosystem II



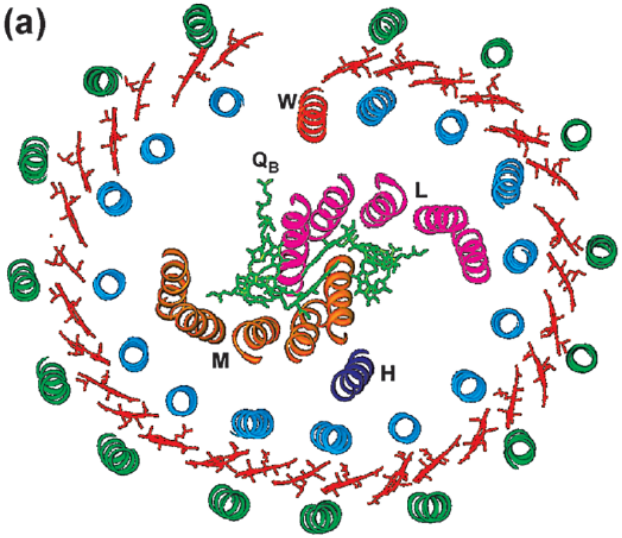
Pg. 186 or 188 in text

Photosystem II- Interacting Molecules

- With chlorophylls next to each other they will have dipole-dipole interactions.

- The dipole interactions span 10nm, whereas the molecules span 1nm.

- Thus any excited state will be a linear combination of the other chlorophyll states.



Percentage of exciton

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

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

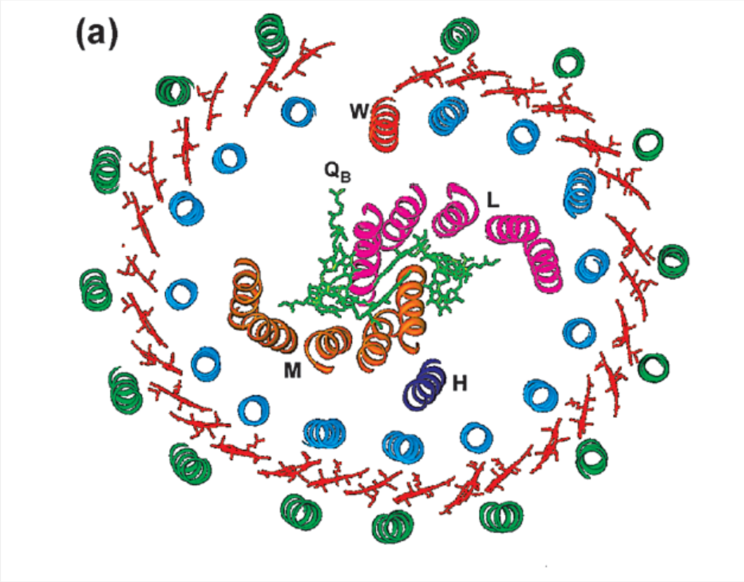
How does the electron move ?

- First their should be some overlapping electronic states.

$$< \psi_k \| \psi_l >= \sum_{n,m} C_{kn}^{*} C_{lm} \langle \varphi_n \| \varphi_m \rangle = \sum_{n,m} C_{kn} C_{lm}$$

- The total transition should be:

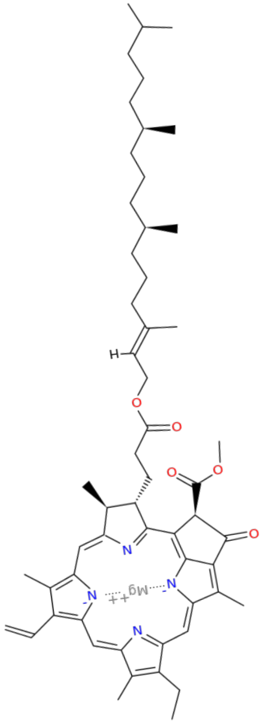
$$W_{kl} = \left\{ \sum_{n,m} C_{kn}^{*} C_{ln} C_{km}^{*} C_{lm} \langle V_n^{*} V_m \rangle \right\} J_{kl}$$



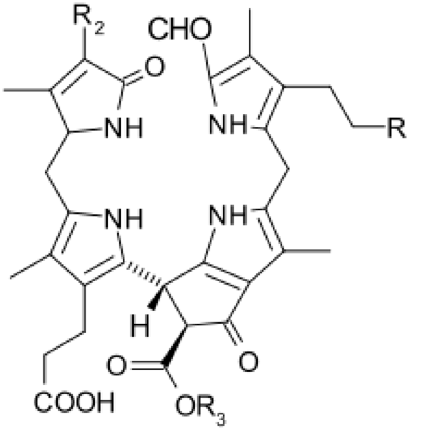
- J_{kl} relates to density of states.
- $<V_n{}^*V_m>$= related coupling to pigment vibration.

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.

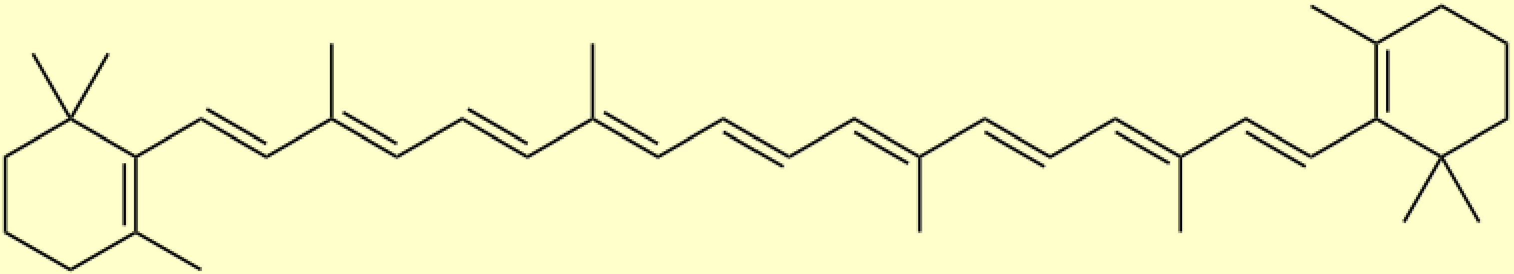


Chlorophyll a



Color change of leaves in autumn

Beta-Carrotene



- What wavelength light does it absorb?

- β-Carotene has a mass of 9.1×10^{-31} kg and a length of 1.83 nm.

Beta-Carrotene

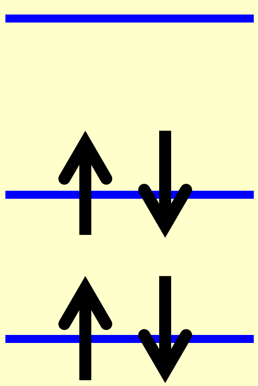
- Quantum mechanics allows us to calculate β-Carotene absorption.
- β-Carotene has 22 delocalized atoms, a mass of $9.1\text{x}10^{-31}$ kg and a length of 1.83 nm.
- This can be modeled as 1-D particle in a box.

$E_n = n^2E_0$

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

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

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



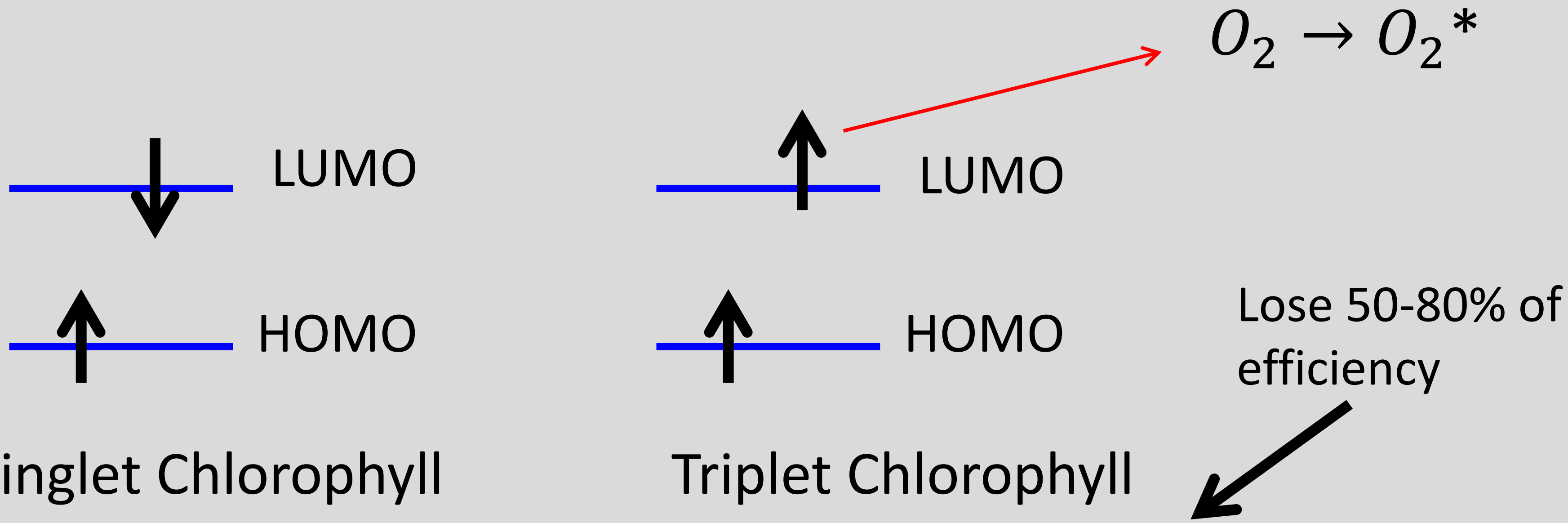
$E_{12} = 144E_0$ LUMO

$E_{11} = 121E_0$ HOMO

$E_{10} = 100E_0$

Beta-Carrotene

- 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.



Singlet Chlorophyll
(low light intensities)

Triplet Chlorophyll
(high light intensities)

Beta-Carrotene

- The β-Carotene easily accepts the electron.


$O_2{}^*$ O_2

- By simply heating the original β-Carotene is regenerated.

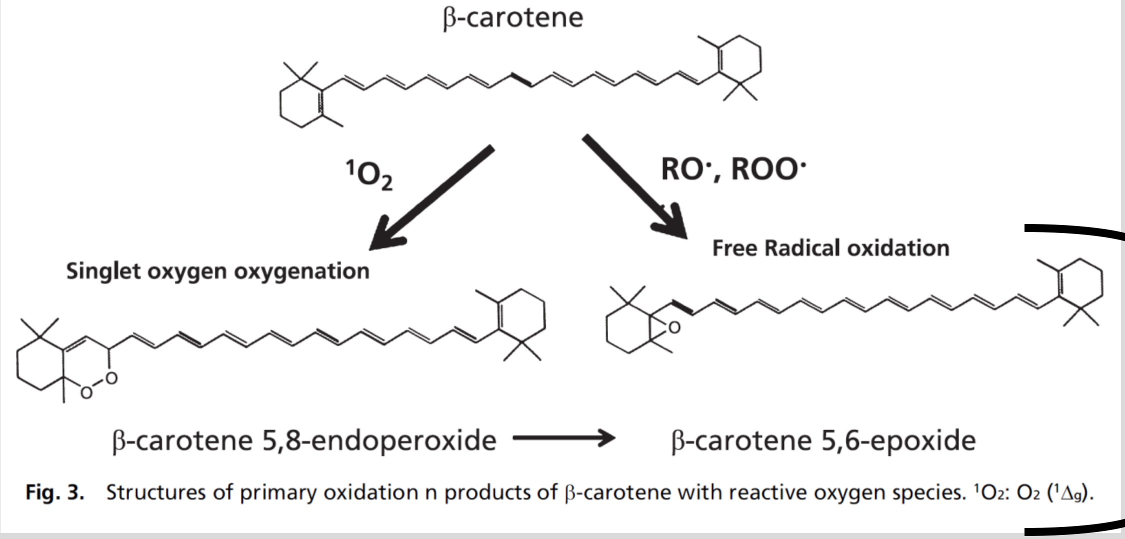
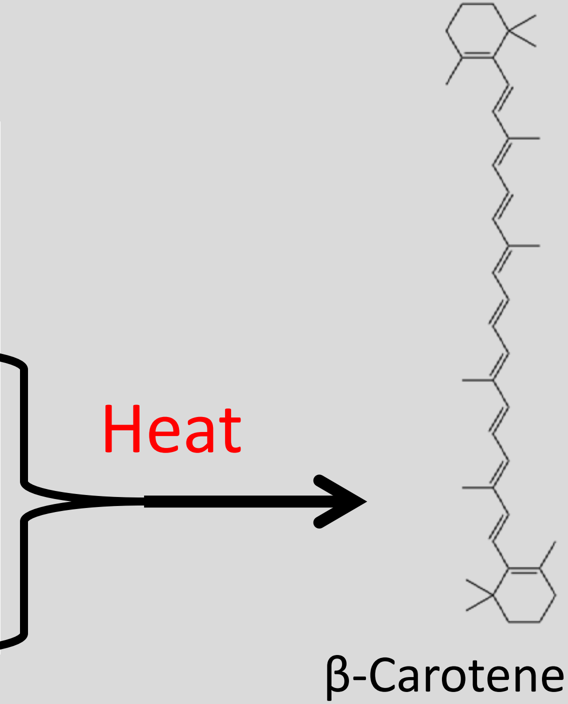
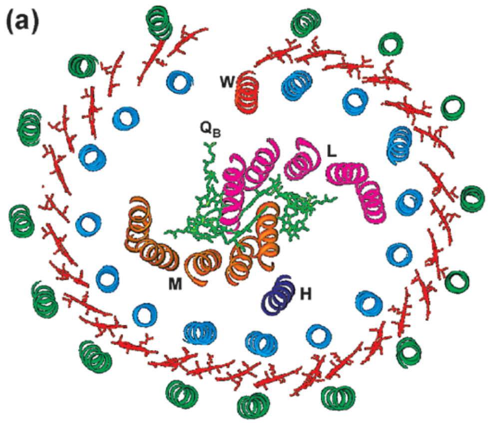


Fig. 3. Structures of primary oxidation n products of β-carotene with reactive oxygen species. $^1O_2$: O_2 ($^1\Delta_g$).

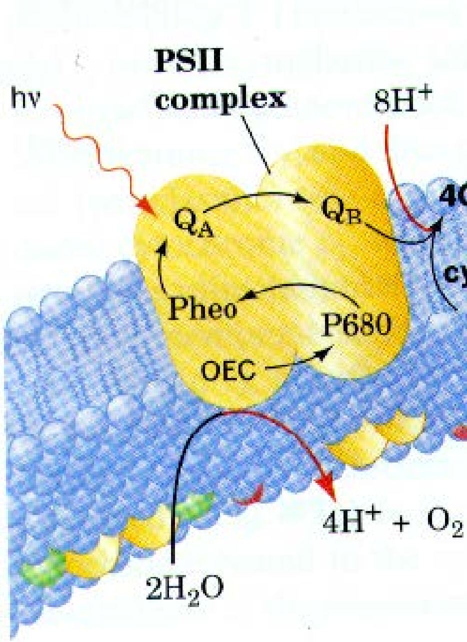


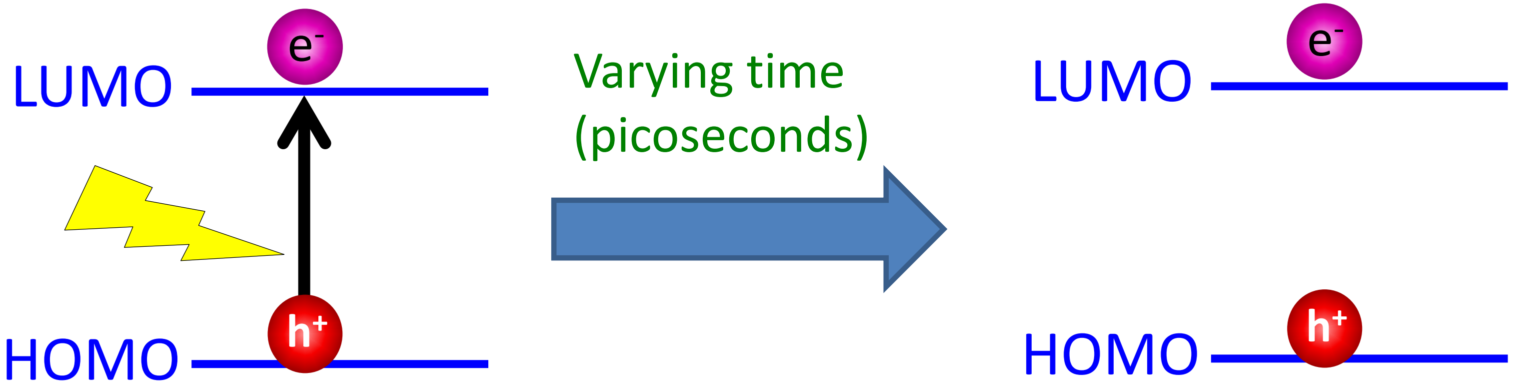
β-Carotene

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.



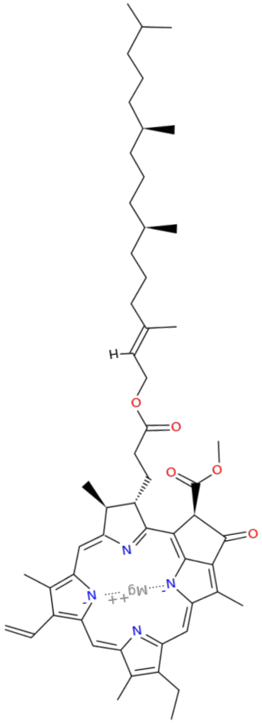


P680-attenae

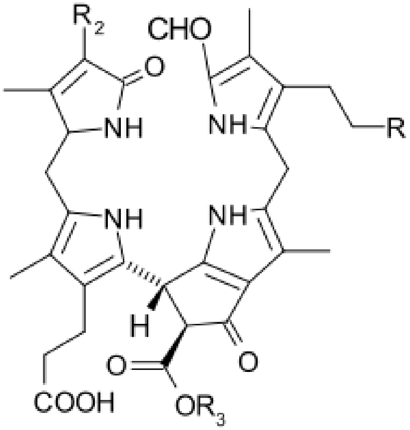
P680-dimer

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



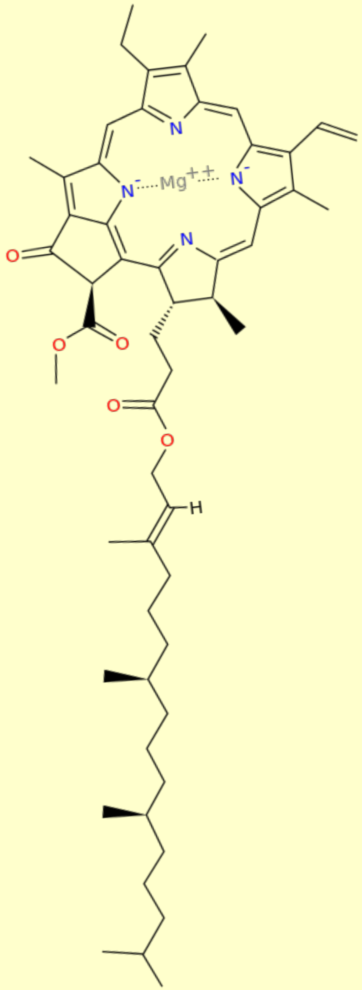
Color change of leaves in autumn

Photosystem II- Side note

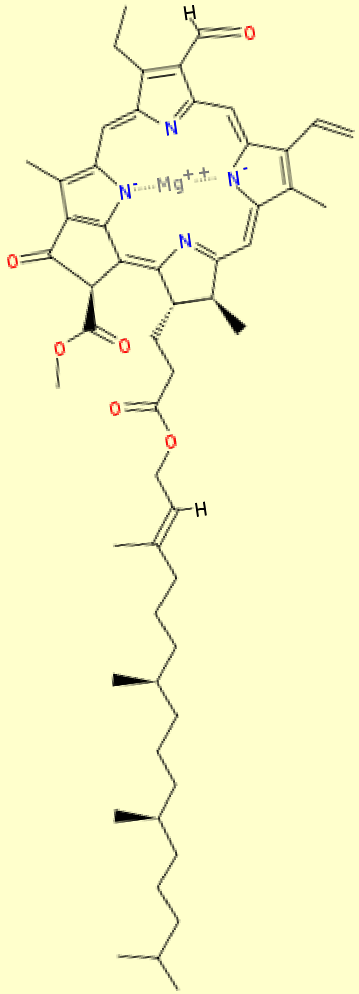
- Sometimes a plant will have Chlorophyll b instead of Chlorophyll a.

- Would you expect Chlorophyll a and Chlorophyll b to absorb at the same wavelength?

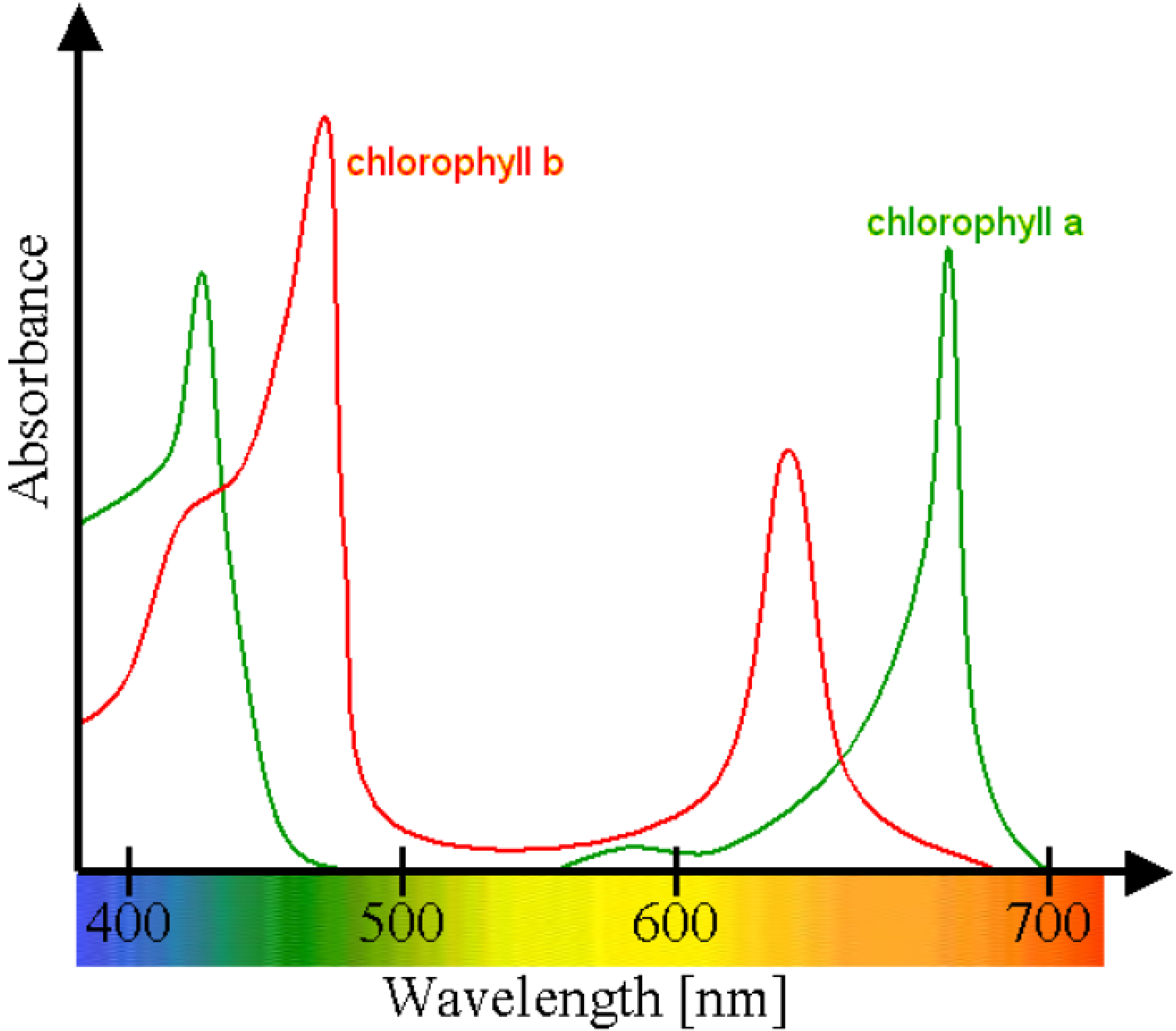
- Can a mixture of Chlorophyll A and Chlorophyll B work for a single plant?

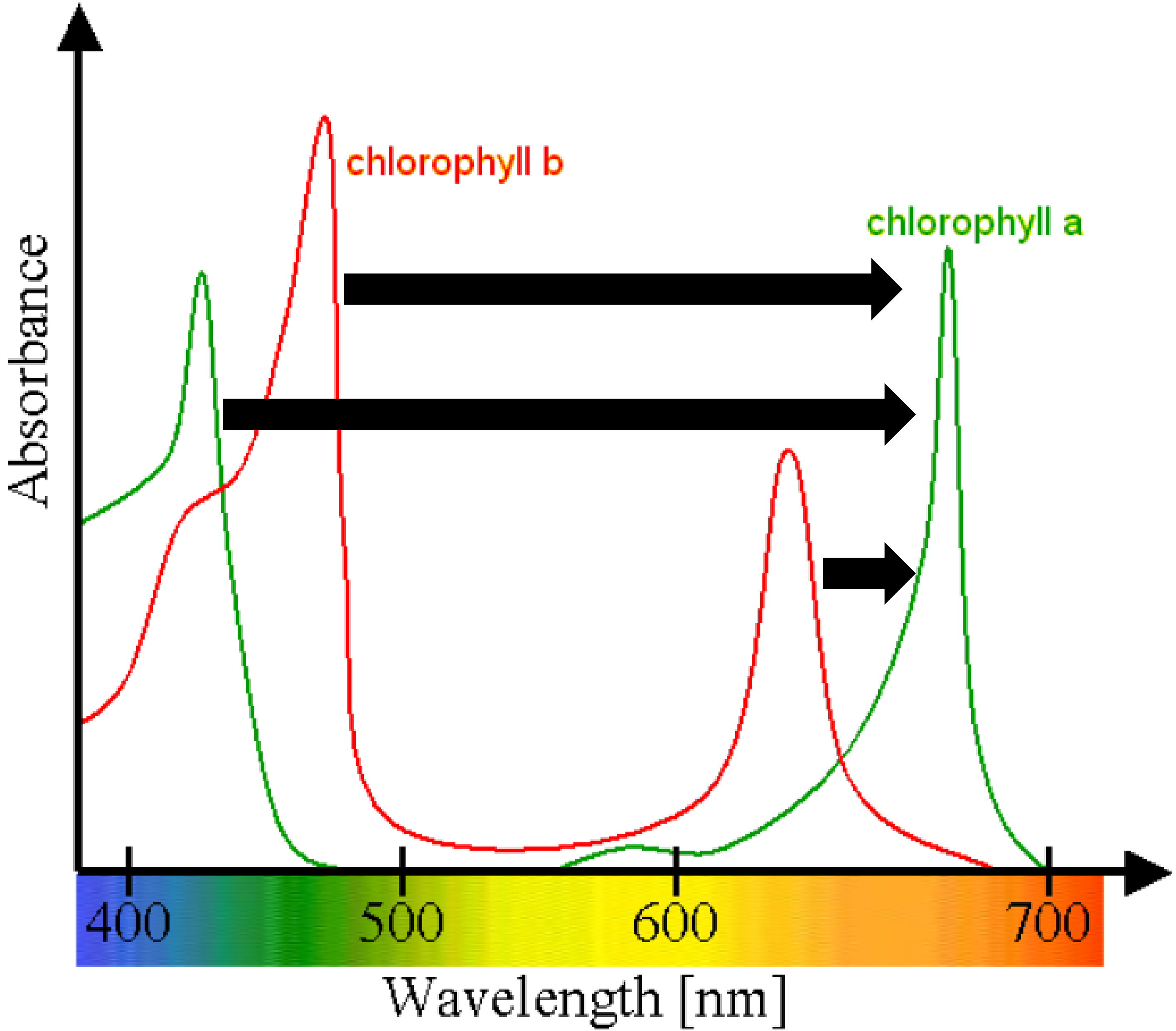


Chlorophyll A



Chlorophyll B


chlorophyll b
chlorophyll a
Absorbance
400
500
600
700
Wavelength [nm]

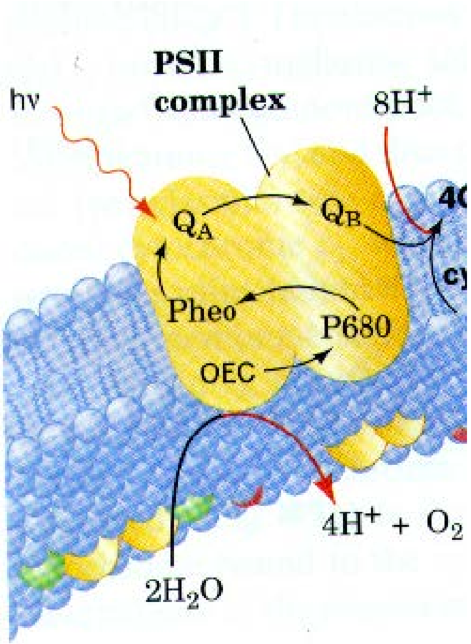

chlorophyll b
chlorophyll a
Absorbance
400
500
600
700
Wavelength [nm]

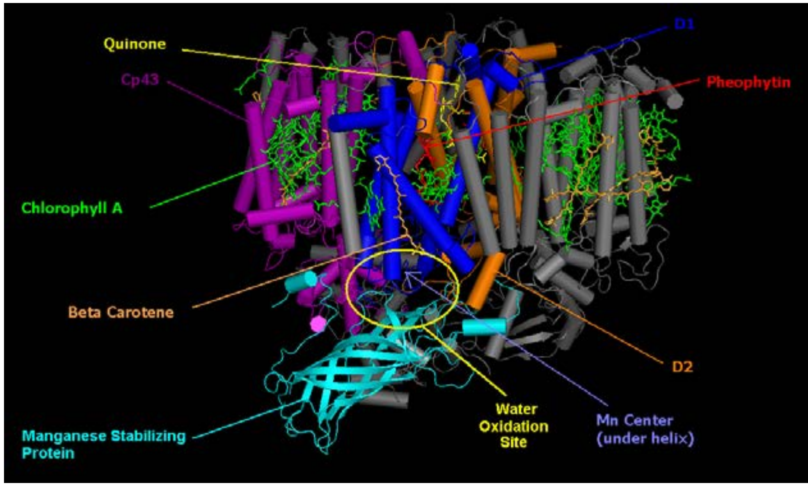
Overall Efficiency

- 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 chlorophyl) → 32% efficient conversion of ATP and NADPH to d-glucose, leaving
- 9% (collected as sugar) → 35–40% of sugar is recycled/consumed by the leaf in dark and photo-respiration, leaving
- 5.4% net leaf efficiency

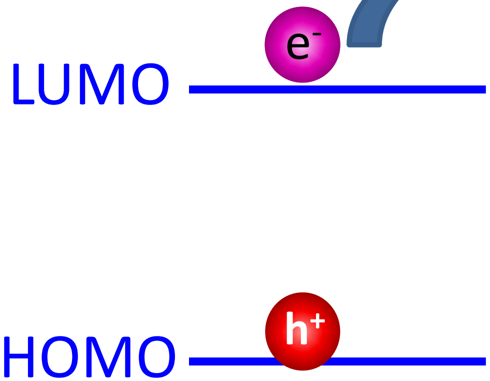
- In reality, the energy conversion efficiency is much less.
- Most photosynthetic processes are 0.1 %, with the most efficient at 1%.

Photosystem II

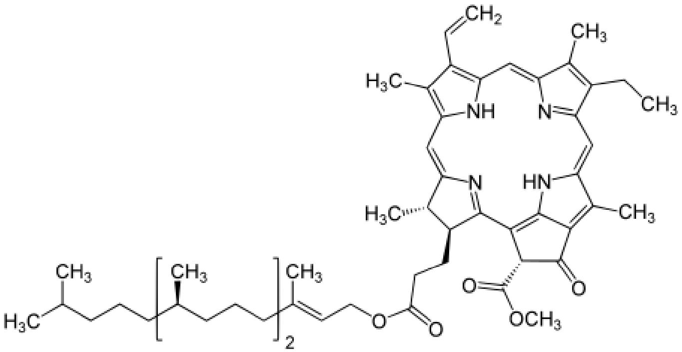




0.6-3 picoseconds

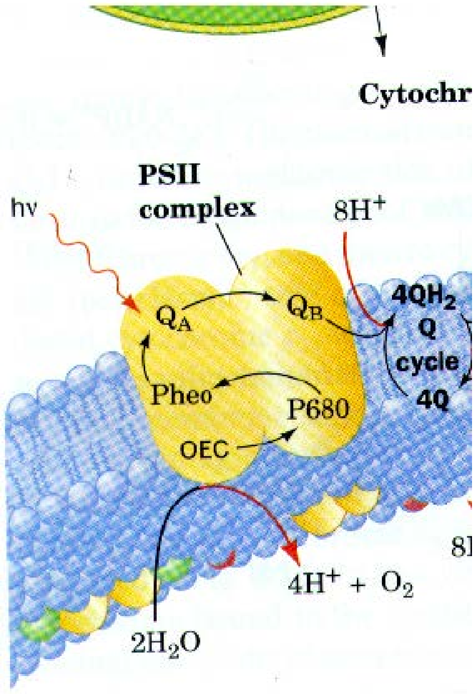


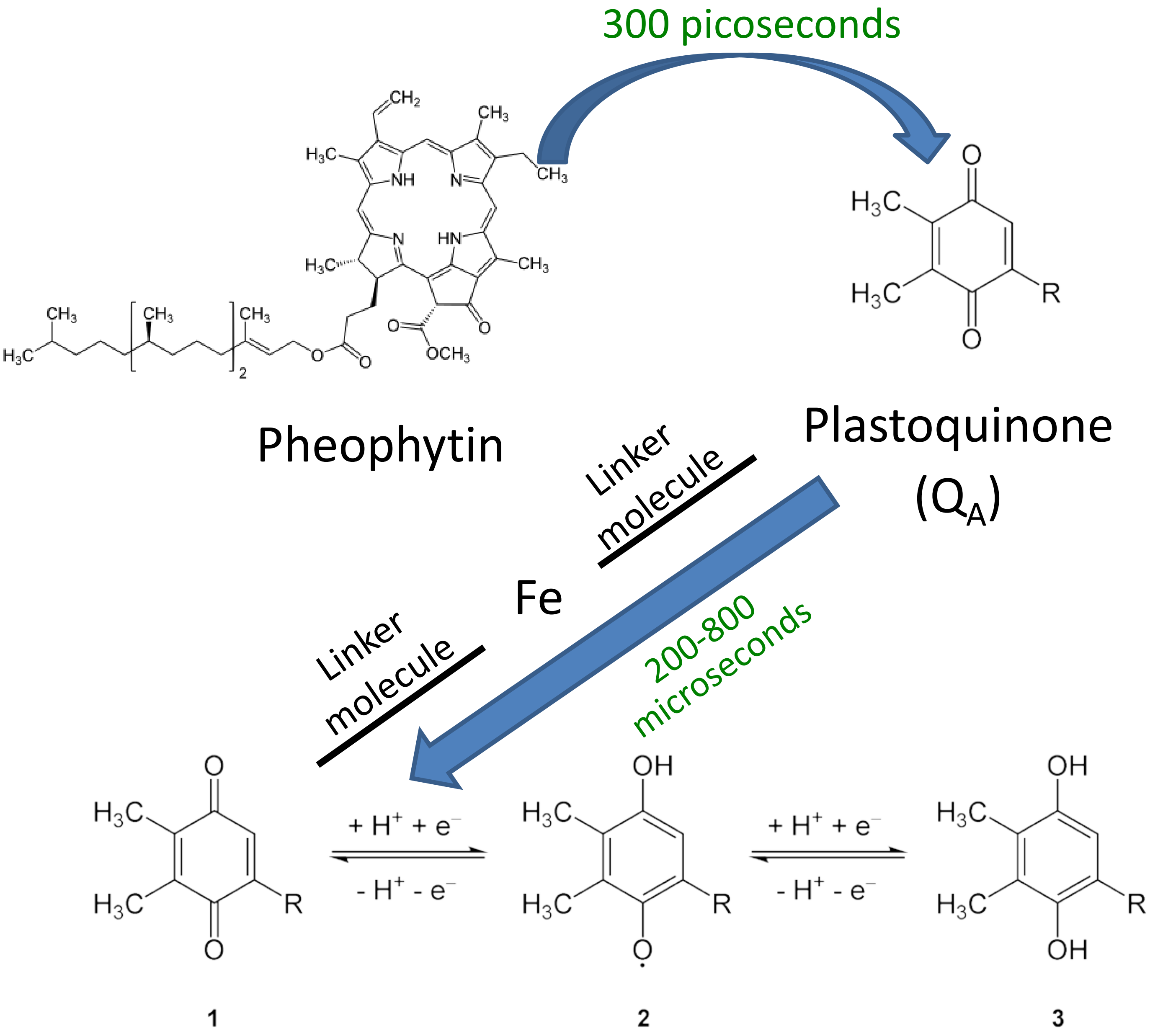
P680-dimer



Pheophytin

(i.e. chlorophyll without Mg)





300 picoseconds

Pheophytin

Plastoquinone (Q_A)

Linker molecule

Fe

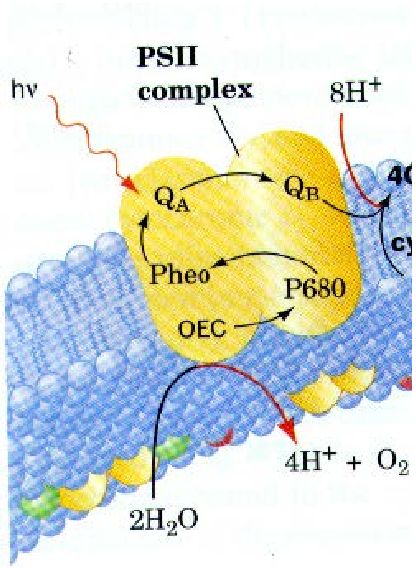
200-800 microseconds

Linker molecule

Plastoquinone (Q_B)

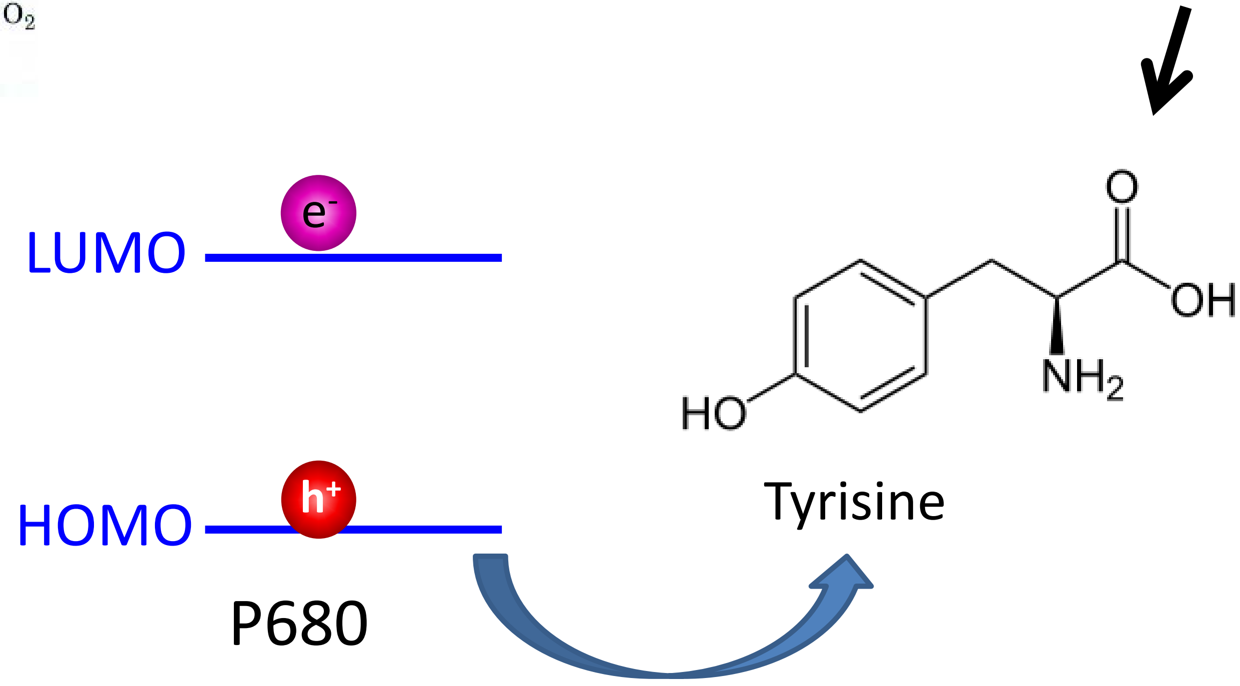
Plastoquinal (Q_B)

Photosystem II-What about the hole?



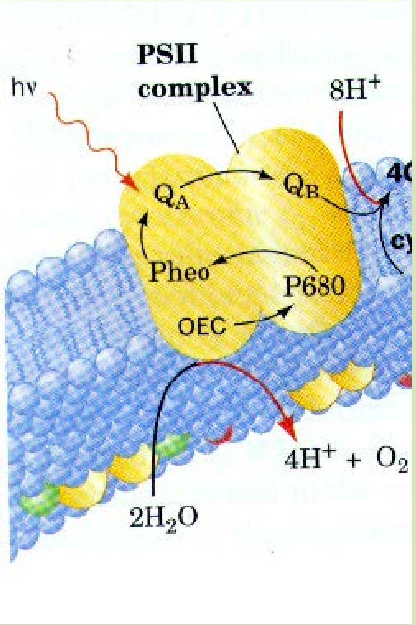
- The hole first transfers to a linker molecule (Tyrisine)

This can also take an electron from radical absorbed beta-carrotene

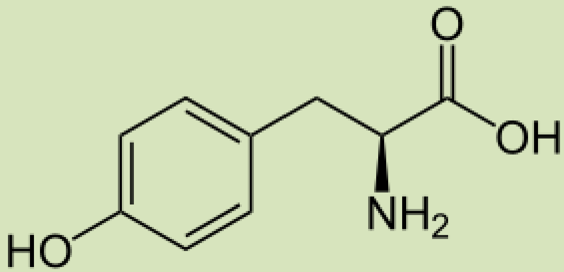


25 ns to 50 μs

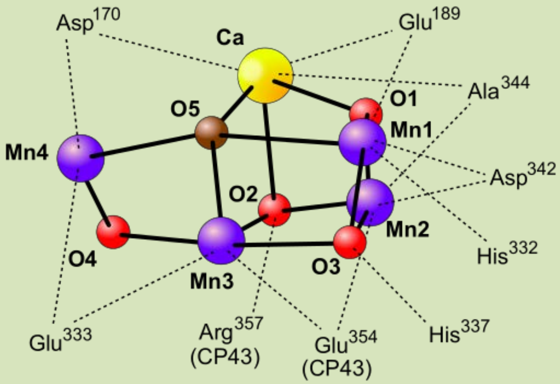
Photosystem II-Water oxidation



- Tyrisine then transfers the hole to the water oxidation catalyst .
- The actual structure of the catalyst is unknown.
- Nevertheless it is a really good catalyst.

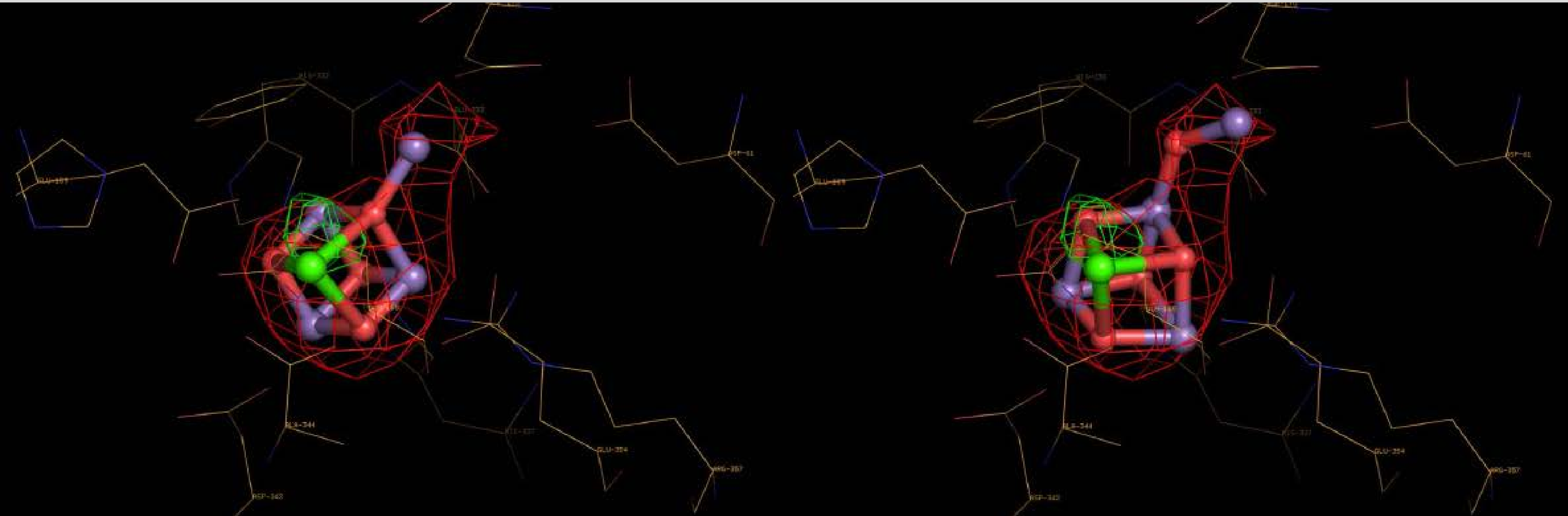


Tyrisine



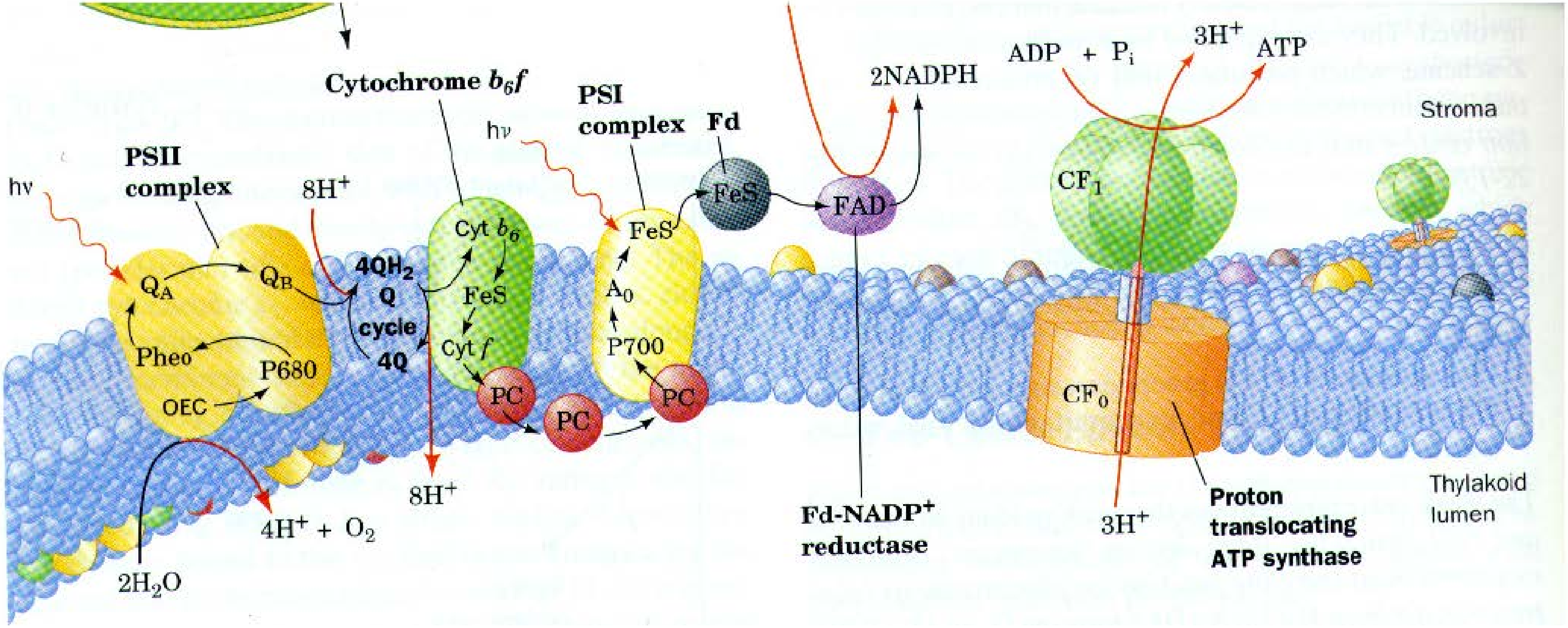
Water oxidation catalyst

- No-one has been able to reproduce this catalyst synthetically.
- The x-ray structure may be inaccurate because the x-rays may damage the sample during testing.
- Understanding this reaction (and maybe this catalyst) is one of the biggest keys to sustainable energy.

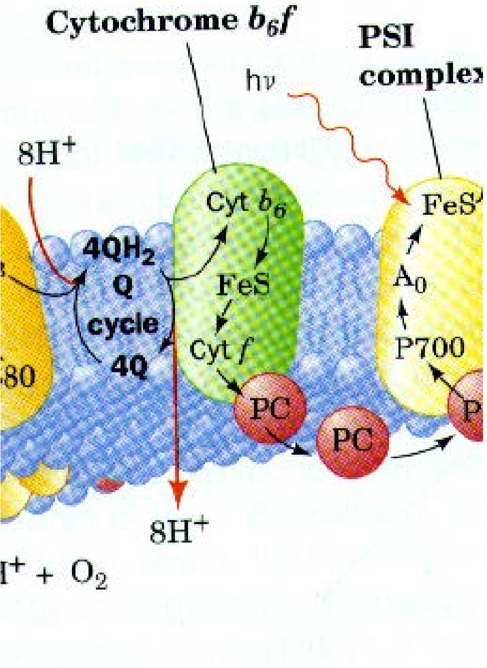


X-Ray structure

Calculated structure

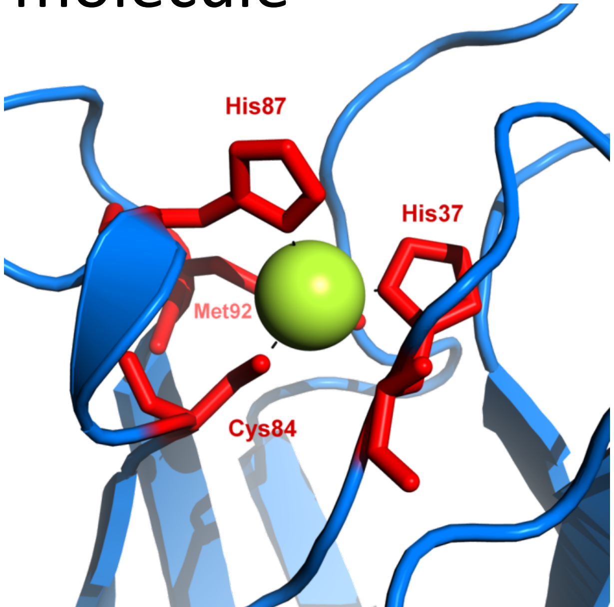

Cytochrome b_6f
PSI complex
Fd
2NADPH
ADP + P_i
$3H^+$
ATP
Stroma
hν
PSII complex
hν
$8H^+$
Cyt b_6
FeS
Cyt f
$4QH_2$
Q cycle
4Q
Q_A
Q_B
Pheo
P680
OEC
FeS
A_0
P700
FeS
FAD
CF_1
CF_0
PC
PC
PC
$8H^+$
$2H_2O$
$4H^+ + O_2$
$Fd\text{-}NADP^+$ reductase
$3H^+$
Proton translocating ATP synthase
Thylakoid lumen

Moving on- Cytochrome b_6f

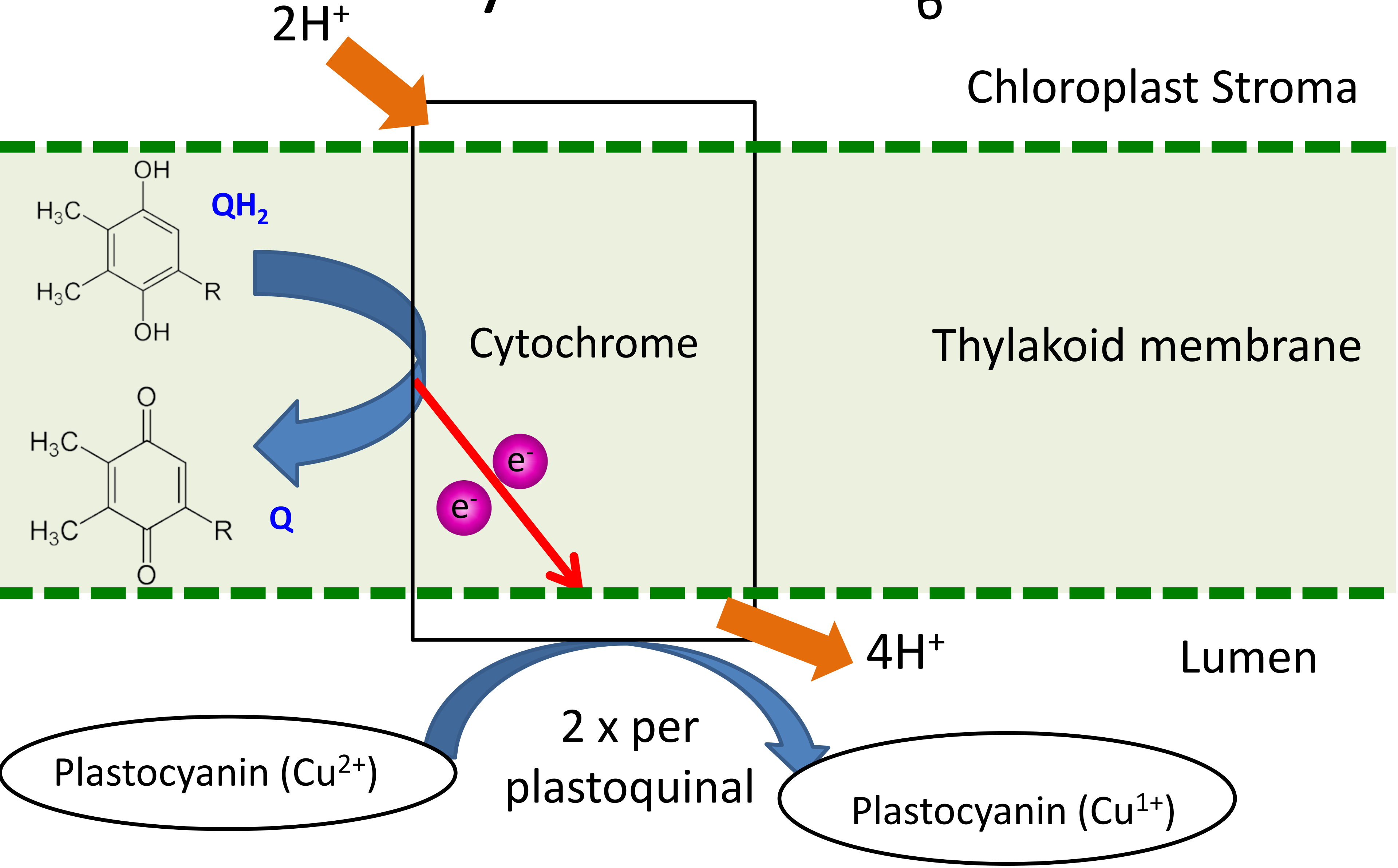


- The cytochrome works to pump protons up hill.
- This creates an bias that the system will use at a later point .
- Plastocyanin is a huge enzyme that works as an electron transfer molecule

- A Cu in plastocyanin converts between 2+ and 1+ to transfer electrons.



Cytochrome b_6f



$2H^+$

Chloroplast Stroma

QH_2

Cytochrome

Thylakoid membrane

Q

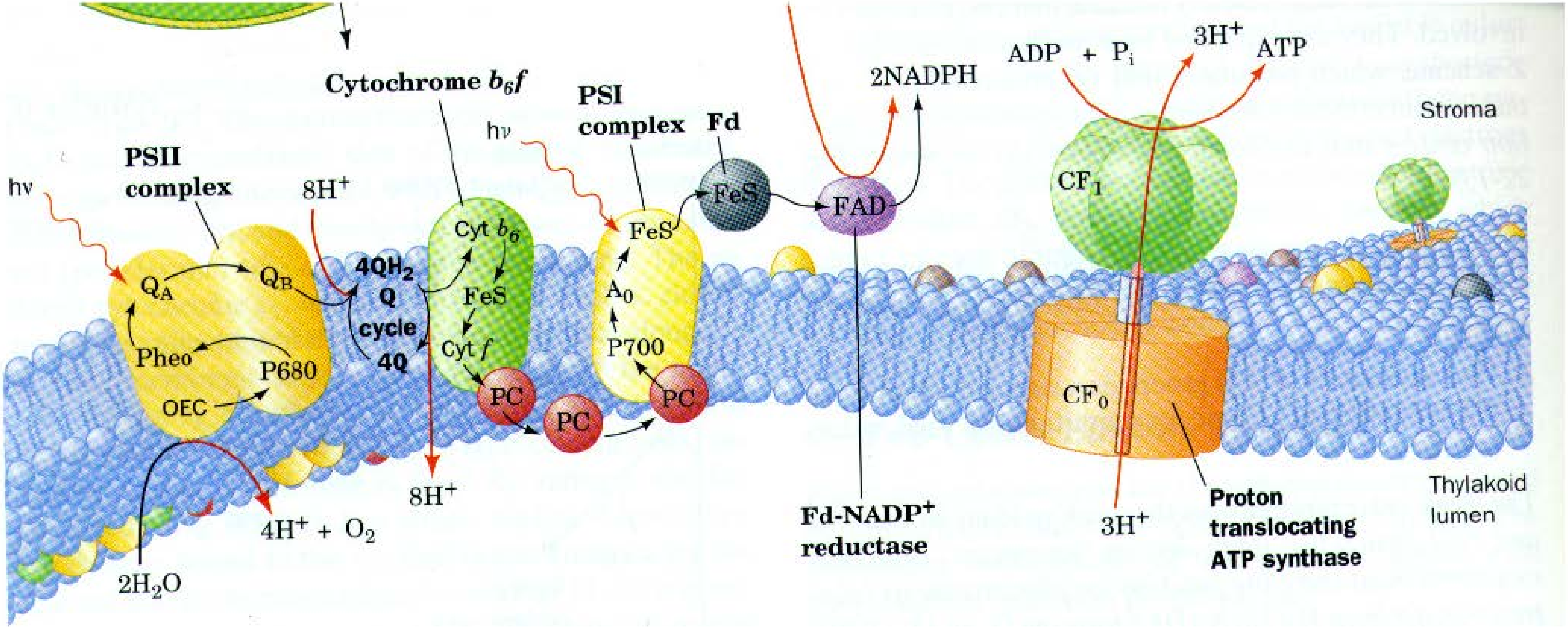
$4H^+$

Lumen

Plastocyanin (Cu^{2+})

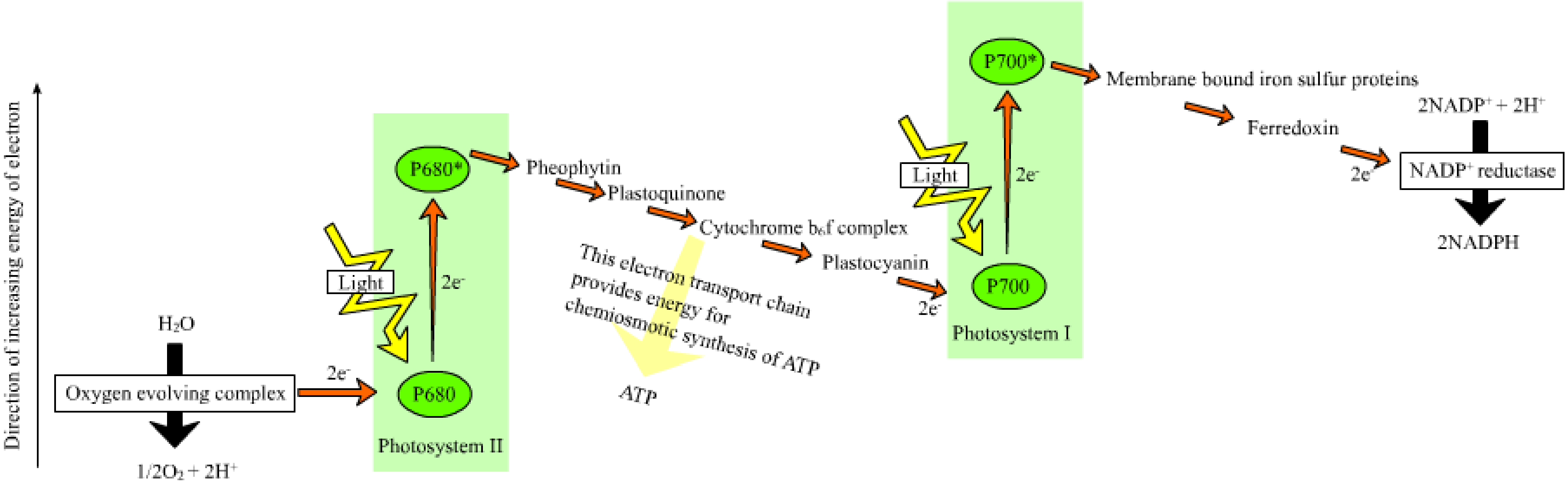
2 x per plastoquinal

Plastocyanin (Cu^{1+})

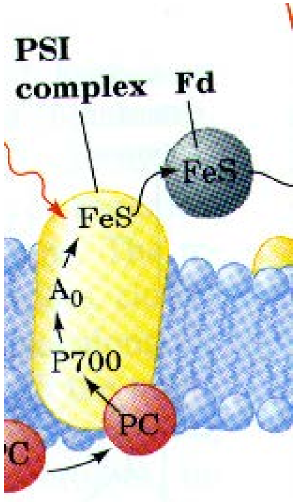

Cytochrome b_6f
PSI complex
Fd
2NADPH
ADP + P_i
$3H^+$
ATP
Stroma
hν
PSII complex
hν
$8H^+$
CF_1
Cyt b_6
FeS
FeS
FAD
Q_A
Q_B
$4QH_2$
Q cycle
4Q
FeS
A_0
Cyt f
P700
Pheo
P680
OEC
PC
PC
PC
CF_0
$8H^+$
$4H^+ + O_2$
$2H_2O$
Fd-NADP$^+$ reductase
$3H^+$
Proton translocating ATP synthase
Thylakoid lumen

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.



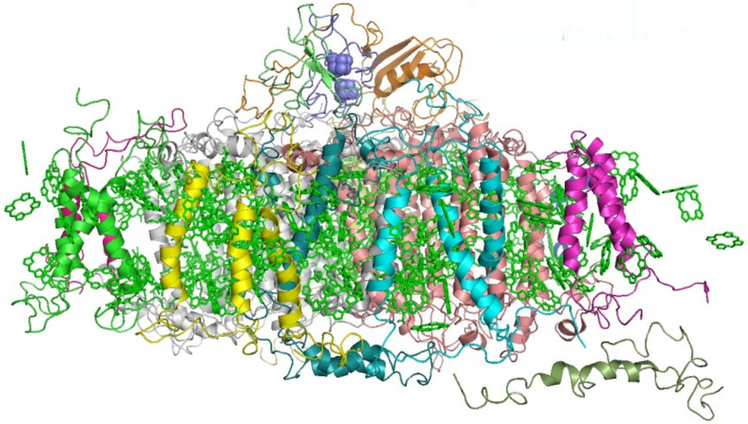
Photosystem I



- This is called #1 because it was the first photosystem produced by cells.

- Some bacteria don’t have PSII and basically run on just PSI.

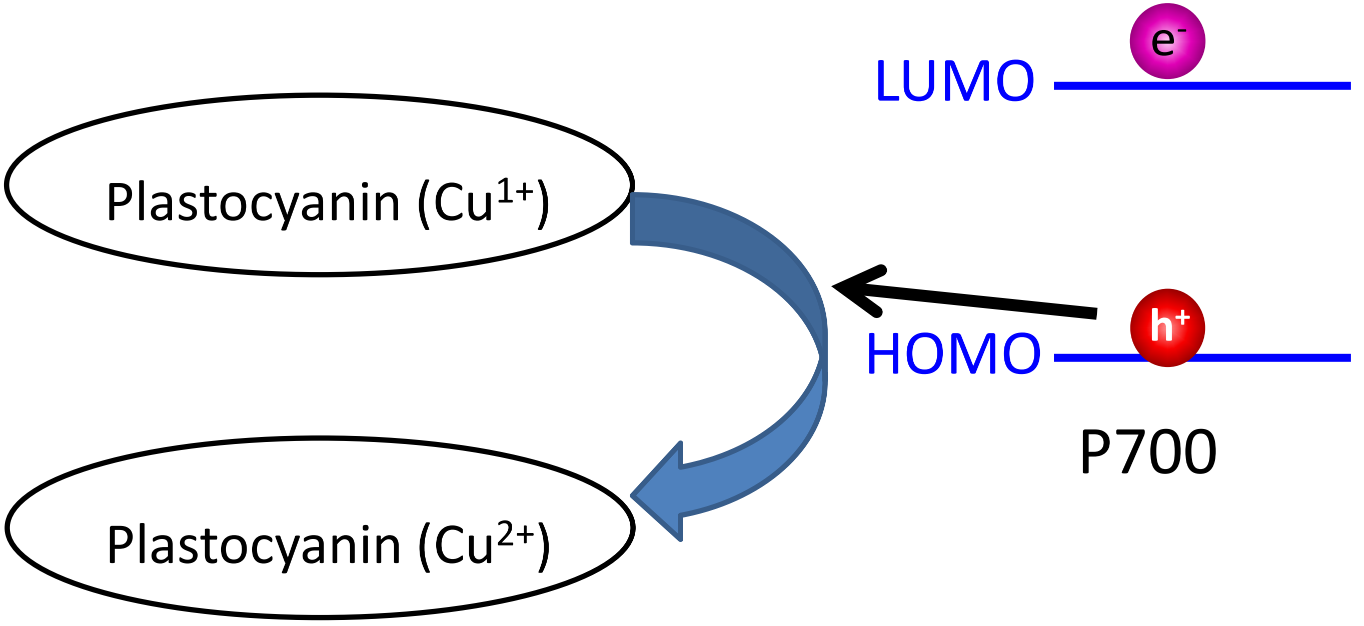
- Photosystem I contains
  - 110 cofactors (random helper molecules)
  - 154 Chlorophyll
  - 13 more Chlorophyll’s in reaction center
  - 22 beta-carotene
  - 4 different types of lipids



Photosystem I

Plastocyanin-Photosystem I

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



Plastocyanin (Cu^{1+})

Plastocyanin (Cu^{2+})

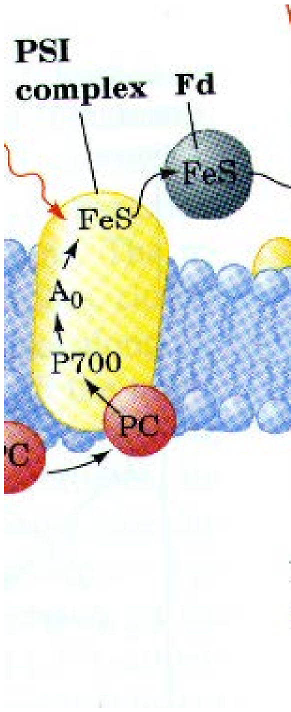
LUMO

e^-

HOMO

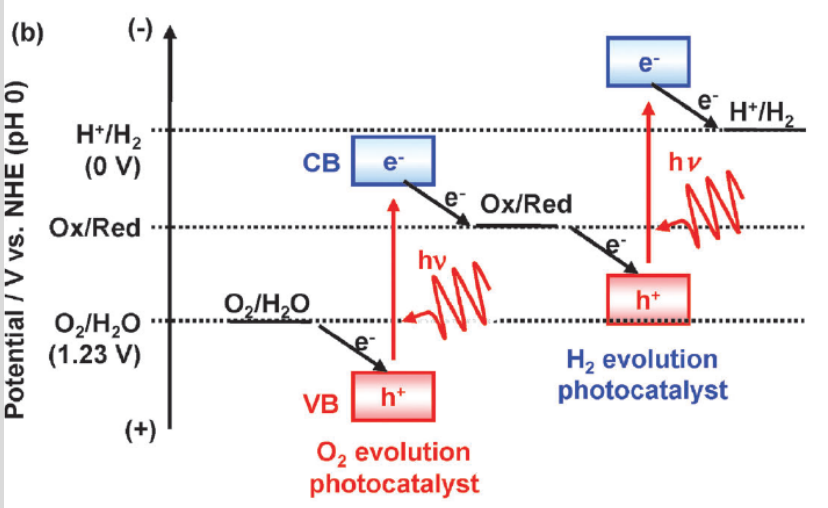
h^+

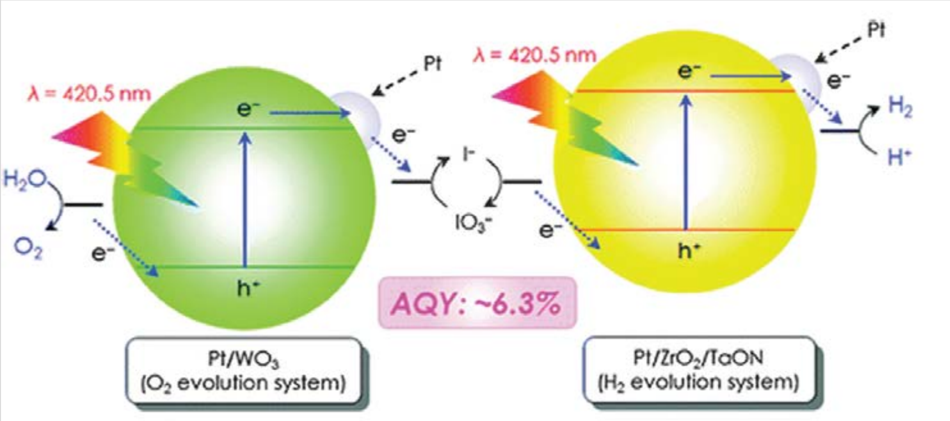
P700



Just Like Photoelectrochemistry

- There are a few people working on this approach, but it is under investigated.
- Typically an I/IO_3^- redox couple is used as an intermediate material.
- The fundamental issues with this approach closely mimick that of a Type 1 approach.

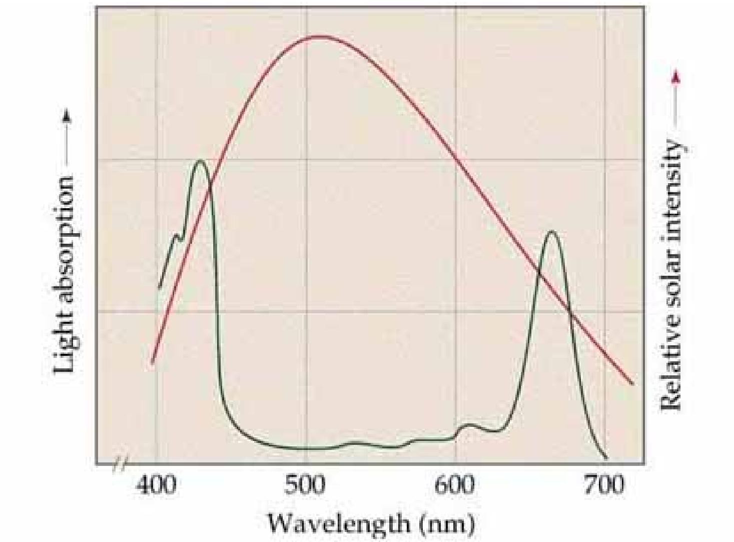




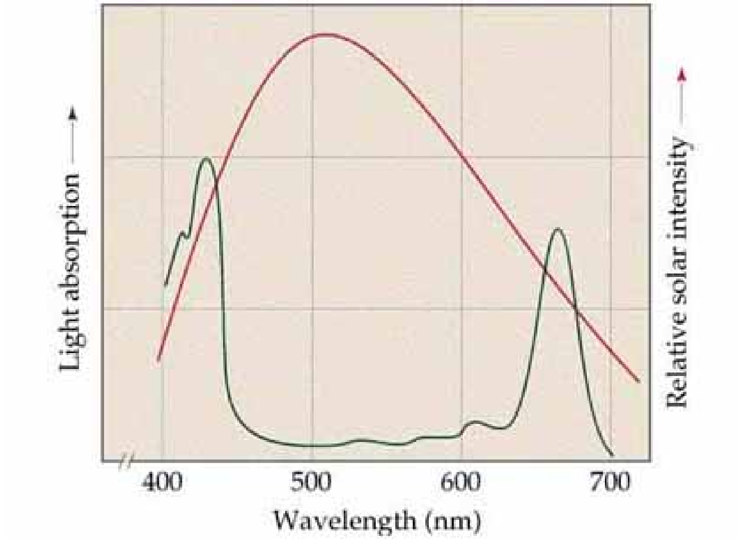
Domen, Chem. Rev., 2014

Evolution- not always smart

- Both Photosystem I and Photosystem II use chlorophyll.
- Thus both photoabsorbers absorb the same wavelength.



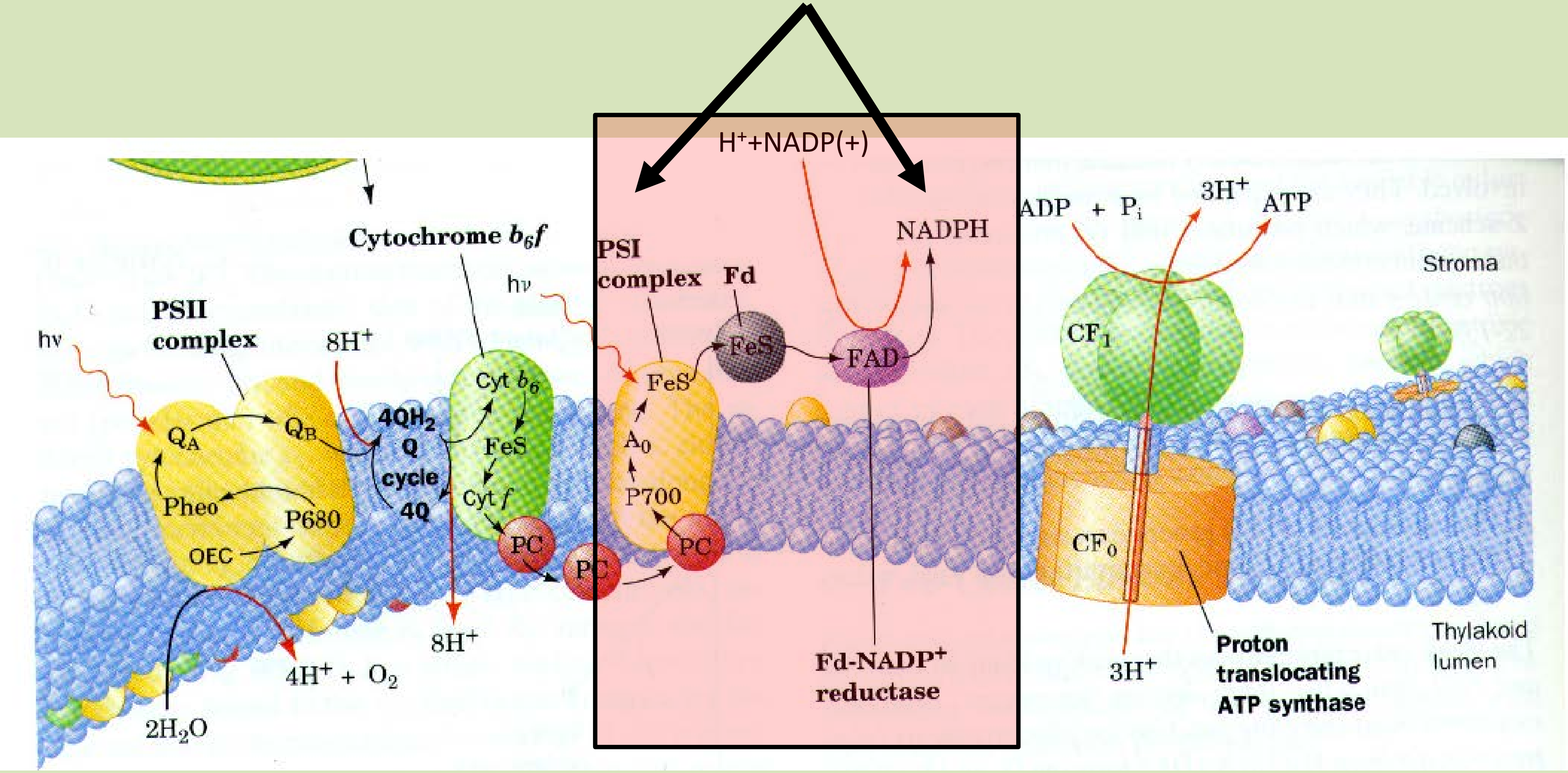
Light absorption from Photosystem I



Light absorption from Photosystem II

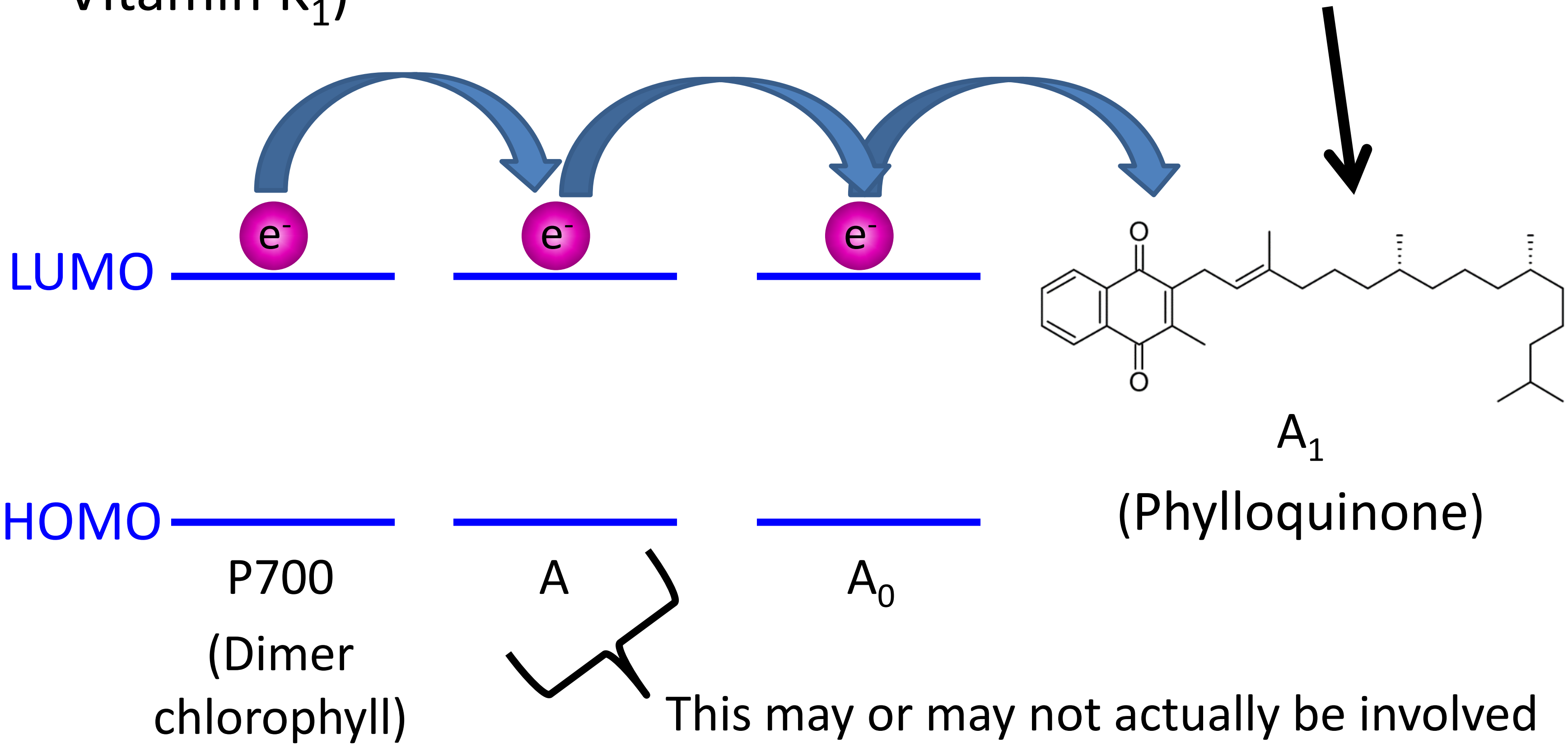
Not very efficient

Photosystem 1 produces NADPH



Photosystem I- Electron transfer

- The electron transfers first to a hetero-dimer chlorophyll (A), then a monomer chlorophyll (A_0) .
- Next it goes to A1, which is typically Phylloquinone (i.e. Vitamin K_1)



P700
(Dimer chlorophyll)

A

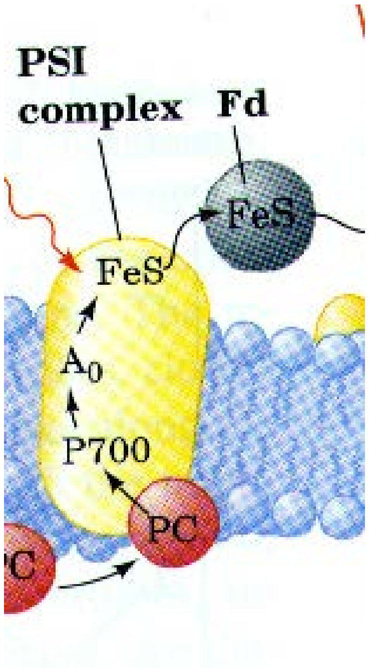
A_0

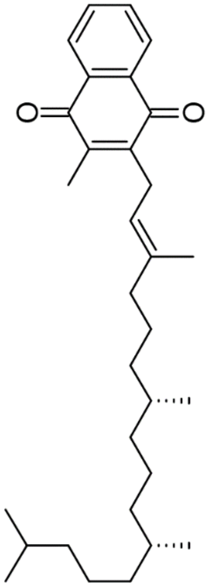
A_1
(Phylloquinone)

This may or may not actually be involved

Photosystem I- Electron transfer

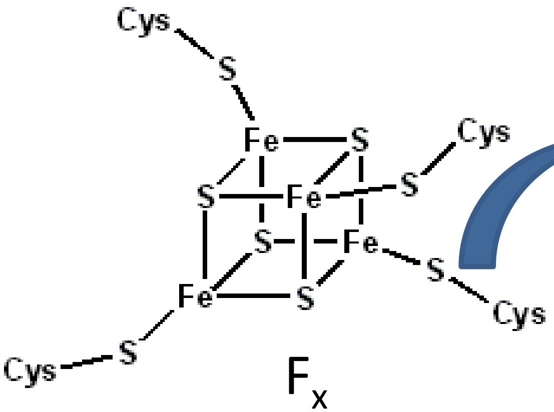
- The electron then transfers through a set of iron-sulfide cubanes.





A_1

(Phylloquinone)



F_x

(Fe_4S_4)

F_a

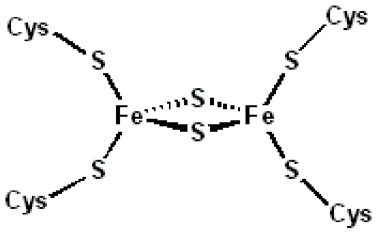
(Fe_4S_4)

F_b

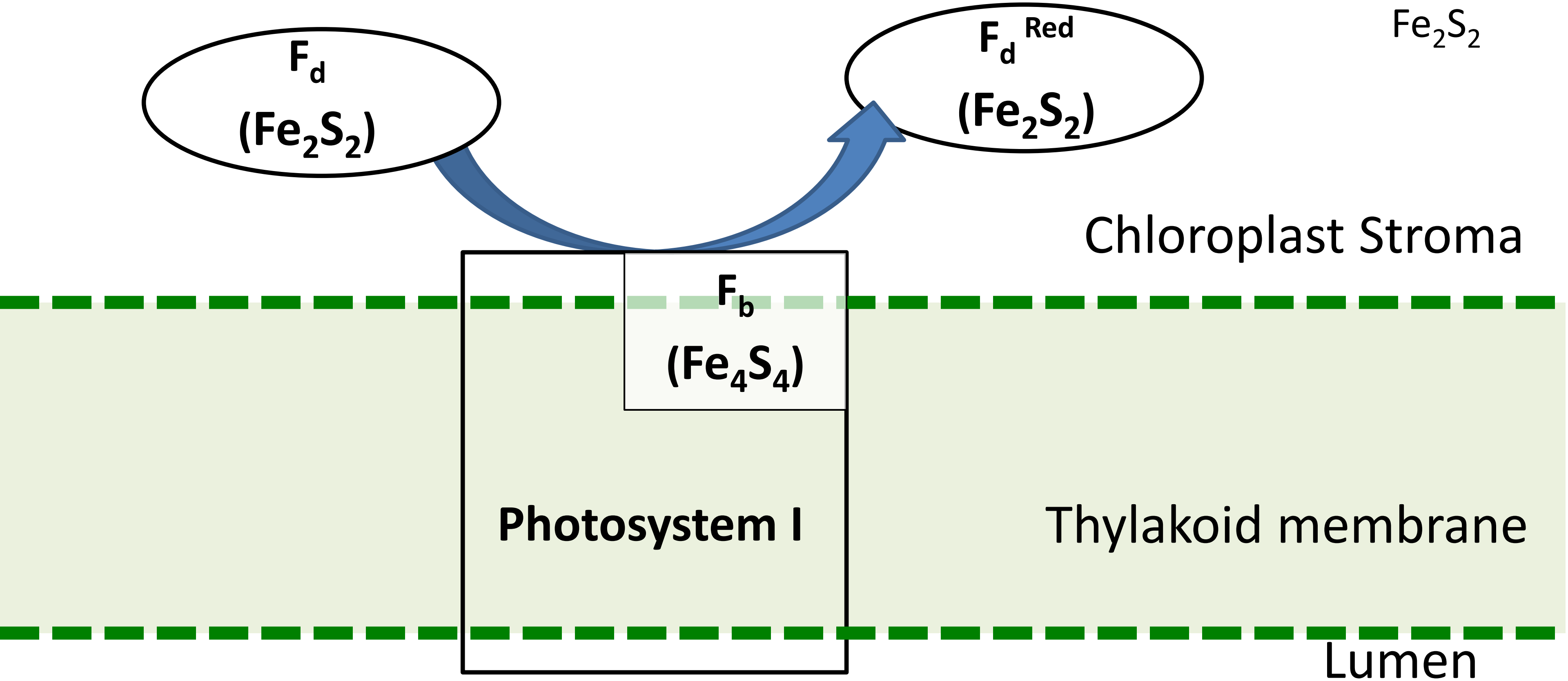
(Fe_4S_4)

Ferrodoxin

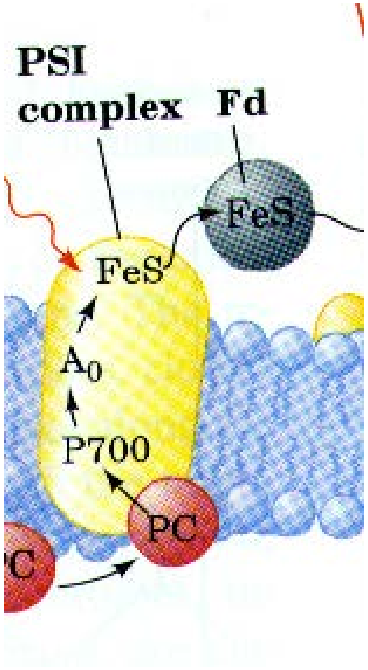
- Ferrodoxin is a protein with a Fe_2S_2 active site that accepts electrons.
- *The Fe oxidation state varies between 3^+ and 2^+ to accept charge.*

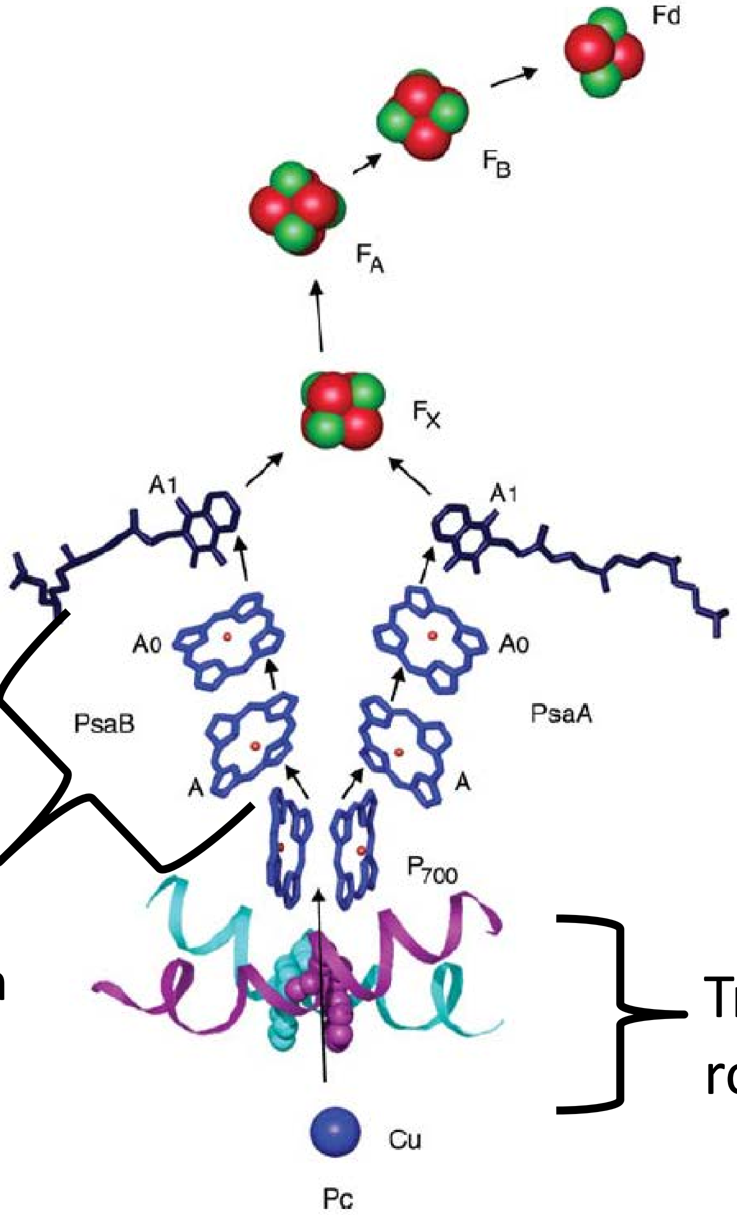


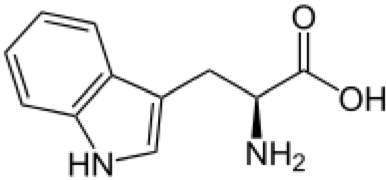
Fe_2S_2



Photosystem I- All together







Side B is thought to be much more active than side a

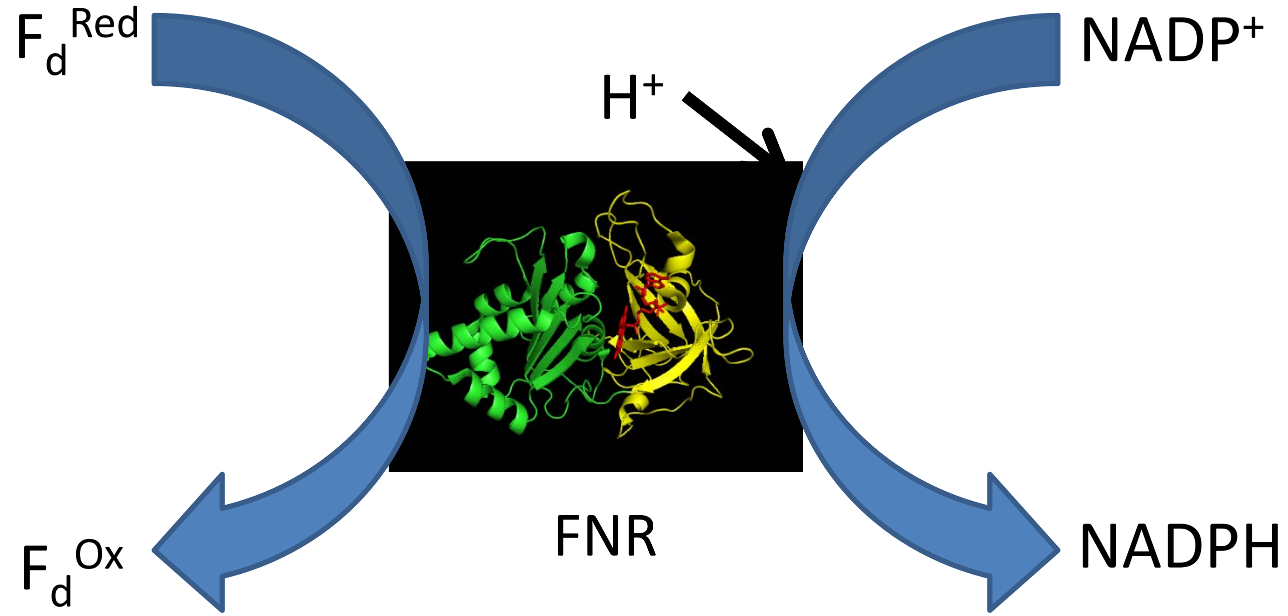
Tryptophan *might* play a role in this transfer

Ferredoxin—NADP(+) reductase

- Ferredoxin—NADP(+) reductase (FNR) is an enzyme that works as a catalyst.

Thus 2 electrons / photons needed for NADP formation

$$2{F_d}^{Red} + H^+ + NADP^+ \rightarrow NADPH + 2{F_d}^{Ox}$$



${F_d}^{Red}$

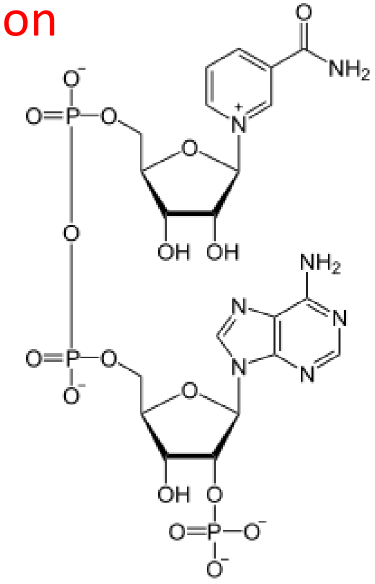
$NADP^+$

H^+

${F_d}^{Ox}$

FNR

NADPH



$NADP^+$

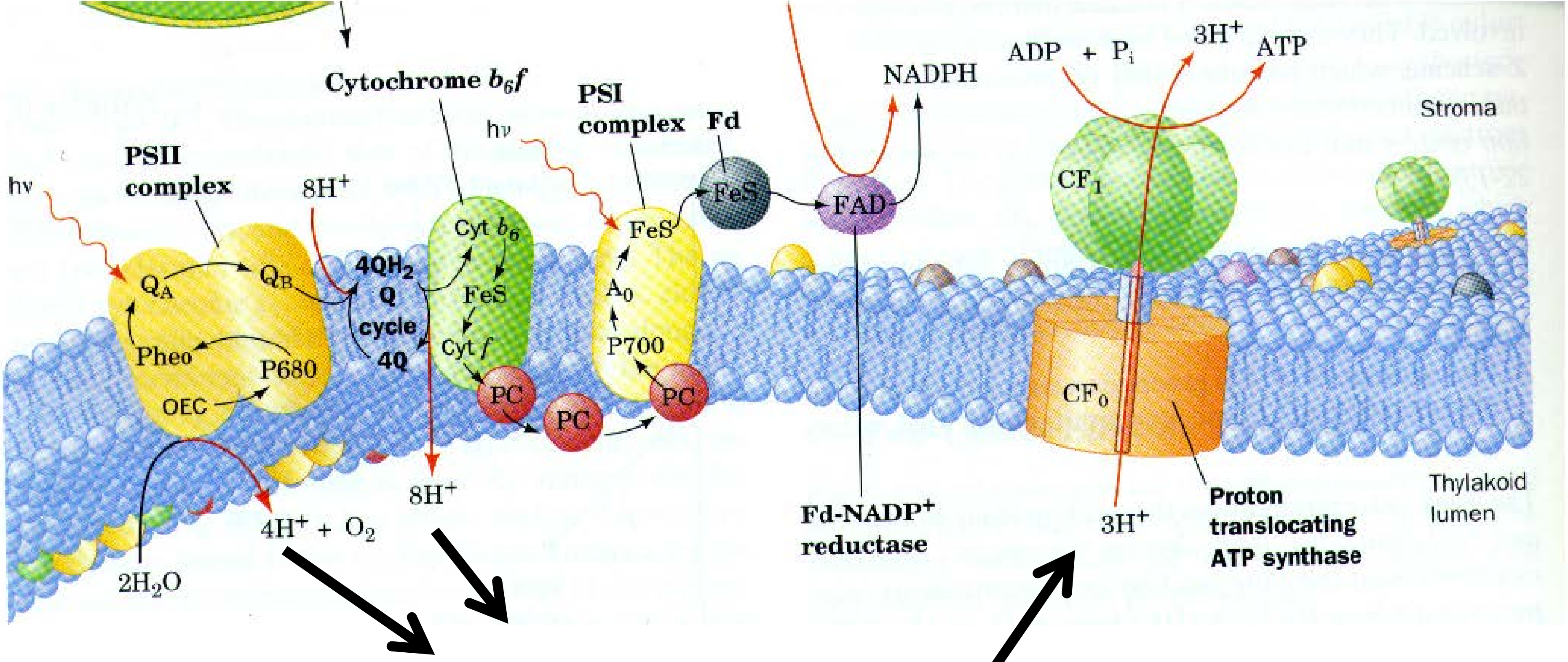
Break

Serious Build-up of Protons

PS 2: $2H_2O + 4hv \rightarrow 4e^- + 4H^+ + O_2$

PS 1: $2e^- + H^+ + 2hv + \mathrm{NADP}^+ \rightarrow \mathrm{NADPH}$

H⁺+NADP(+)

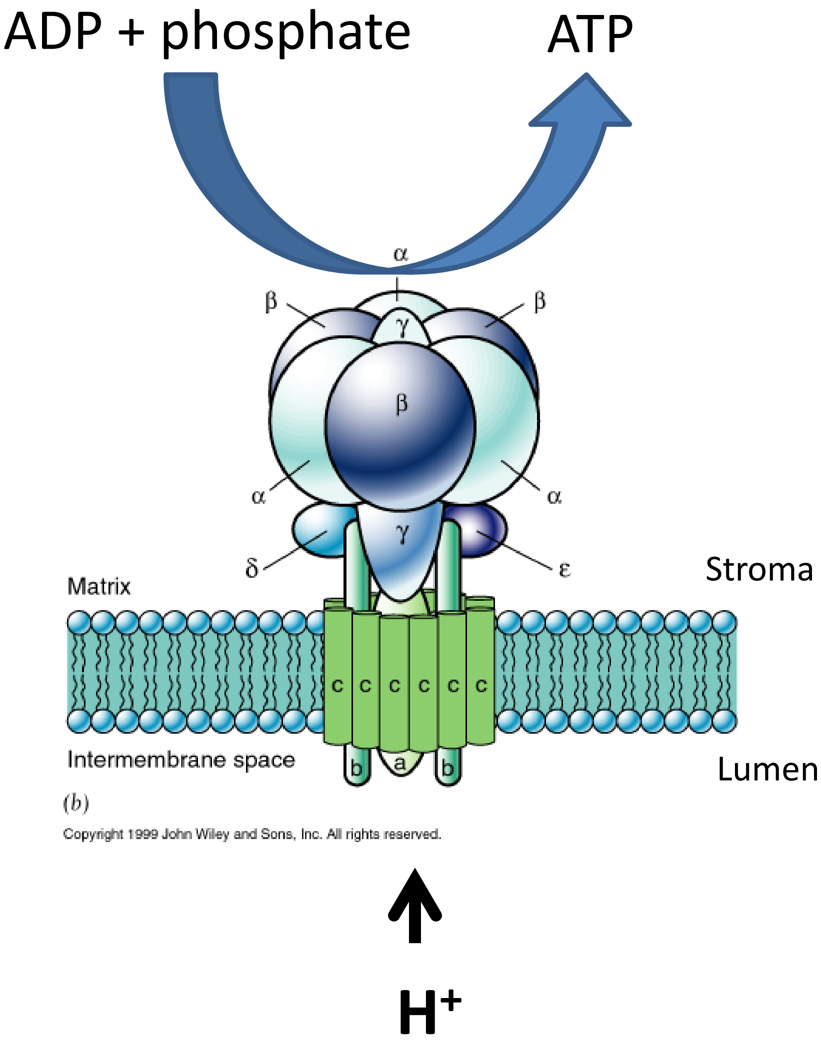


12 protons being pumped in

$2\ H_2O + 2\ NADP^+ + 3\ ADP + 3\ P_i + \text{light} \rightarrow 2\ NADPH + 2\ H^+ + 3\ ATP + O_2$

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 neccessary for charge balancing



ADP + phosphate

ATP

Stroma

Lumen

H^+

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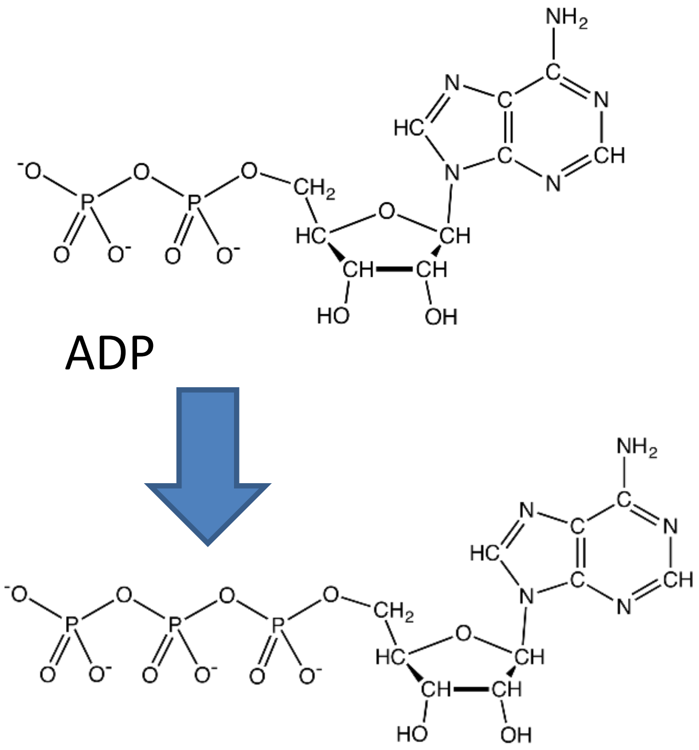
ATP

$$\overbrace{[ADP]^{3-} + PO_4^{3-}}^{\text{Inside (Lumen)}} + 2H^+ \rightarrow \overbrace{[ATP]^{4-} + H_2O}^{\text{Outside (Stroma)}}$$



ADP

ATP

Gibbs Free Energy

$$\Delta G = RTLn\left(\frac{Products}{Reactants}\right)$$

$$\Delta G = 2.3RTLog\left(\frac{Products}{Reactants}\right)$$

- For this reaction ΔG = 30.5 kJ/mol.

Electrochemistry

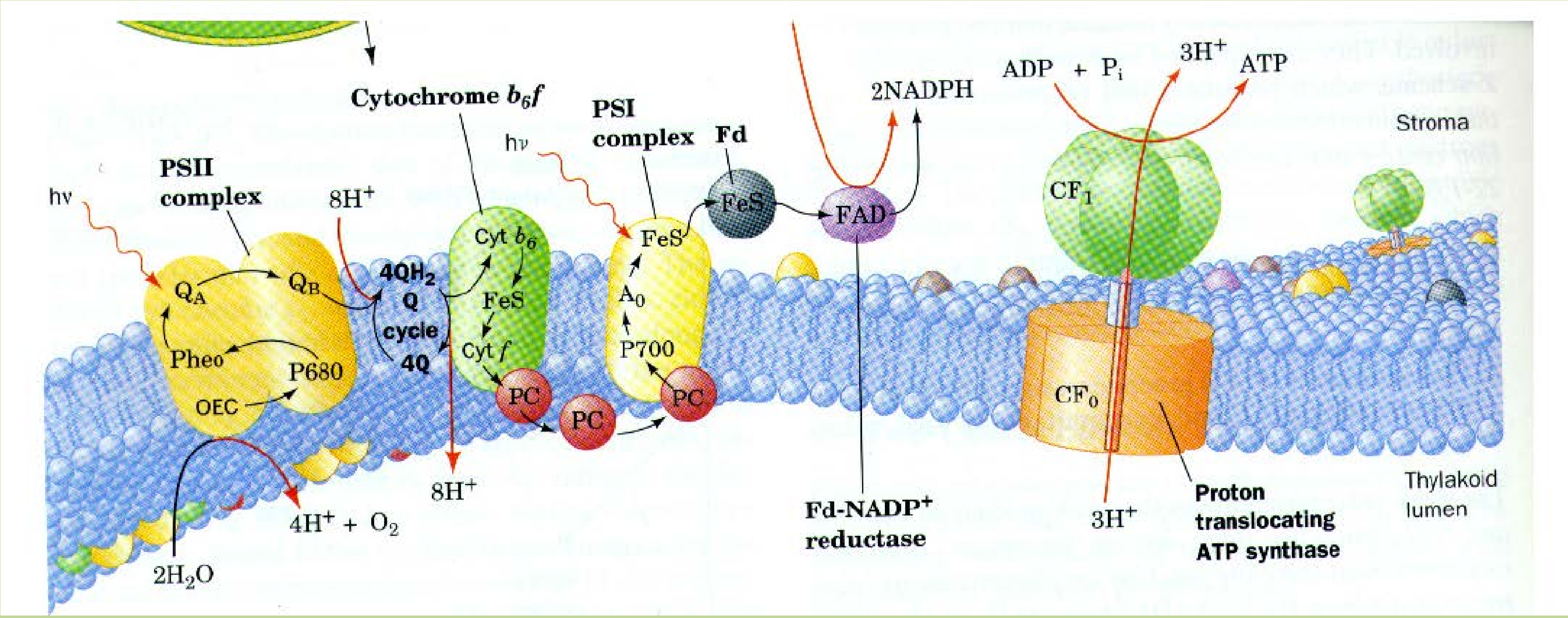
$$\Delta G = -n \times F \times \Delta E$$

@T=25C →

$$\Delta E = 59\ meV\ Log\left(\frac{Products}{Reactants}\right)$$

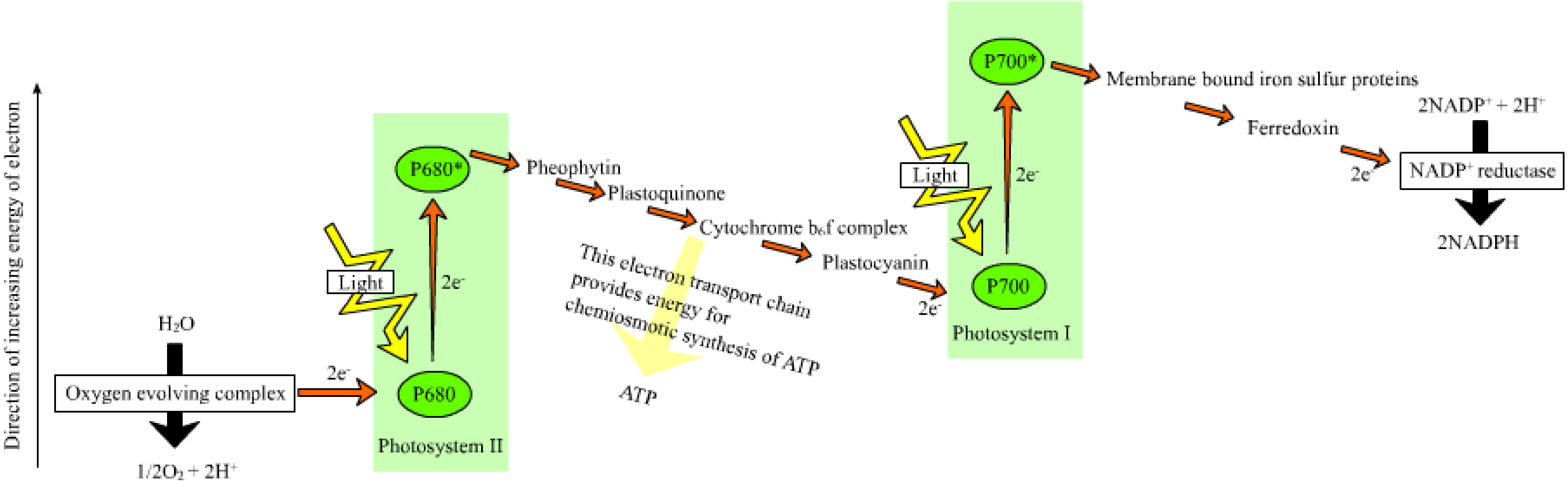
Overall Reaction

$$H_2O + 2\ NADP^+ + [ADP]^{3-} + PO_4^{3-} + \text{light} \rightarrow 2\ NADPH + [ATP]^{4-} + O_2$$



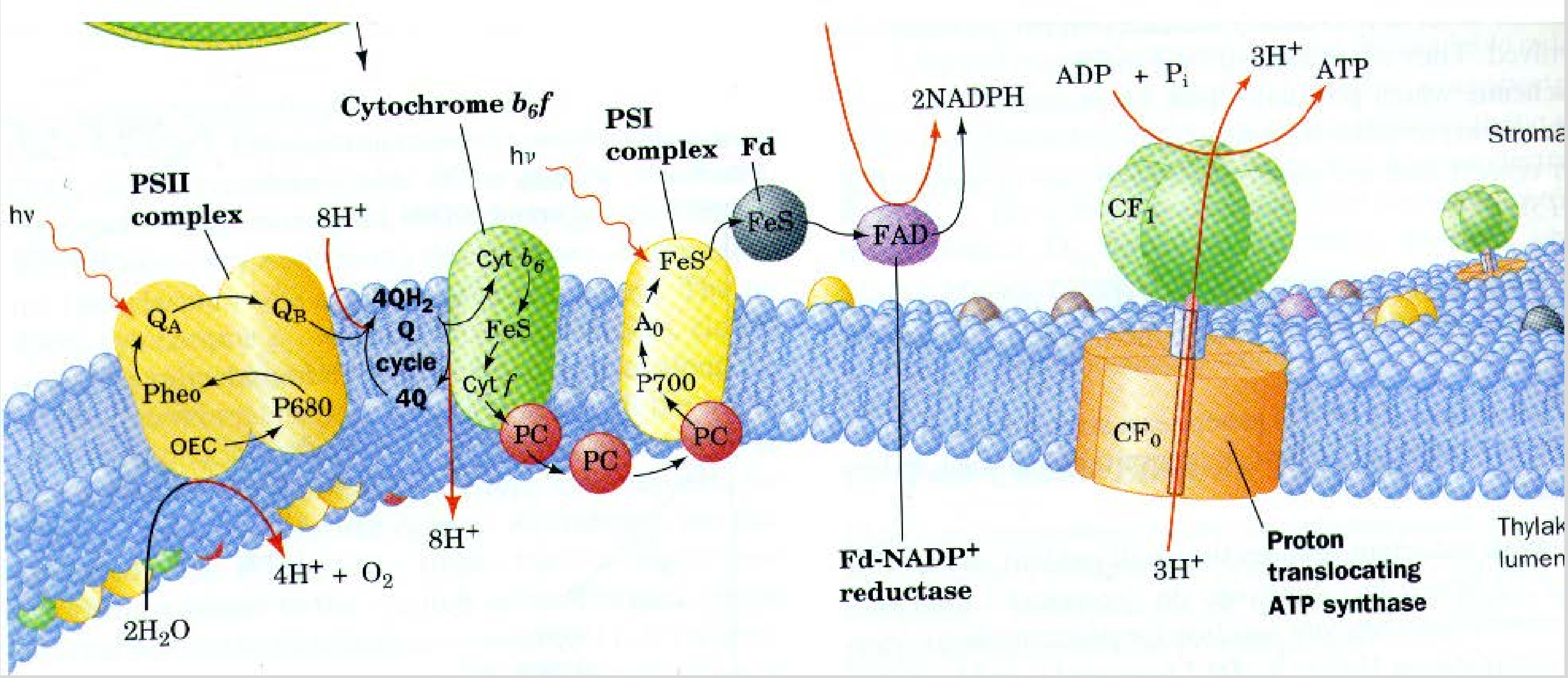
Energetics

- 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.



Who needs Photosystem II ?

- What if we just use photosystem I?
- Could that be more efficient?
- How to do that?



Who needs Photosystem II ?

- Materials such as purple non-sulfur bacterium and green sulfur bacterium don't use PSII

- For an oxidizing agent they use H_2 or H_2S giving the following reaction.

$$2\,H_2S + 2\,NADP^+ + 3\,ADP + 3\,P_i + \text{light} \rightarrow 2\,NADPH + 2\,H^+ + 3\,ATP + 2S$$

- Compare this to that for the combined Photosystem I + II system. Which can you gain more energy from?

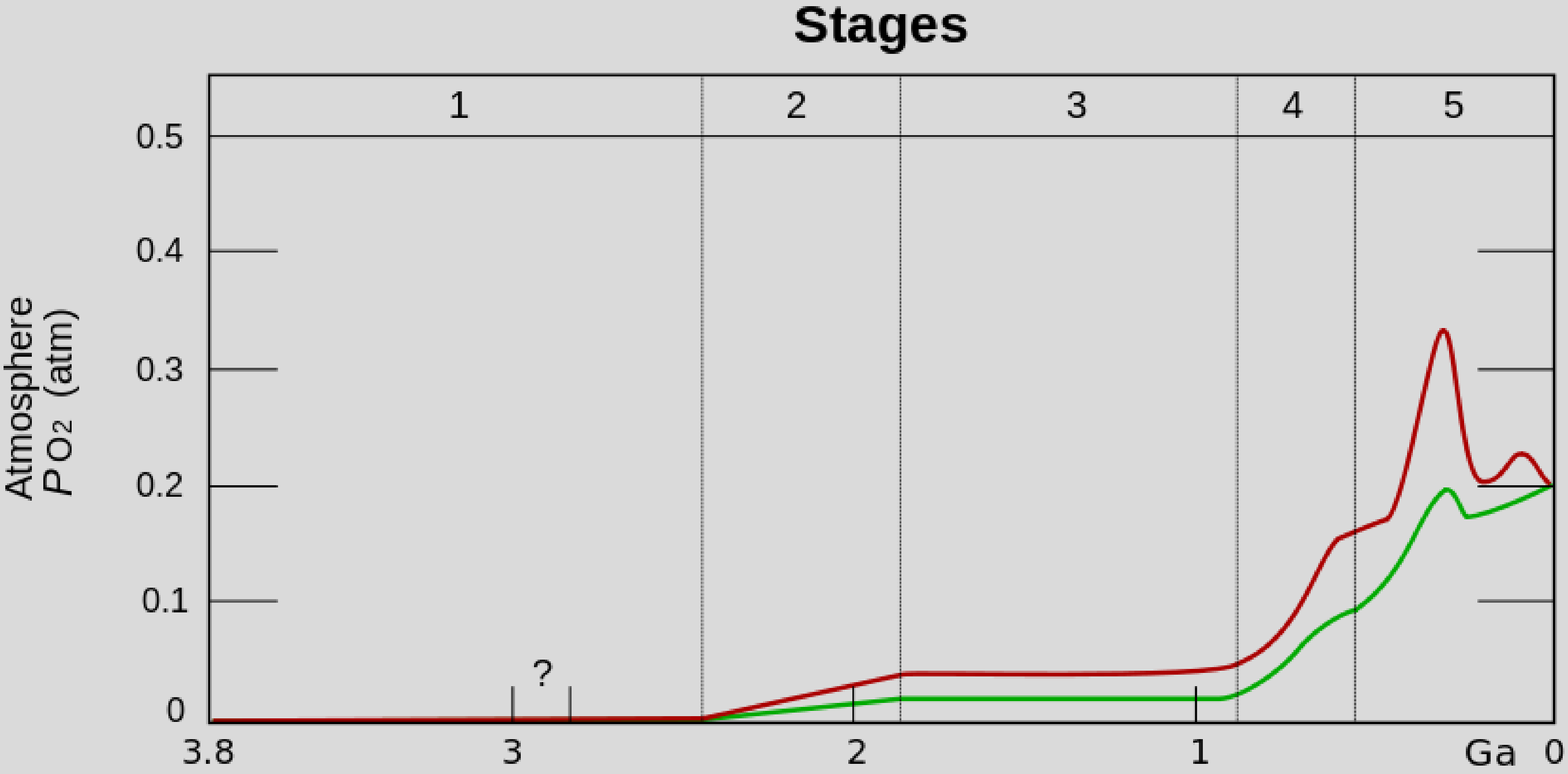
$$2\,H_2O + 2\,NADP^+ + 3\,ADP + 3\,P_i + \text{light} \rightarrow 2\,NADPH + 2\,H^+ + 3\,ATP + O_2$$

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 CO_2 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.



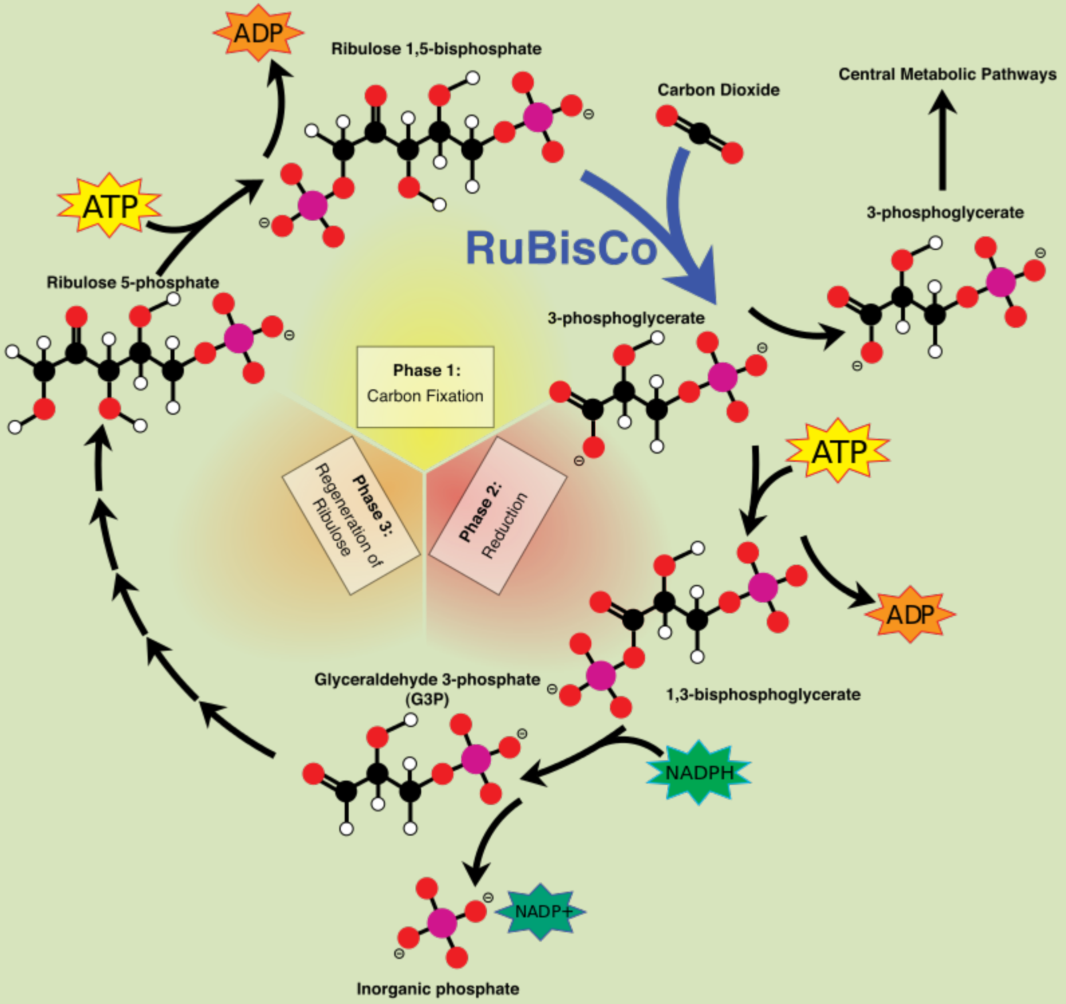
Billions of years

Non-Photosynthesis Reactions

Calvin Cycle

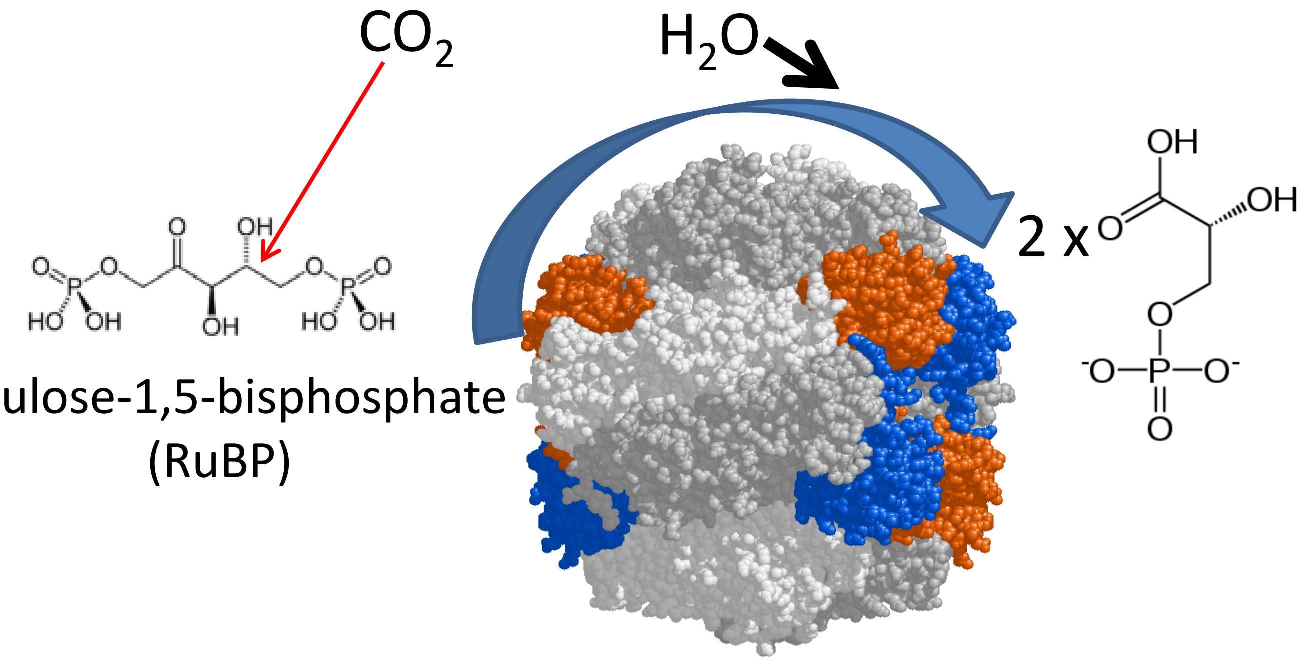
- The Calvin cycle converts CO_2 to hydrocarbons.

$$3\ CO_2 + 9\ ATP + 6\ NADPH + 6\ H^+ \rightarrow C_3H_6O_3\text{-}PO_3 + 9\ ADP + 8\ P_i + 6\ NADP^+ + 3\ H_2O$$



CO_2 adsorption

- The CO_2 basically splits a RuBP into 2 molecules.
- ΔG = -35 kJ/mol.



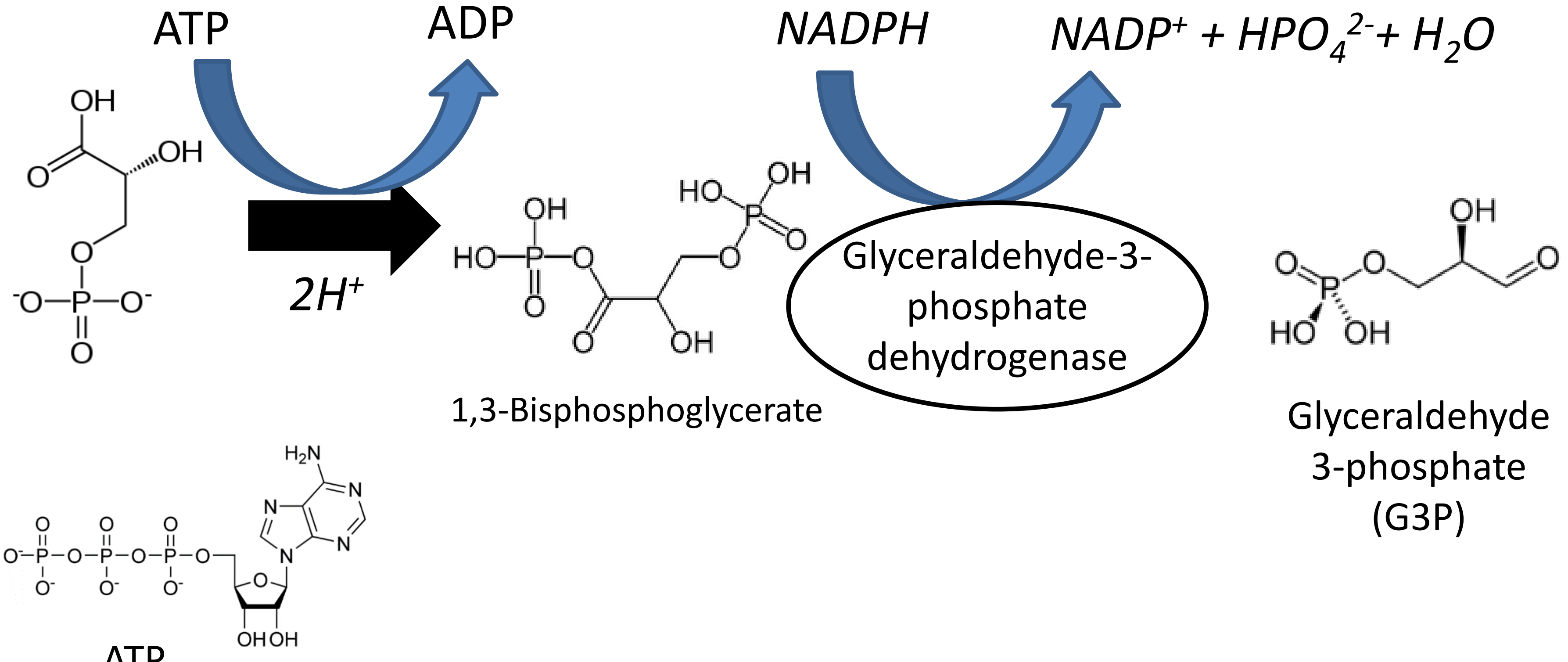
Ribulose-1,5-bisphosphate (RuBP)

Ribulose-1,5-bisphosphate carboxylase/oxygenase (colors denote dimers)

RuBisCO

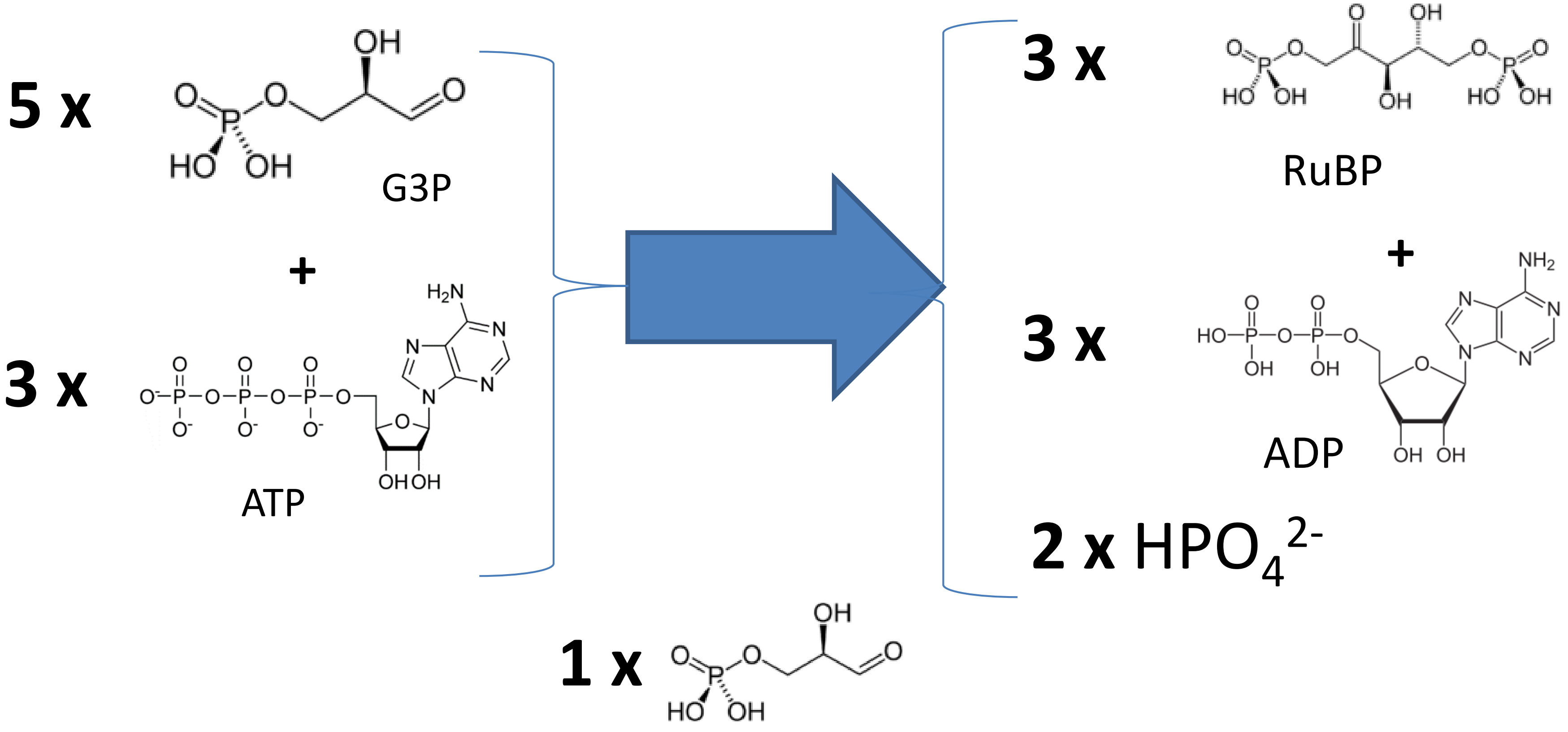
ATP

- 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

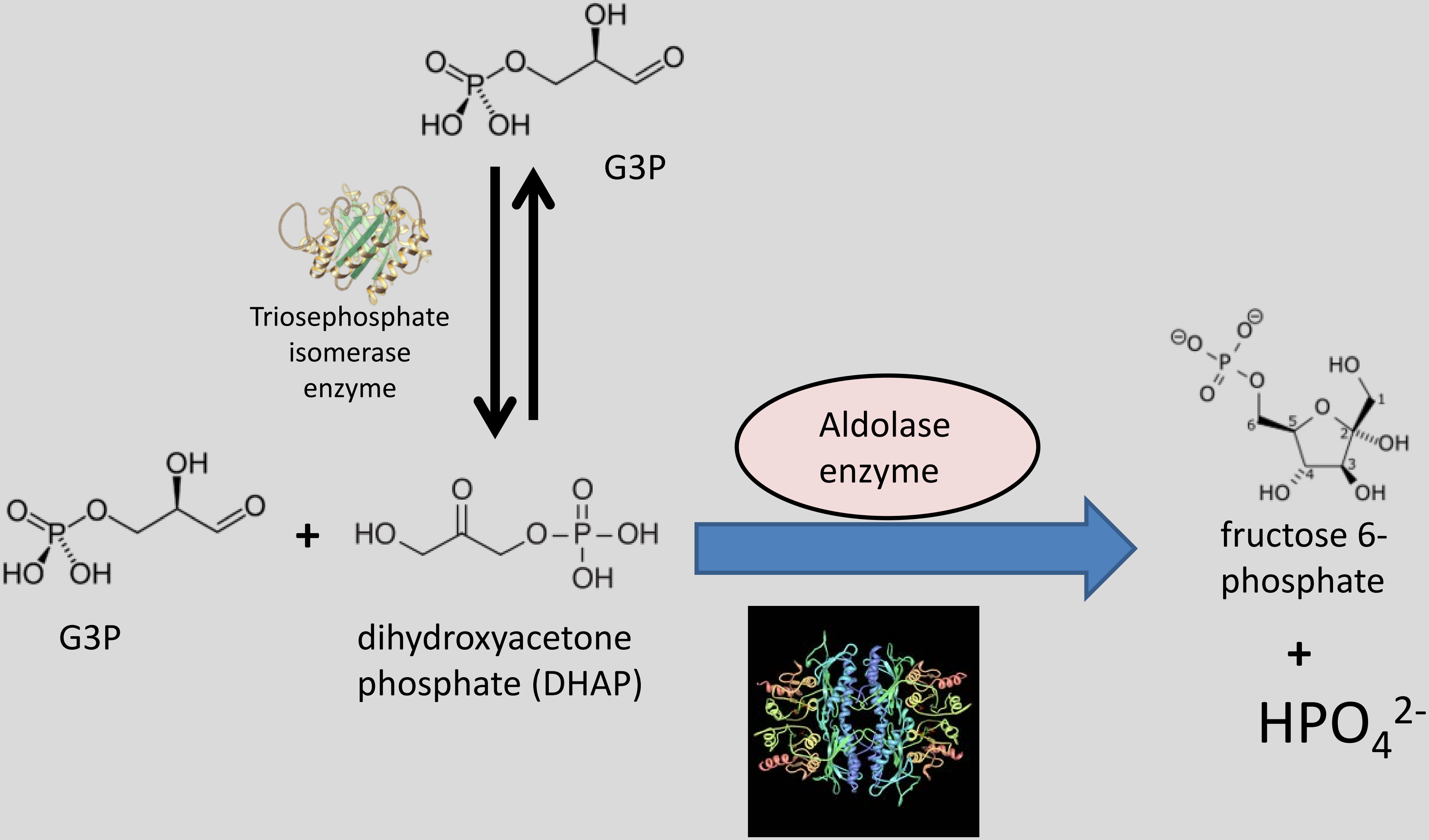
- The reaction below is for 3 absorbed CO_2 molecules.



Overall Reaction

$$3\ CO_2 + 9\ ATP + 6\ NADPH + 6\ H^+ \rightarrow C_3H_6O_3\text{-}PO_3 + 9\ ADP + 8\ P_i + 6\ NADP^+ + 3\ H_2O$$

This is what we gain (for 24 photons)



G3P

Triosephosphate
isomerase
enzyme

G3P + dihydroxyacetone phosphate (DHAP)

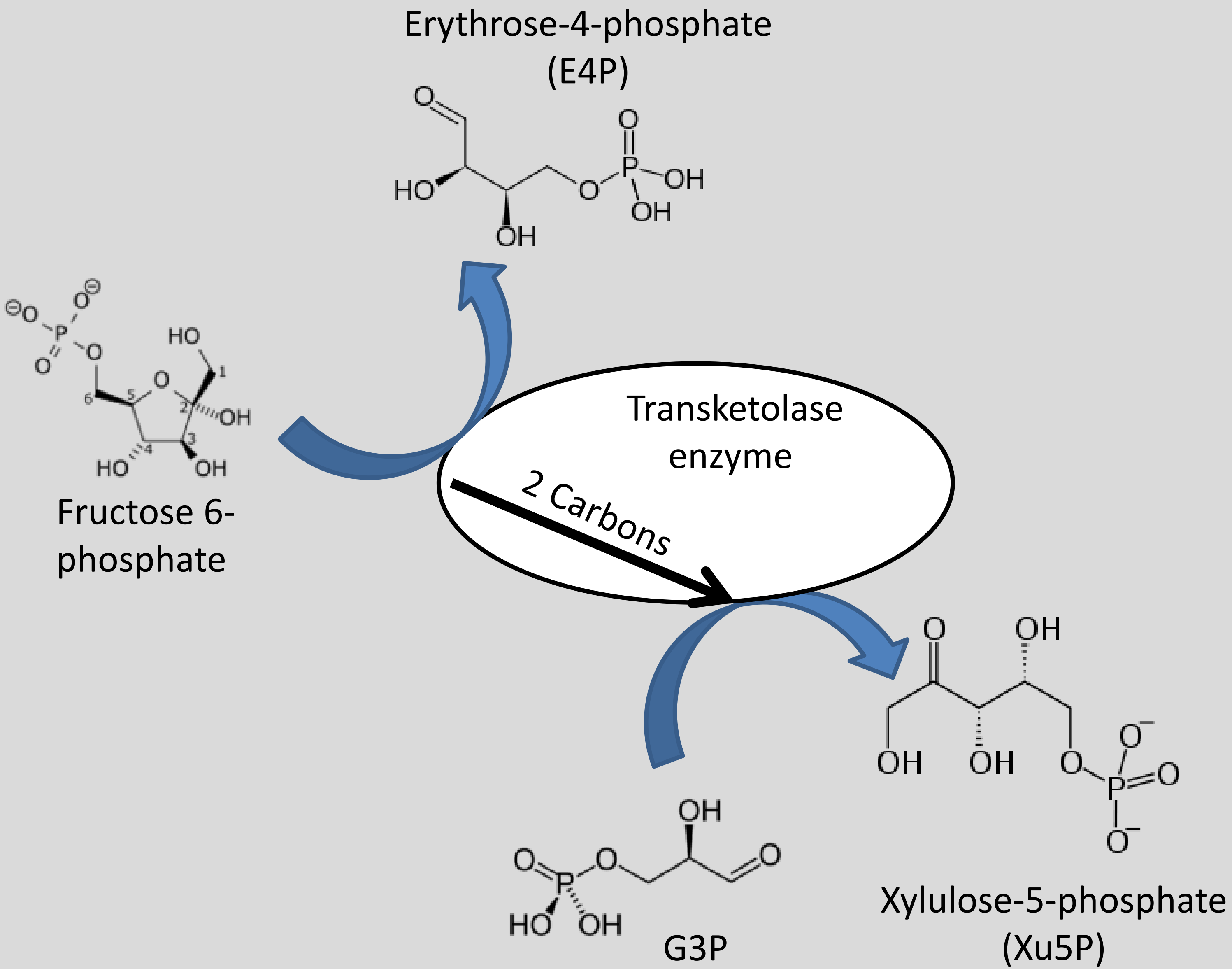
Aldolase enzyme

Fructose 1,6-bisphosphatase enzyme

fructose 6-phosphate

+

HPO_4^{2-}



Erythrose-4-phosphate (E4P)

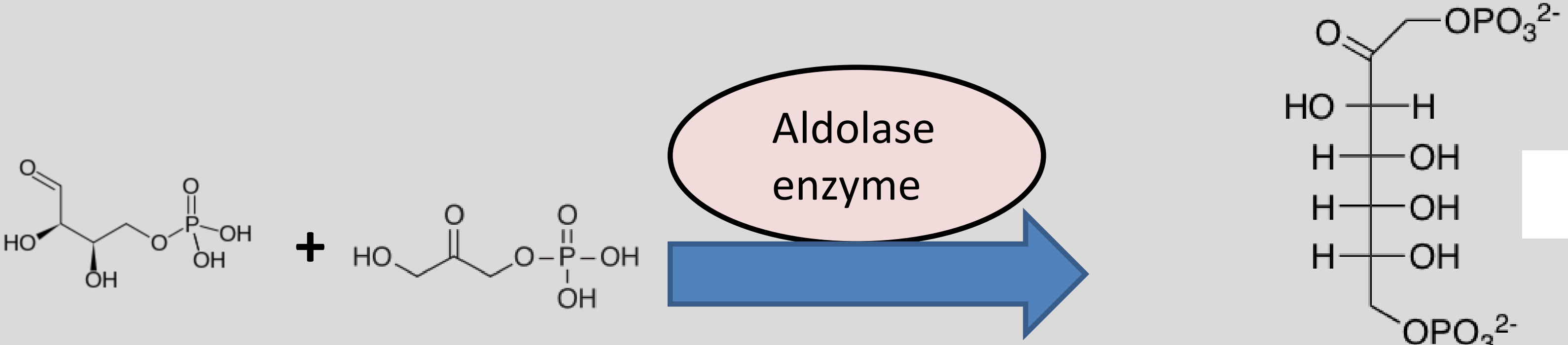
Fructose 6-phosphate

Transketolase enzyme

2 Carbons

G3P

Xylulose-5-phosphate (Xu5P)



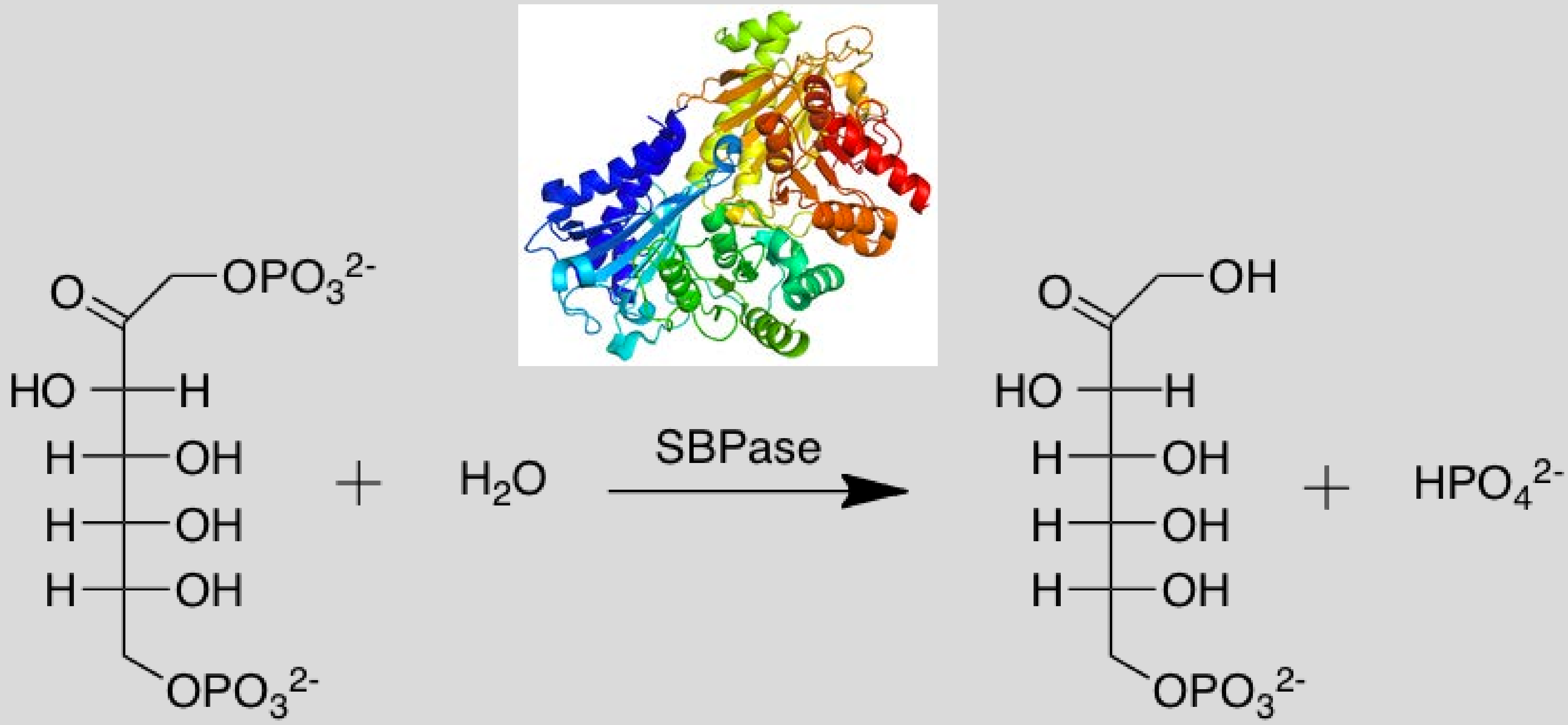
Aldolase enzyme

E4P

DHAP

sedoheptulose-1,7-bisphosphate (7C)

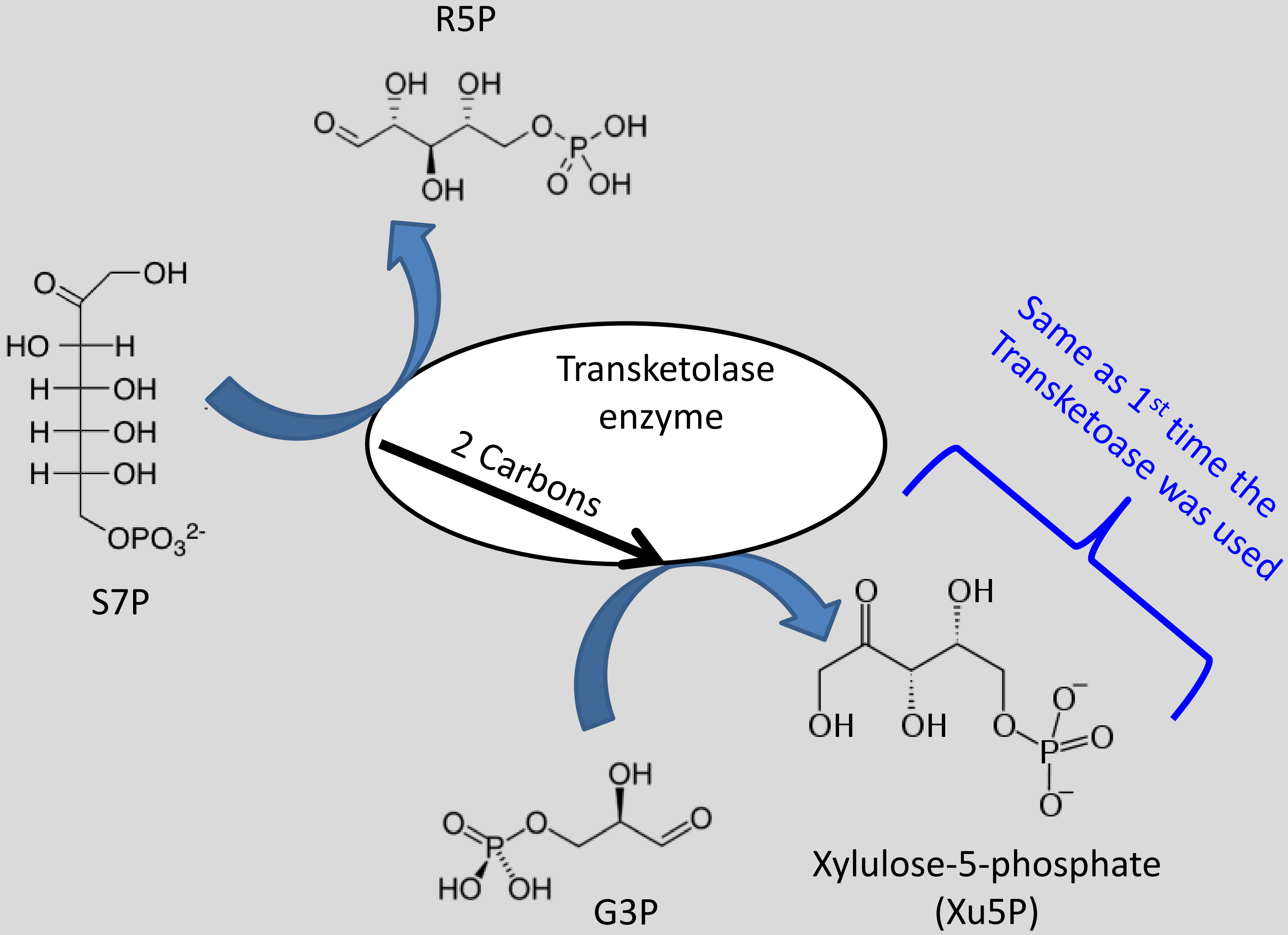
Sedoheptulose-1,7-bisphosphatase



sedoheptulose-1,7-bisphosphate

sedoheptulose-7-bisphosphate

(S7P)



R5P

S7P

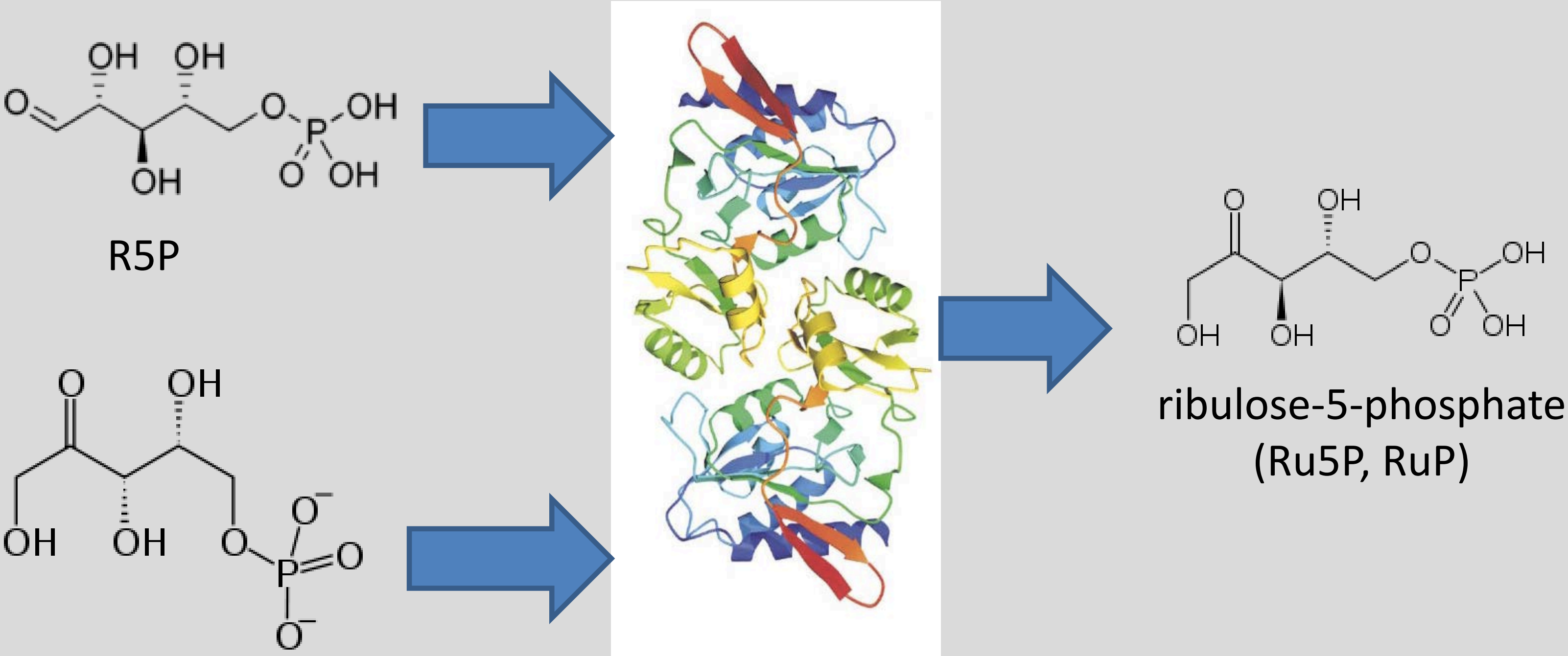
Transketolase enzyme

2 Carbons

G3P

Xylulose-5-phosphate (Xu5P)

Same as 1st time the Transketoase was used



2 x

R5P

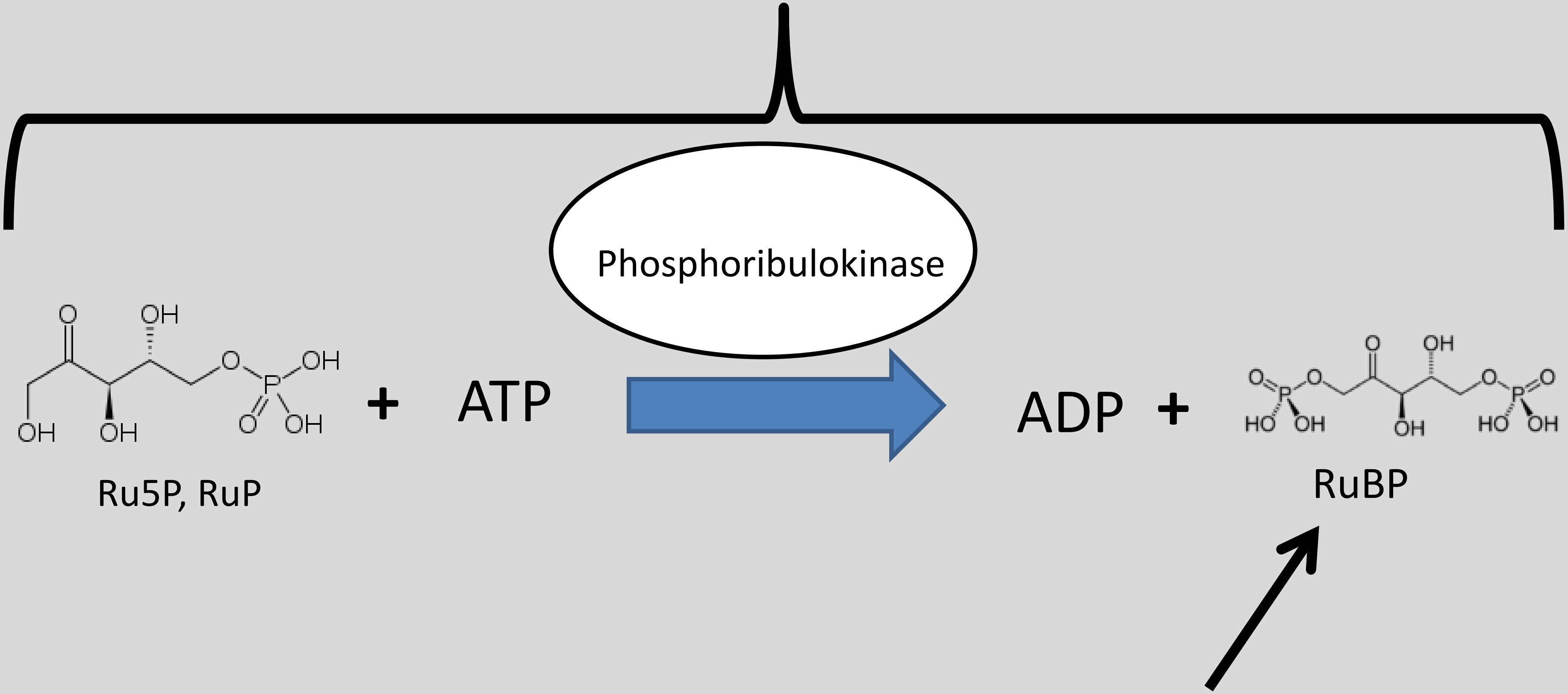
Xylulose-5-phosphate (Xu5P)

Phosphopentose epimerase enzyme

ribulose-5-phosphate (Ru5P, RuP)

Since we used the Transketolase twice, we will have 2 of these.

- We need to do this 3 times since we have 3 Ru5P, RuP



Phosphoribulokinase

Ru5P, RuP + ATP → ADP + RuBP

This is our starting material in the Calvin Cycle

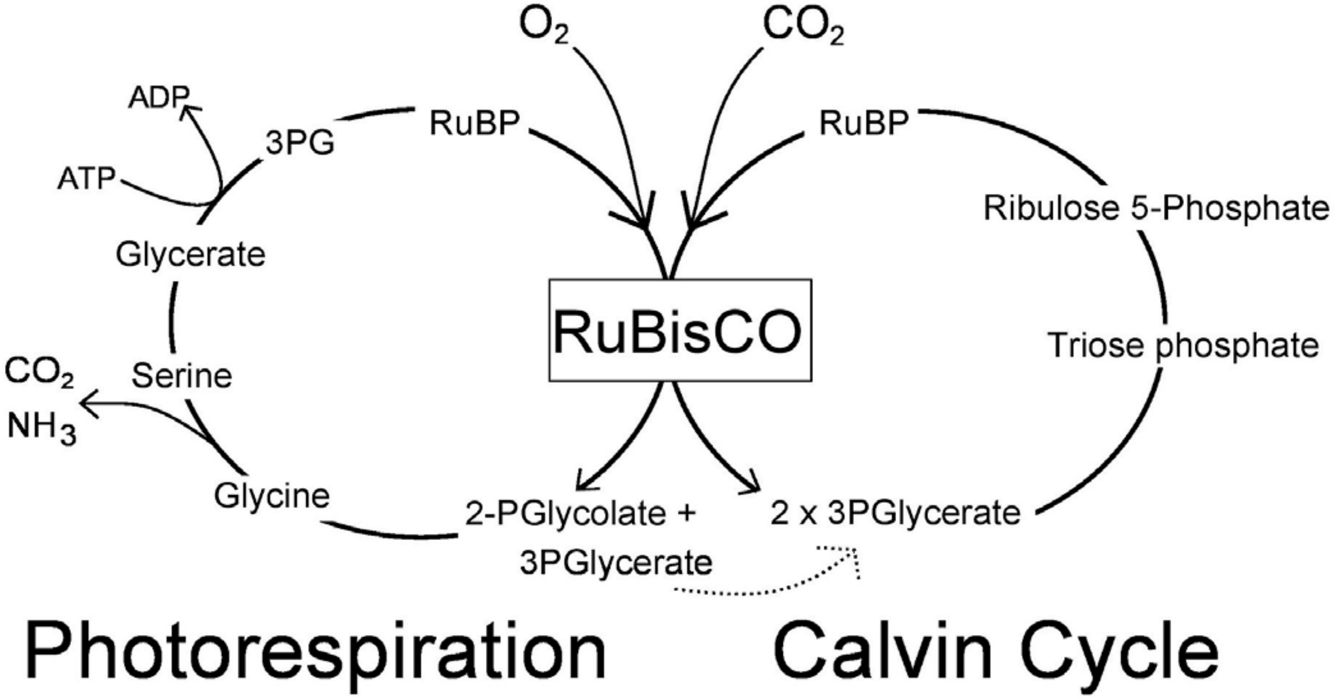
Overall Efficiency

- 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 chlorophyl) → 68% lost in conversion of ATP and NADPH to d-glucose, leaving
- 9% (collected as sugar) → 35–40% 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%.

Photorespiration- O_2 causing trouble

- Photorespiration is simply O_2 reacting with RuBP-CO_2 molecule while in the RuBisCO enzyme.
- This basically an annoying, useless process.
- This process happens about 35-40% of the time, thus really hurting efficiency



Overall Efficiency

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- **5.4% net leaf efficiency**

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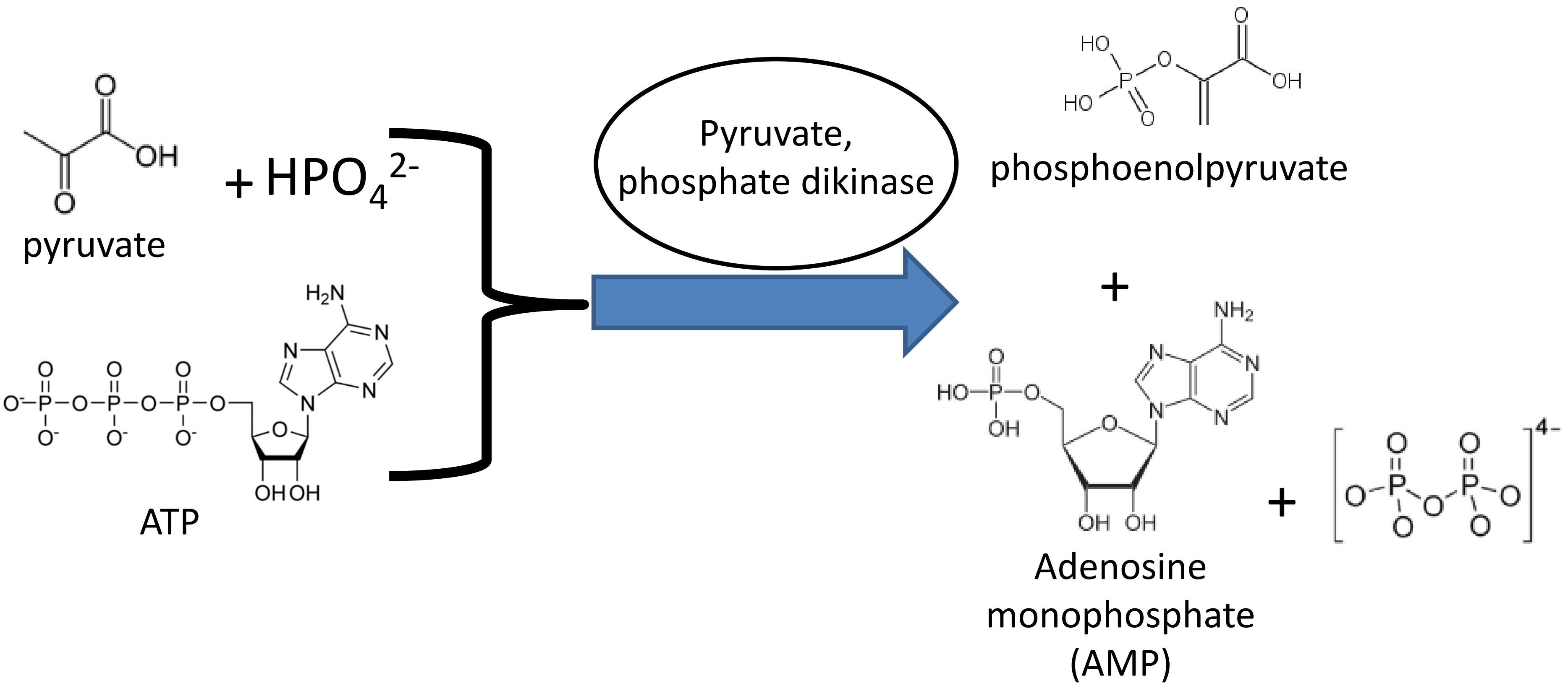
C_4 Photosynthesis

- C_4 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.



pyruvate $+ HPO_4^{2-}$

ATP

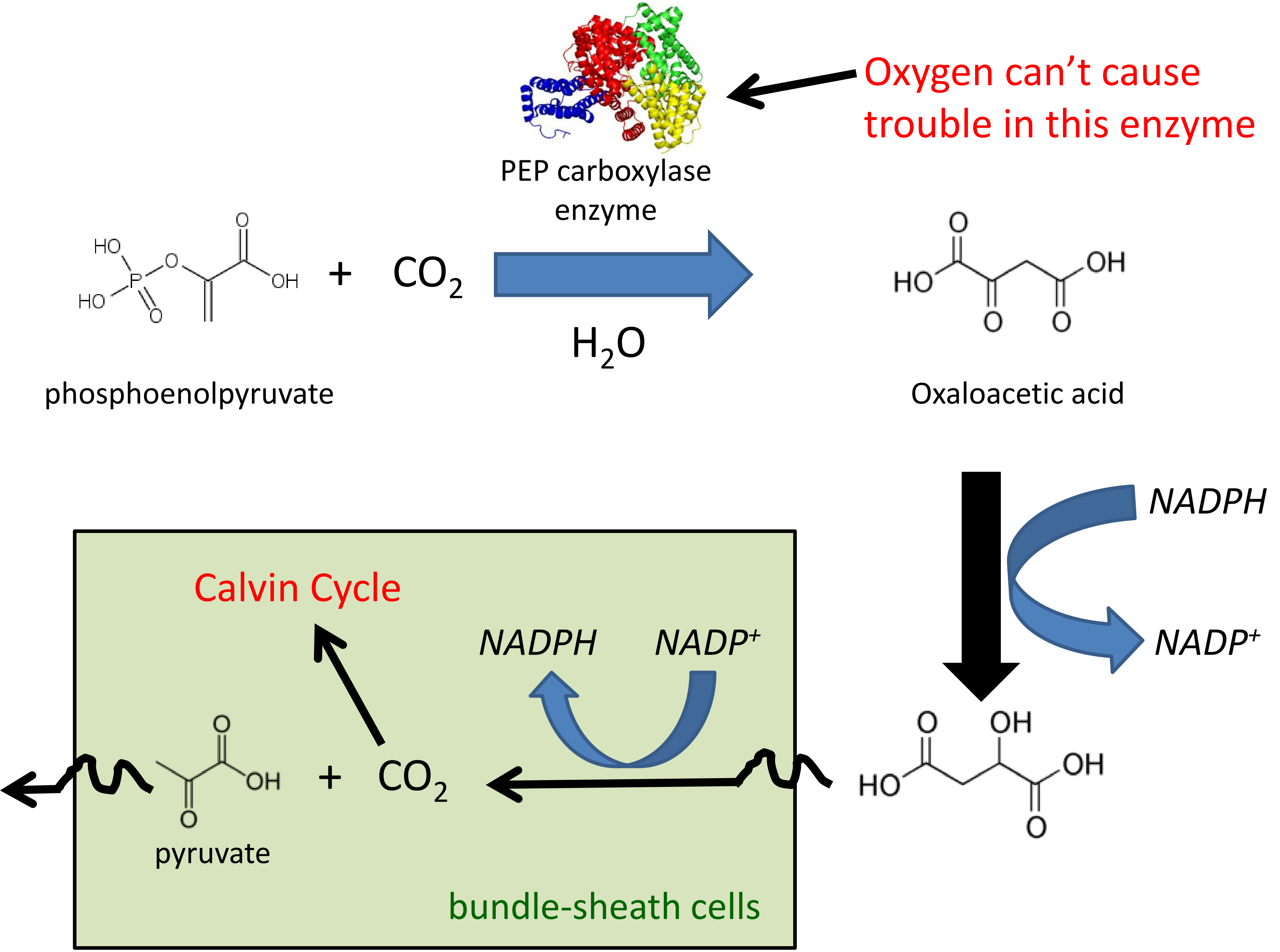
Pyruvate, phosphate dikinase

phosphoenolpyruvate

+

Adenosine monophosphate (AMP)

+



Oxygen can’t cause trouble in this enzyme

PEP carboxylase enzyme

phosphoenolpyruvate + CO_2

H_2O

Oxaloacetic acid

NADPH

$NADP^+$

Calvin Cycle

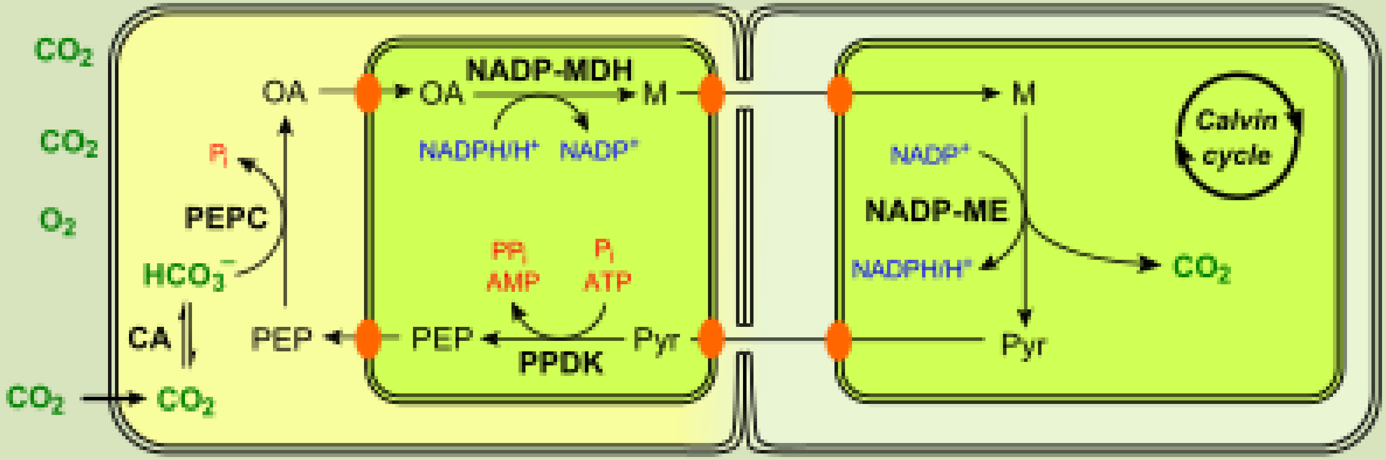
NADPH *$NADP^+$*

pyruvate + CO_2

bundle-sheath cells

C_4 Photosynthesis

- To fix 1 CO_2 molecule
  - For C_3 you need 3 ATP and 2 NADPH
  - For C_4 you need 5 ATP and 3 NADPH
- C_4 does not get effected by O_2
- C_4 can ‘upconcentrate’ CO_2



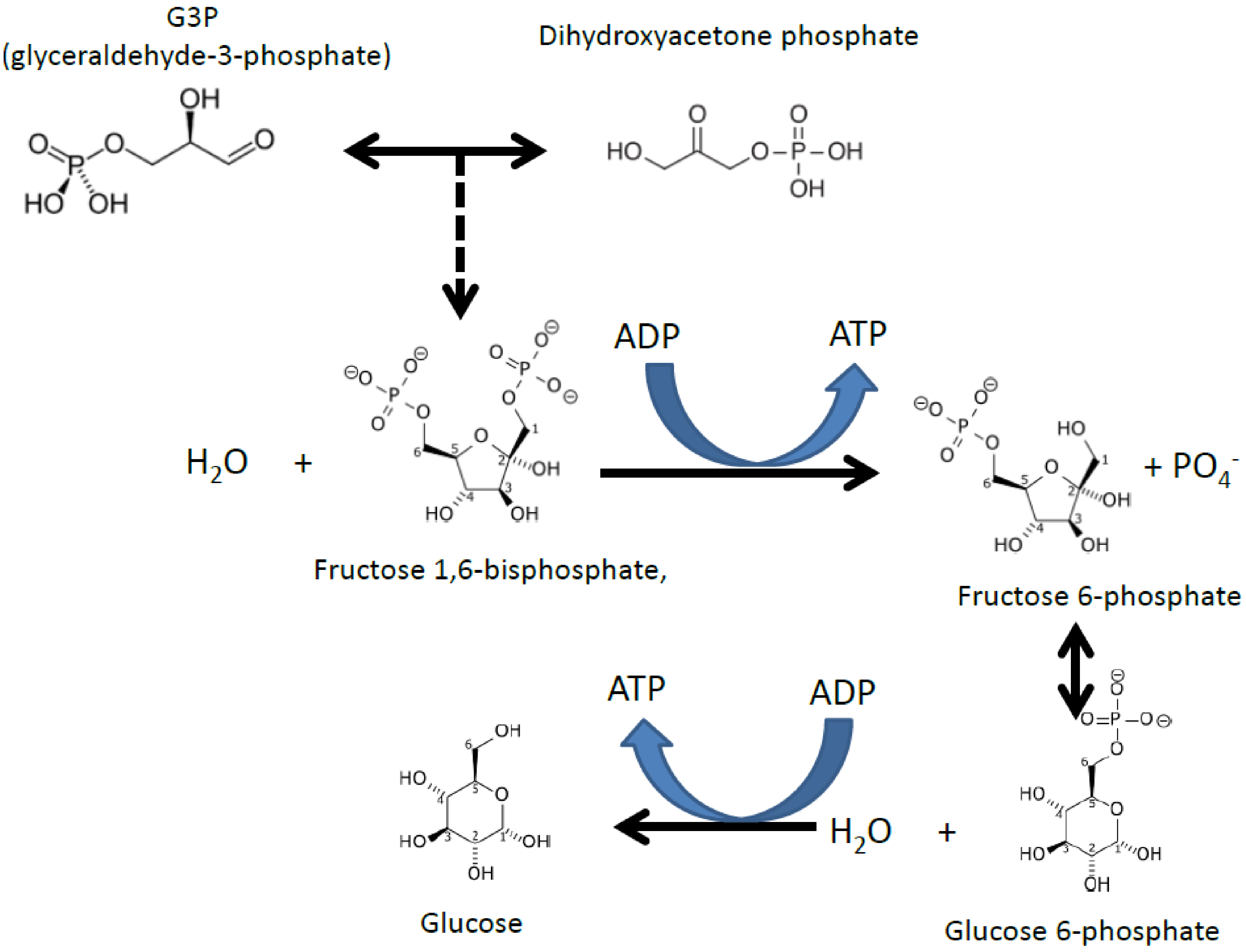
- Can you change a C_3 plant into a C_4 plant ? Some scientists think its possible (See C_4 Rice project - [http://c4rice.irri.org/)](http://c4rice.irri.org/)

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)


G3P
(glyceraldehyde-3-phosphate)
Dihydroxyacetone phosphate
H_2O +
Fructose 1,6-bisphosphate,
ADP
ATP
+ PO_4^-
Fructose 6-phosphate
ATP
ADP
H_2O +
Glucose
Glucose 6-phosphate

Lecture - Learning Objectives

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

- Explain the basic’s concepts relating to photoelectrochemistry.
- Understand the entire photosynthesis process from light absorption to sugar production.
- Understand why photosynthesis is as efficient/inefficient as it is.
- Understand the Calvin Cycle.

Exercises

- What is the minimum pH gradient across the Thylakoid membrane assuming no catalytic losses in the ATP Synthase . Calculate it from slide 76.

- How do you get from G3P to the more commonly used glucose.

- 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 for just the 620 nm light (Basically if we assume the sun just produces 620nm light)?