# Plant biochemistry

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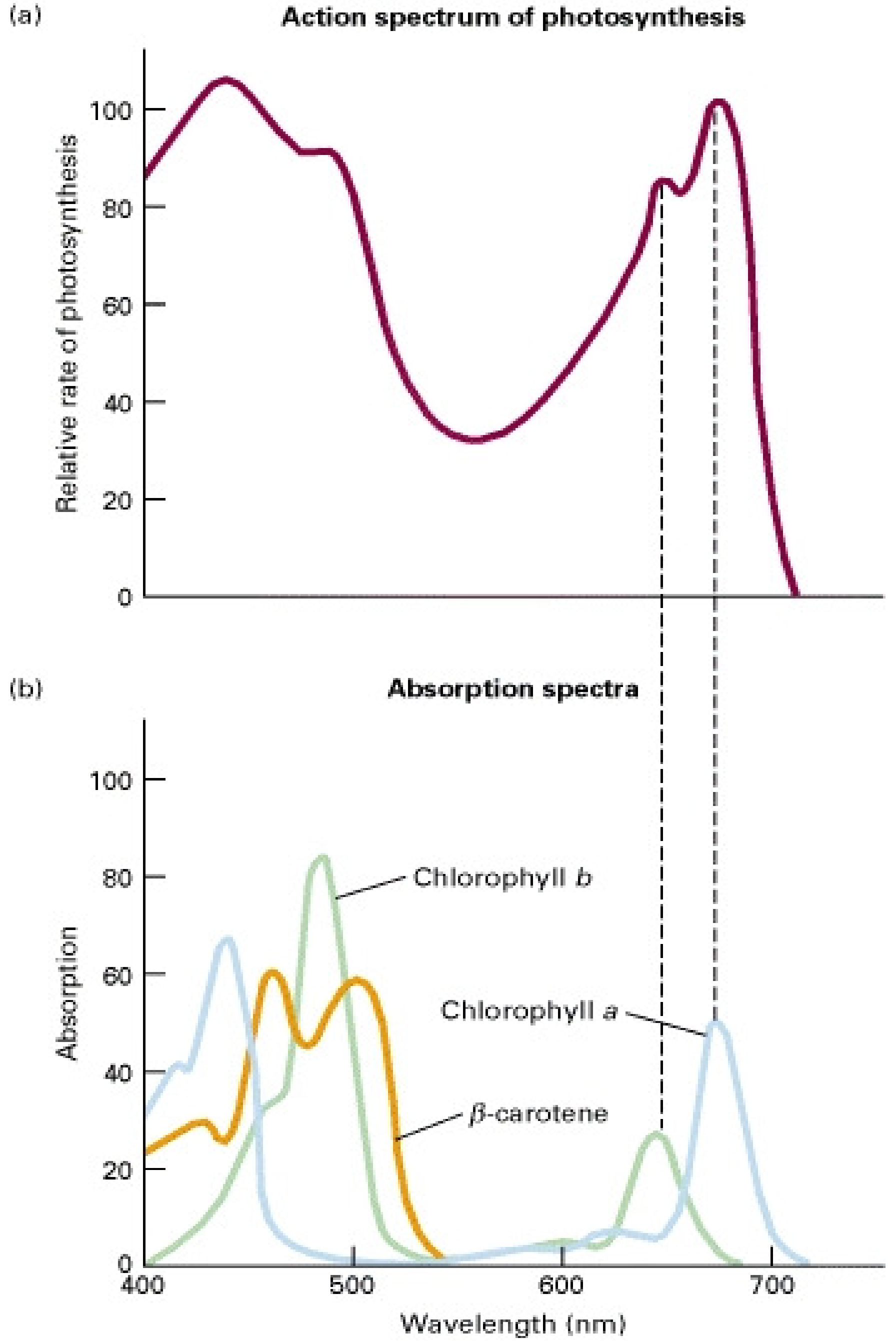
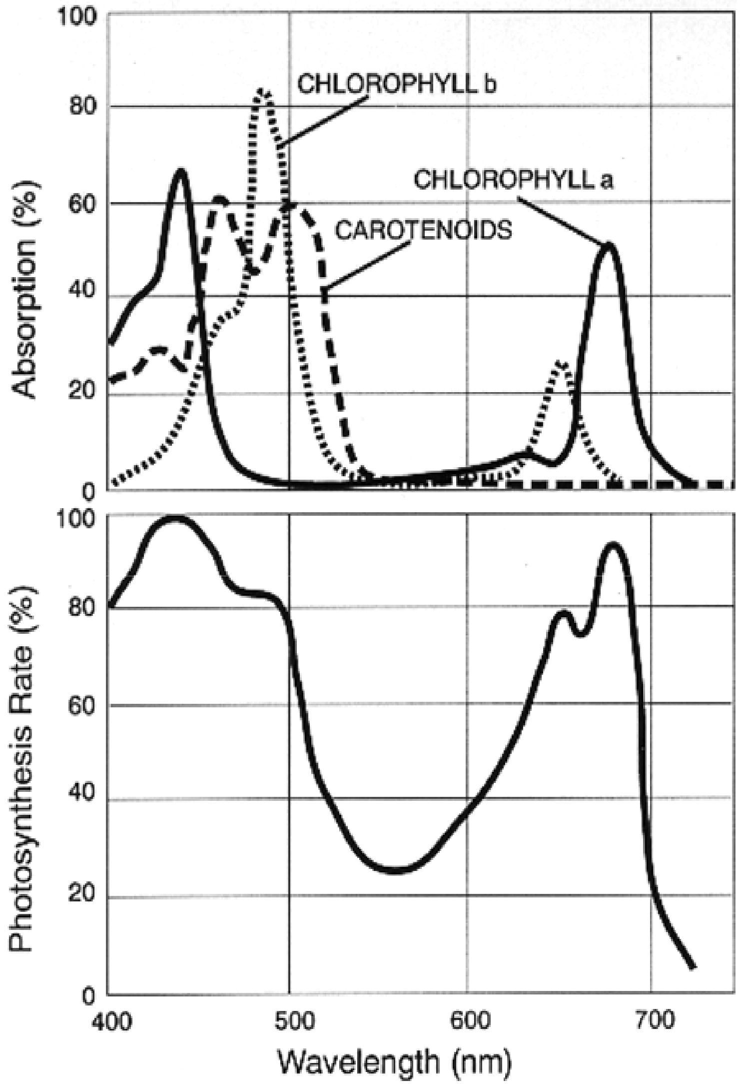
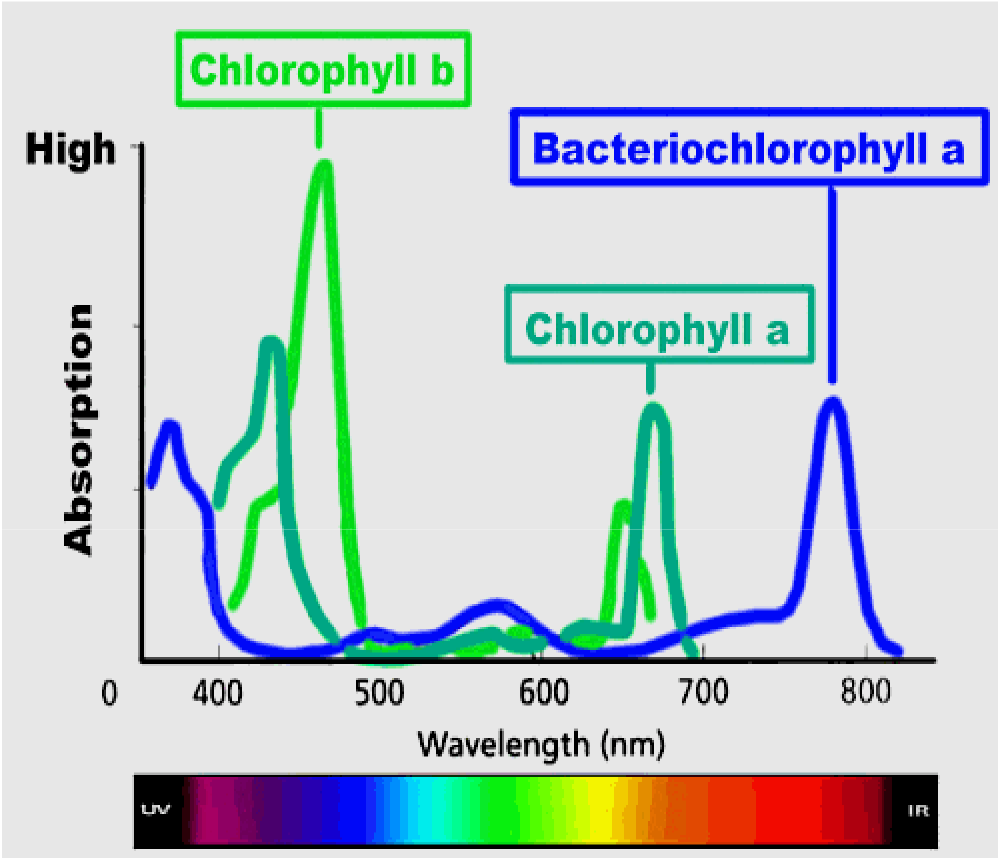
# Chlorophyll

The absorption spectra of chlorophylls " a" and " b" are different, light that is not appreciably absorbed by chlorophyll a at certain wave length ( 460 nm for example ) is absorbed by chlorophyll b .


(a)
Action spectrum of photosynthesis
Relative rate of photosynthesis
0
20
40
60
80
100
(b)
Absorption spectra
Absorption
0
20
40
60
80
100
Chlorophyll b
Chlorophyll a
β-carotene
400
500
600
700
Wavelength (nm)



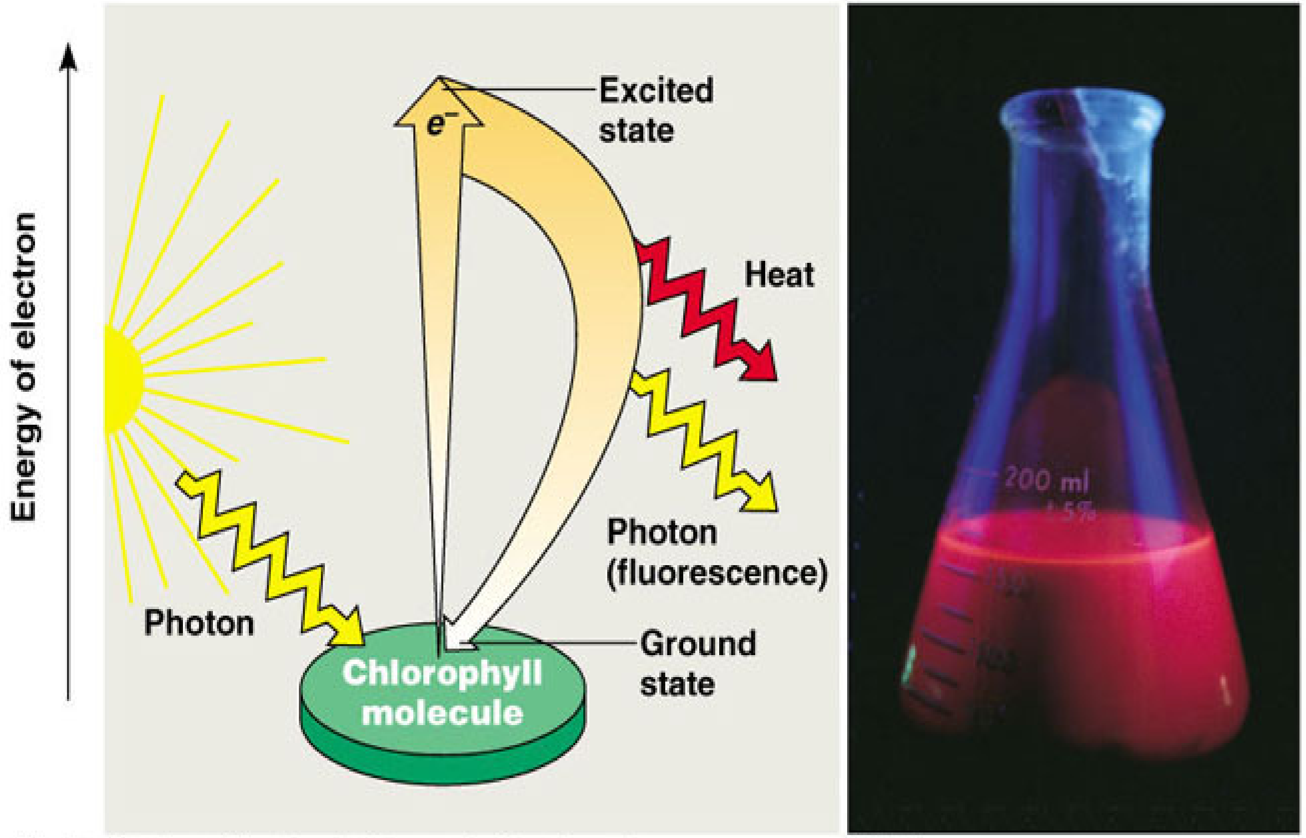
100
80
60
40
20
0
Absorption (%)
CHLOROPHYLL b
CHLOROPHYLL a
CAROTENOIDS
100
80
60
40
20
0
Photosynthesis Rate (%)
400
500
600
700
Wavelength (nm)



Chlorophyll b
Bacteriochlorophyll a
Chlorophyll a
High
Absorption
0
400
500
600
700
800
Wavelength (nm)
UV
IR

- when light strikes the chlorophyll molecule , one of the electron in it is raised to a higher energy level and is said to be in an " excited state “.

- chlorophyll molecules are arranged in such away that the excited electrons don't immediately return to their ground state but are transferred to other molecules resulting in an increase in the free energy or the chemical potential, of the acceptor molecules.




**(a) Excitation of isolated chlorophyll molecule** **(b) Fluorescence**

- Thus light energy is converted into chemical energy .

- The electron " hole" left in the chlorophyll molecule is replaced by an electron donated by water , in this process the water is oxidized and molecular oxygen is given off

- **chlorophyll**, is an intermediate in the pathway of electrons from a low energy level in water to a high energy level in the final electron acceptor .
- **light reactions** of photosynthesis depend on the interplay of two photosystems :

- **photosystem I** , which can be excited by light of wave length shorter than 700 nm generates a strong reductant that leads to the formation of NADPH.

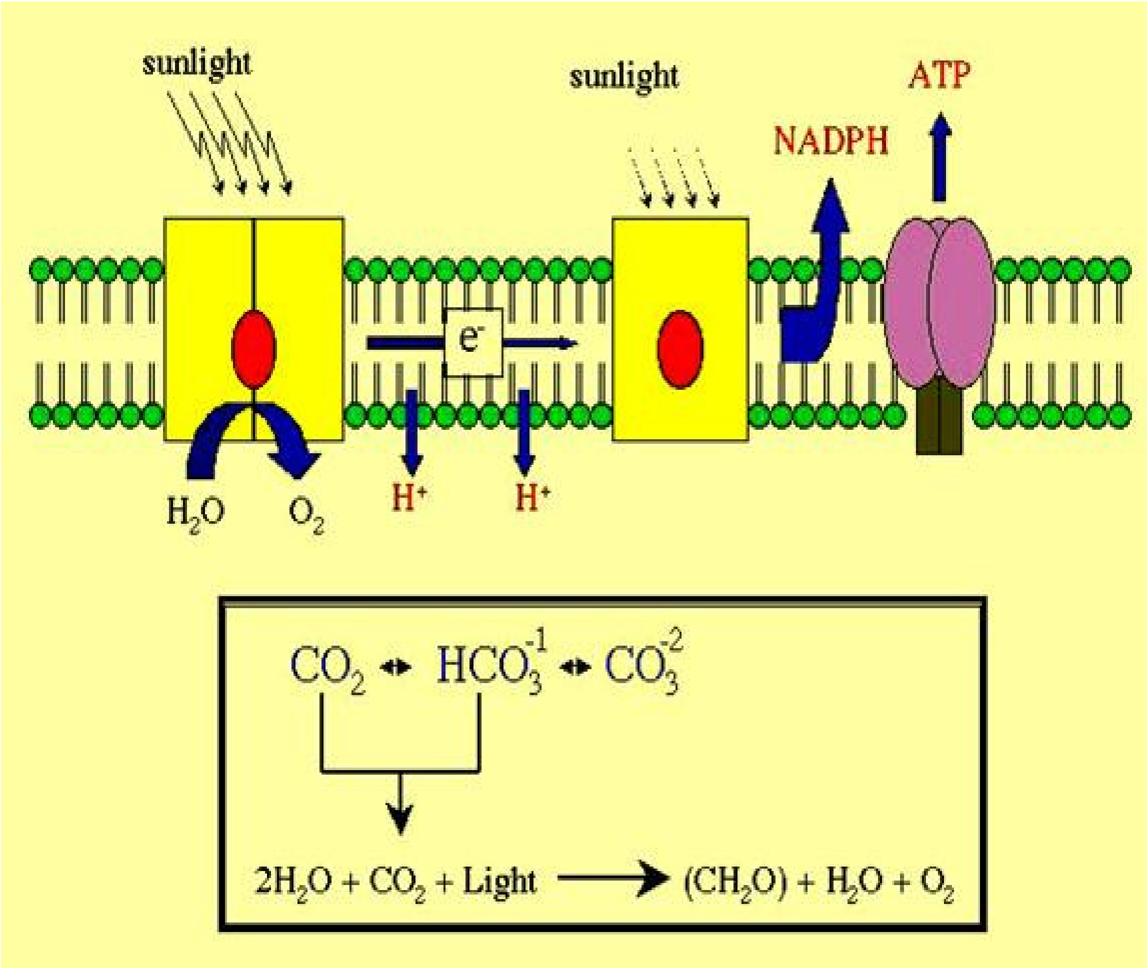
- **Photosystem II**, which requires light of wavelength shorter than 680 nm, produces a strong oxidant that leads to the formation of $O_2$

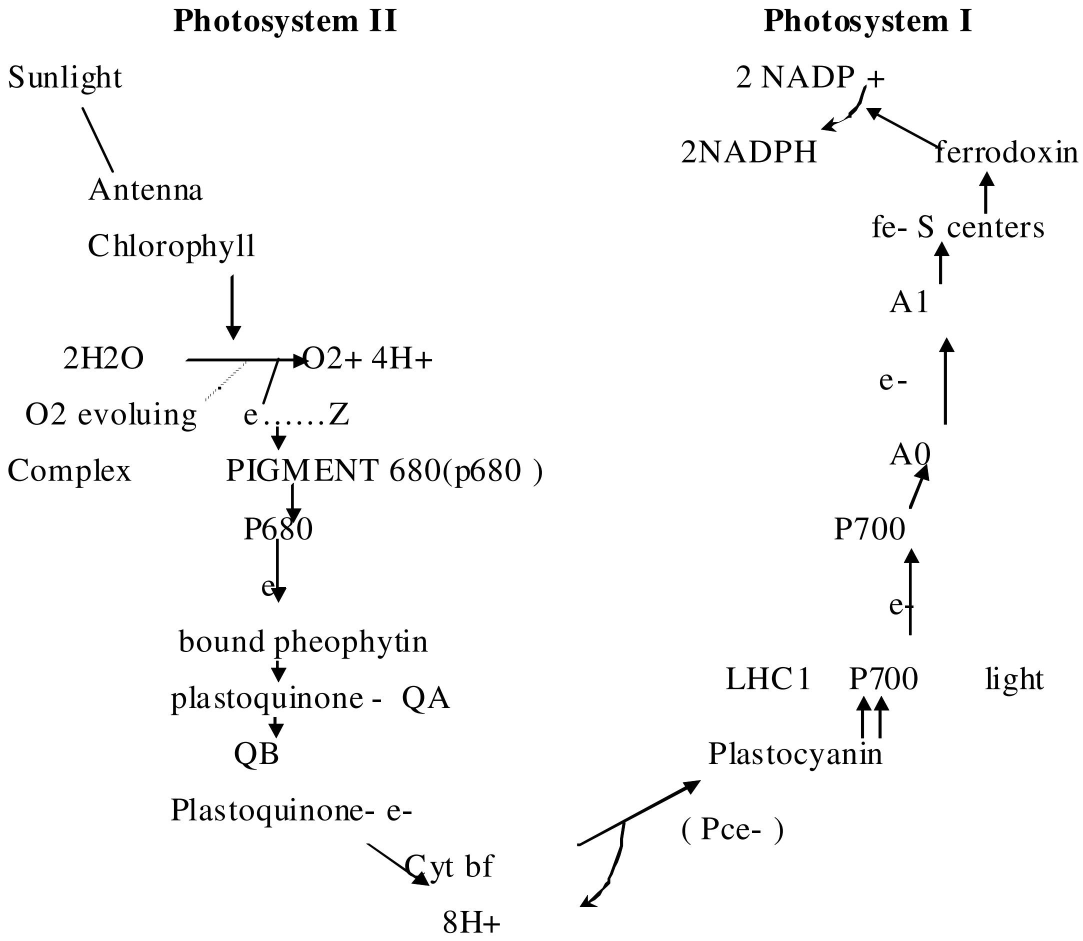
# Photosystem II:

- A transmembrane assembly of more than 10 polypeptide chains [ >600Kd ], Catalyzes the light – driven transfer of electrons from water to plastoquinone .

- It consists of a 1. light – harvesting complex, 2. a core with a reaction center and an 3. oxygen evolving complex .

- The light –harvesting complex [ LHCII ] contains about 200 ,molecules of chlorophyll a and chlorophyll b bound to several polypeptide chains.


sunlight
sunlight
ATP
NADPH
e-
H2O
O2
H+
H+
CO2 ↔ HCO3-1 ↔ CO3-2
2H2O + CO2 + Light → (CH2O) + H2O + O2


Photosystem II
Photosystem I
Sunlight
Antenna
Chlorophyll
2H2O
O2+ 4H+
O2 evoluing
Complex
e……Z
PIGMENT 680(p680 )
P680
e
bound pheophytin
plastoquinone - QA
QB
Plastoquinone- e-
Cyt bf
8H+
( Pce- )
Plastocyanin
LHC1
P700
light
e-
P700
A0
e-
A1
fe- S centers
ferrodoxin
2NADPH
2 NADP +

- Electrons are extracted form water by intermediate called " Z", water are splitted by the water splitting enzymes, a constituent of photosystem II, contains a cluster of four manganese ( Mn++ ) ions at catalytic center.

- Electronic excitation energy is funneled from antenna chlorophylls to a reaction center chlorophyll called P680[ Pigment 680].This pigment become excited P680* and an electron is transferred from P680 to bound pheophytin, the electron flow from reduced pheophytin to a plastoquinone. Bound to a protein site called QA, and finally to a second plastoquinone on site QB.

- " At this point the energy of two photons has been safely stored in the reducing potential of QH2 ( reduced plastoquinone ) "

# Cyochrome bf complex :

- Electrons flow through this complex form photosystem II to photosystem I.

- Cytochrome bf catalyzes the transfer of electrons across the thylakaid membrane to plastocyanin ( Pc) .

- It is a transmembrane protein complex .

- After electrons are pumped through bf complex to Pc, Pc becomes reduced

# Photosystem I :

- A transmembrane complex consisting of at least 13 polypeptide chains >800kd) .
- Light is funneled from an accessory antenna protein [ LHC1]containing 70 chlorophyll a and chlorophyll b molecules and a core antenna with 130 chlorophyll a molecules to P 700 , the reaction center .
- An electron is transferred from P 700* , the excited state of the reaction –center chlorophyll , to an acceptor chlorophyll called A0 to form A0-

- ✓ The very high – potential electron of A0- is transferred to A1, and then to series of iron – sulfur centers within photosystem I .

- ✓ The final step is the reduction of ferredoxin. This reaction occurs on the stromal side of the thylakaid membrane .

- ✓ The high – potential electrons two molecules of ferredoxin are then transferred to $NADP^+$ TO form $ANDPH+H^+$ this reaction is catalyzed by ferredoxin – $NADP^+$ reductase .

- ✓ ( Two molecules of reduced ferredoxin $\longrightarrow$ 2 electrons to one $ANDP^+$ )

- The net reaction carried out by photosystem II, cyt bf and photosystem I is .

$$2\,H_2O + 2\,NADP^+ \xrightarrow{\text{light}} O_2 + 2NADPH + 2H^+$$

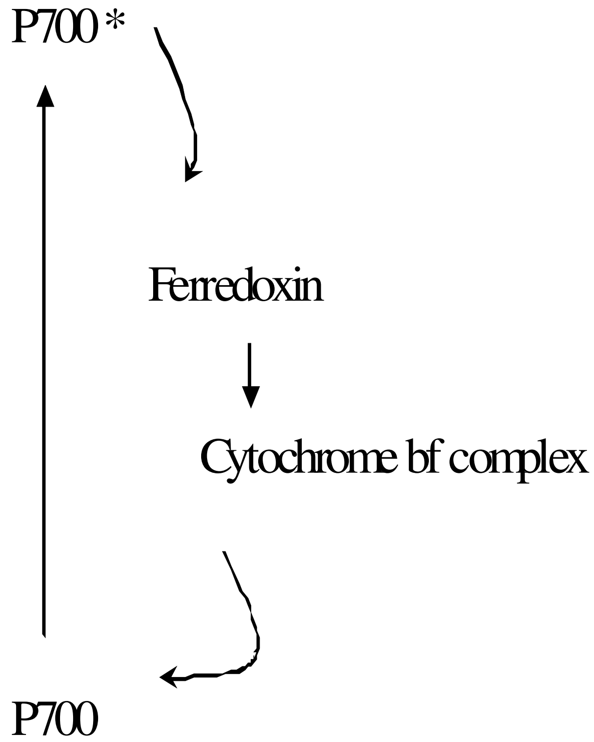
**N.B**

Heme and chlorophyll have similar structure & functions :

- both have protoporhyrin structure .
- both can transport electrons .
- both contain divalent cation
- both have characteristic color due to the presence of the cation ( $Mg^{2+}$ & $Fe^{2+}$ ) .

## "Cyclic phosphorylation"

## "cyclic electron flow"



- An alternative pathway for electrons arising from P700 , the reaction center of photosystem I .

- Electrons form P700* - donot pass to NADP+ .

- The high electron potential in ferredoxin can be transferred to the cyt. Bf complex rather than to NADP+ .

- This electron flows back to the oxidized form of P700 through plastocyonin to Fd .

- Thus , illumination of photosystem I can cause e- to cycle continuously out of the reaction center of photosystem I and back to it ,each e- being propelled around the cycle by the energy yielded by absorption of one photon .

    - This cyclic flow of electrons leads solely to proton pumping by the cytochrome bf complex .

# Cyclic photo phosphorylation .

- The proton gradient then drives the synthesis of ATP

- ATP synthetase of chloroplasts [ CF1-CF0 Complex ]catalyzes the formation of ATP from ADP and Pi

- About 3 protons flow through CF1 – CF0 complex per ATP synthesized .
- The newly synthesized ATP is released in to the stromal space .
- NADPH formed by photosystem I is released into the stromal space.

- Thus , ATP and NADPH , the products of light reactions of photosynthesis , are appropriately positioned for the subsequent dark reactions , in which CO2 is converted to carbohydrate .

- Cyclic electron flow involves only photosystem I .

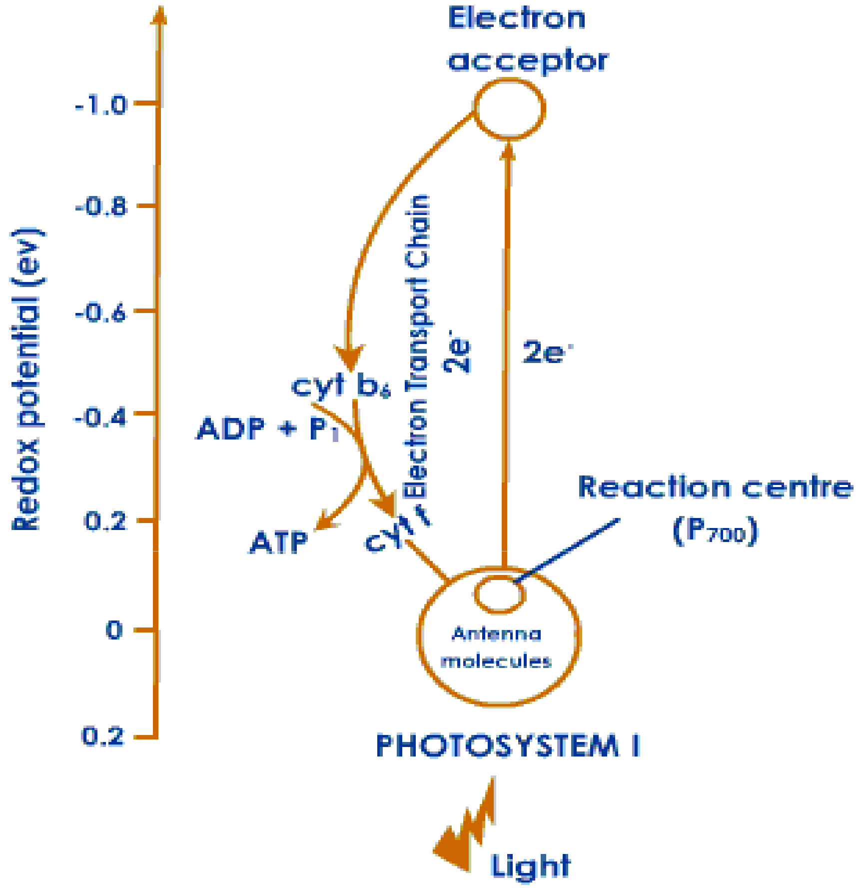
- the overall reaction equation of cyclic electron flow and photo phosphorylation is simply :

$$ADP + Pi \xrightarrow{light} ATP + H_2O$$

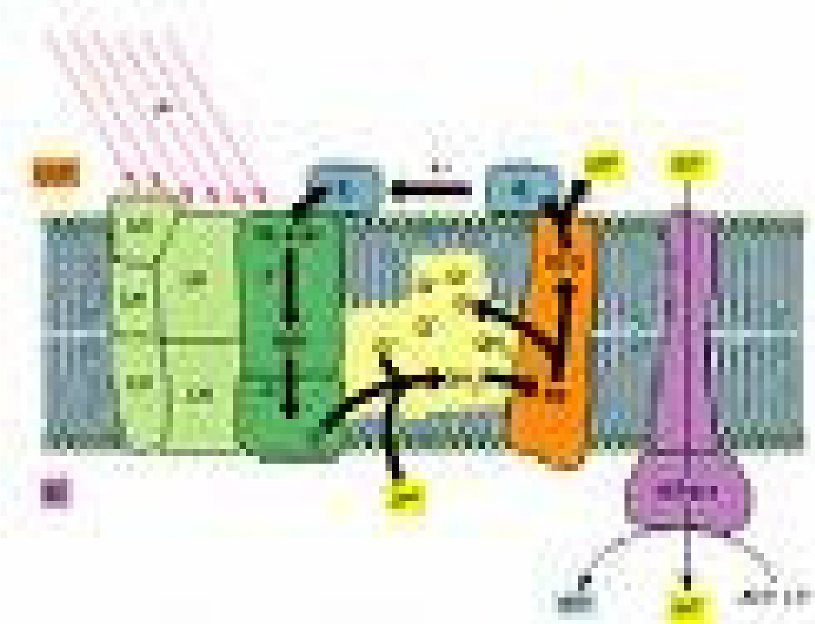
- There is no NADPH or $O_2$ evolution .

- Cyclic flow and photophosphorylation are believed to occur when the plant cell is already amply supplied with reducing power in the form of NADPH but requires additional ATP for other metabolic needs .

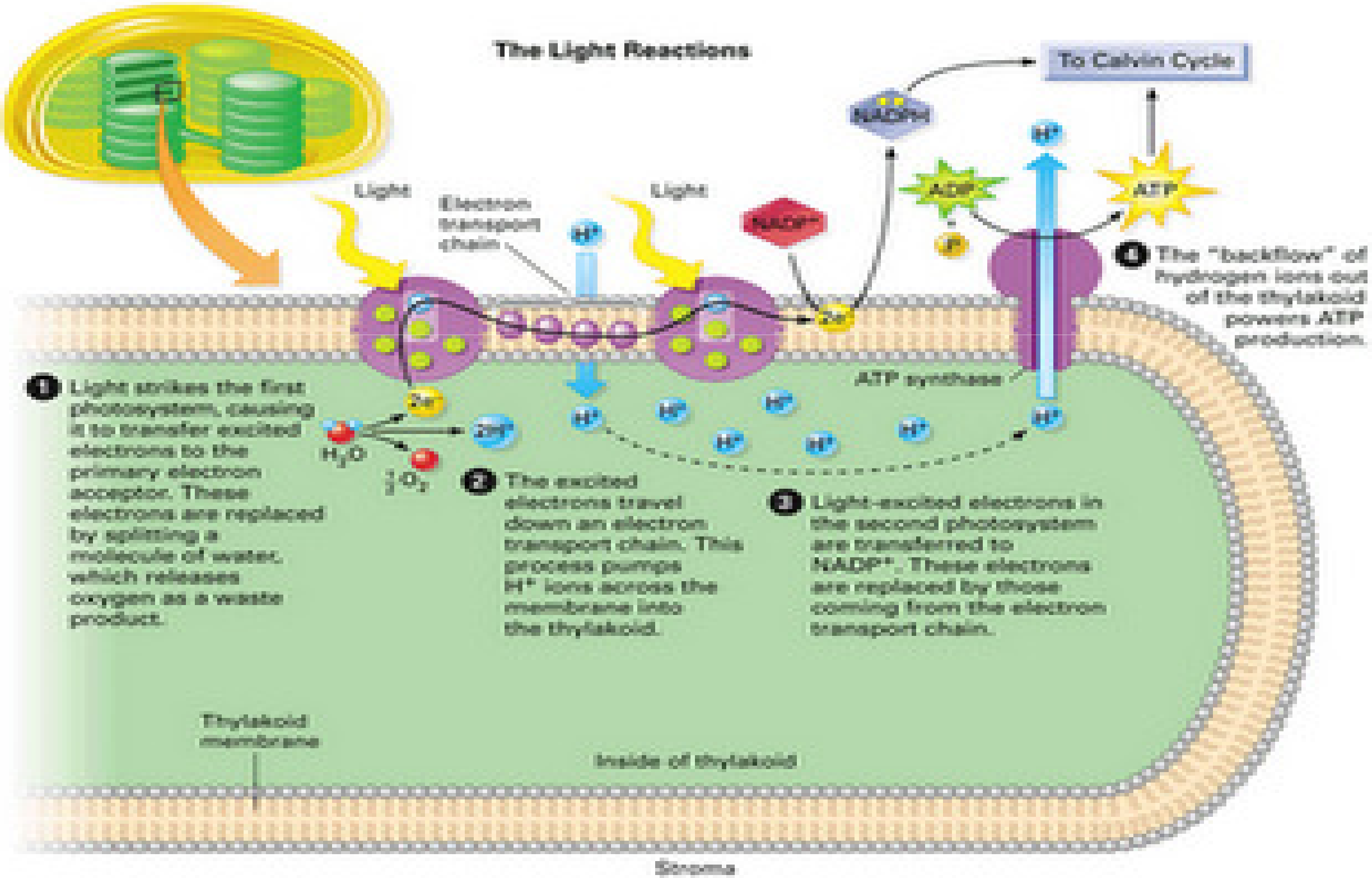
- By regulating the partitioning of electons between $NADP^+$ reduction and cyclic photophosphoryltion , a plant adjust the ratio of NADPH and ATP produced in the light reaction to match its needs .



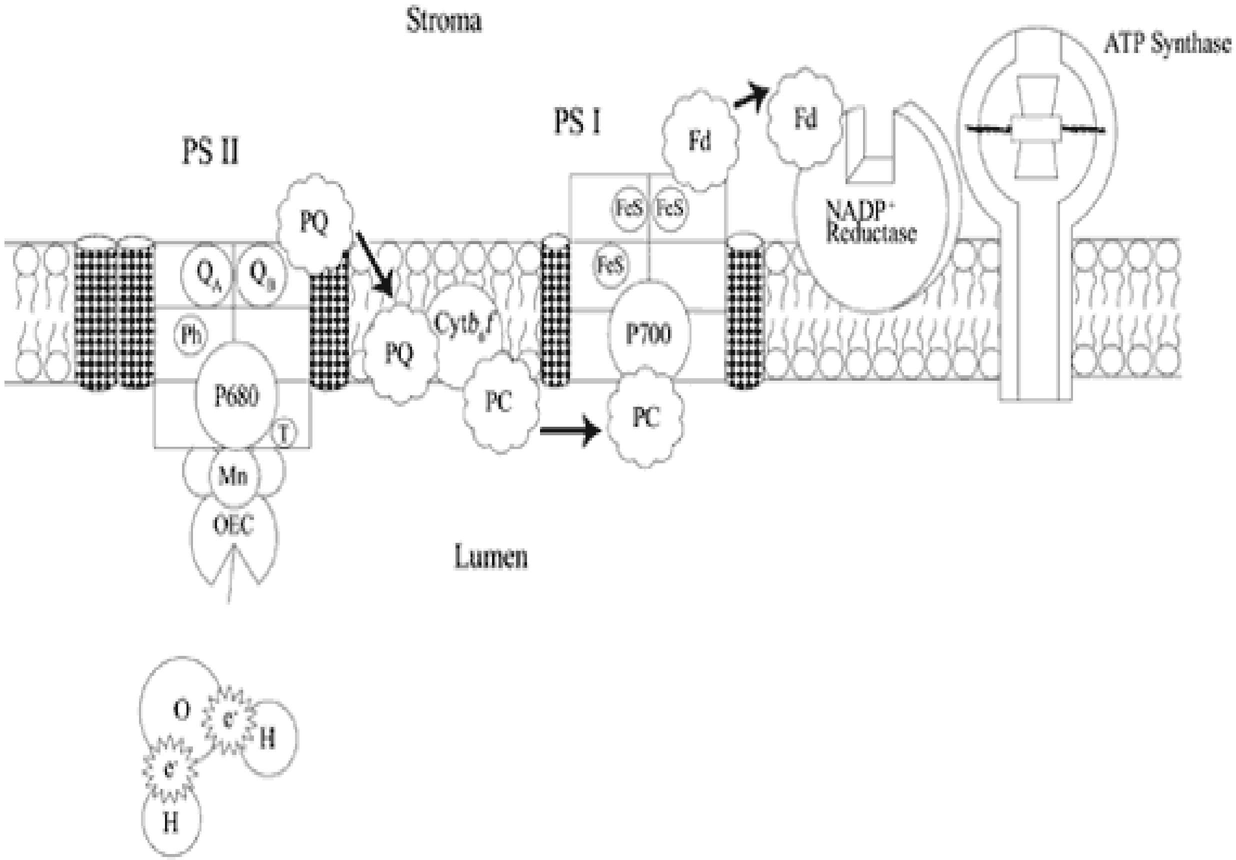
Electron
acceptor
-1.0
-0.8
-0.6
-0.4
0.2
0
0.2
Redox potential (ev)
Electron Transport Chain
2e-
2e-
cyt b6
ADP + P1
ATP
cyt f
Reaction centre
(P700)
Antenna
molecules
PHOTOSYSTEM I
Light



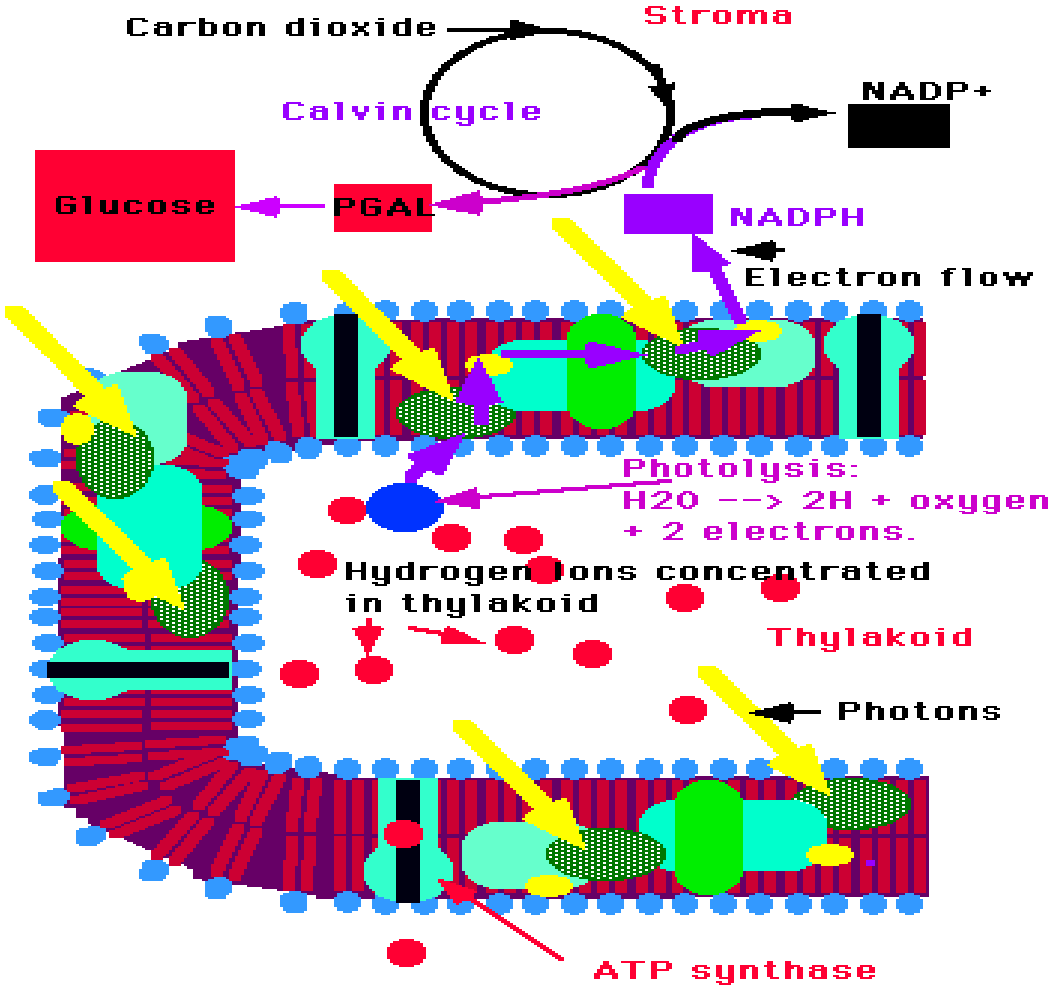
- Electron transferring molecules in the connecting chain between photosystem I and II are oriented asymmetrically in the thylakoid membrane, so that photo induced electron flow results in the net movement of protons across the membrane, from the outside of the thylakoid membrane to the inner component .



The Light Reactions
To Calvin Cycle
NADPH
ADP
ATP
Light
Electron transport chain
Light
NADP+
H+
2e-
ATP synthase
H2O
2H+
1/2 O2
1 Light strikes the first photosystem, causing it to transfer excited electrons to the primary electron acceptor. These electrons are replaced by splitting a molecule of water, which releases oxygen as a waste product.
2 The excited electrons travel down an electron transport chain. This process pumps H+ ions across the membrane into the thylakoid.
3 Light-excited electrons in the second photosystem are transferred to NADP+. These electrons are replaced by those coming from the electron transport chain.
4 The "backflow" of hydrogen ions out of the thylakoid powers ATP production.
Thylakoid membrane
Inside of thylakoid
Stroma



Stroma
ATP Synthase
PS I
Fd
Fd
PS II
PQ
FeS
FeS
NADP+
Reductase
FeS
QA
QB
Ph
PQ
Cytb6f
P700
P680
PC
T
PC
Mn
OEC
Lumen
O
e-
H
e-
H


Carbon dioxide
Stroma
NADP+
Calvin cycle
Glucose
PGAL
NADPH
Electron flow
Photolysis:
H2O --> 2H + oxygen
+ 2 electrons.
Hydrogen Ions concentrated
in thylakoid
Thylakoid
Photons
ATP synthase

# Dark Reactions

- **Photosynthetic carbohydrate synthesis :**

➢ Plants and photosynthetic organisms can make carbohydrates from $CO_2$ and water .

  ➢ They synthesize glucose , sucrose and other carbohydrates by reducing $CO_2$ at the expense of energy furnished by ATP and NADPH generated in the light phase of photosynthesis .

- Green plants contain their chloroplasts unique enzymatic machinery to catalyze the conversion of $CO_2$ to Simple reduced organic compounds [ a process called $CO_2$ fixation ].

- Plants convert their simple products of photosynthesis into more complex biomolecules including sugars, polysaccharides and metabolites derived form them .

# Calvin Cycle

- **Carbon Dioxide Fixation Occurs in 3 Stages :**

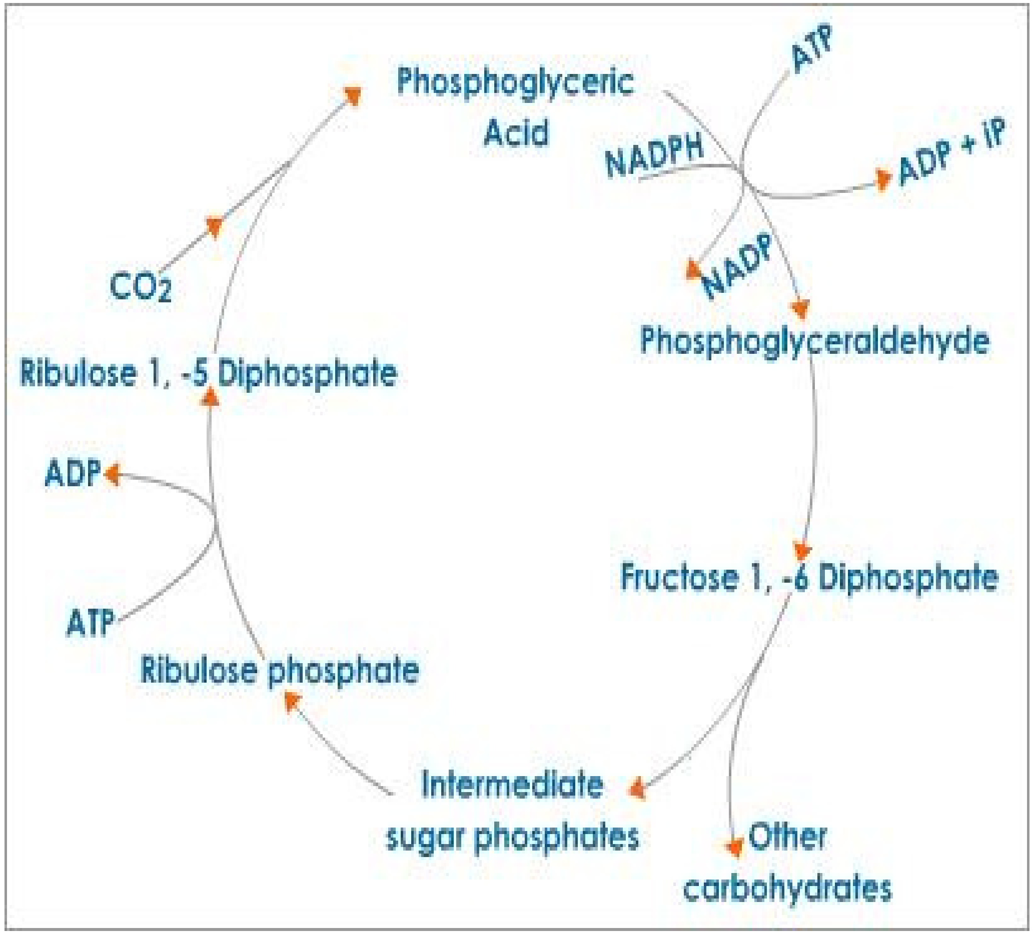
❖ 1) Condensation with a five carbon acceptor ribulose -1.5 diphosphate to form 2molecules of 3- phosphoglycerate.

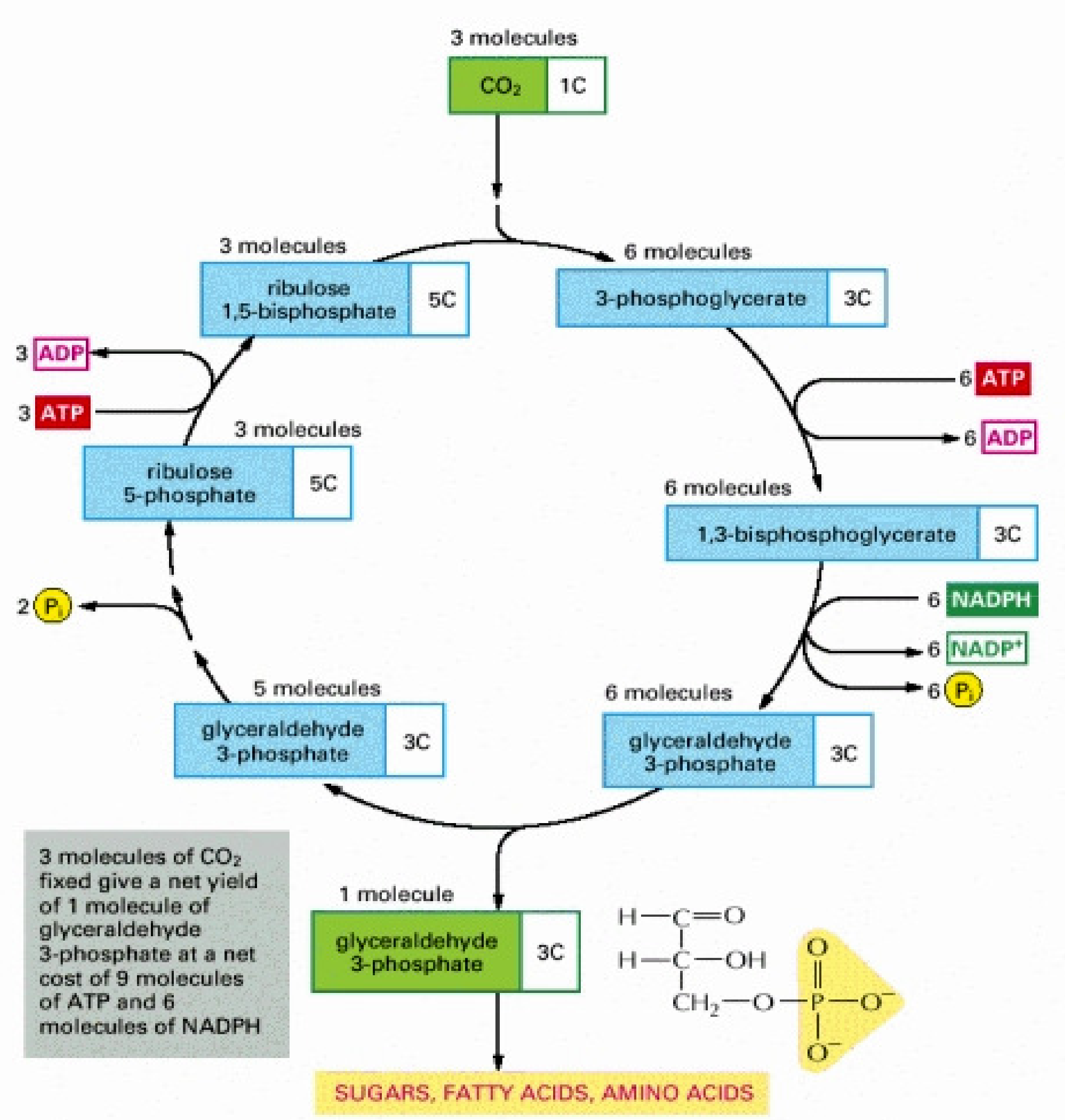
❖ 2) The 3- phosphoglycerate is reduced to glyceraldehydes-3 phosphate [6-molecules] .

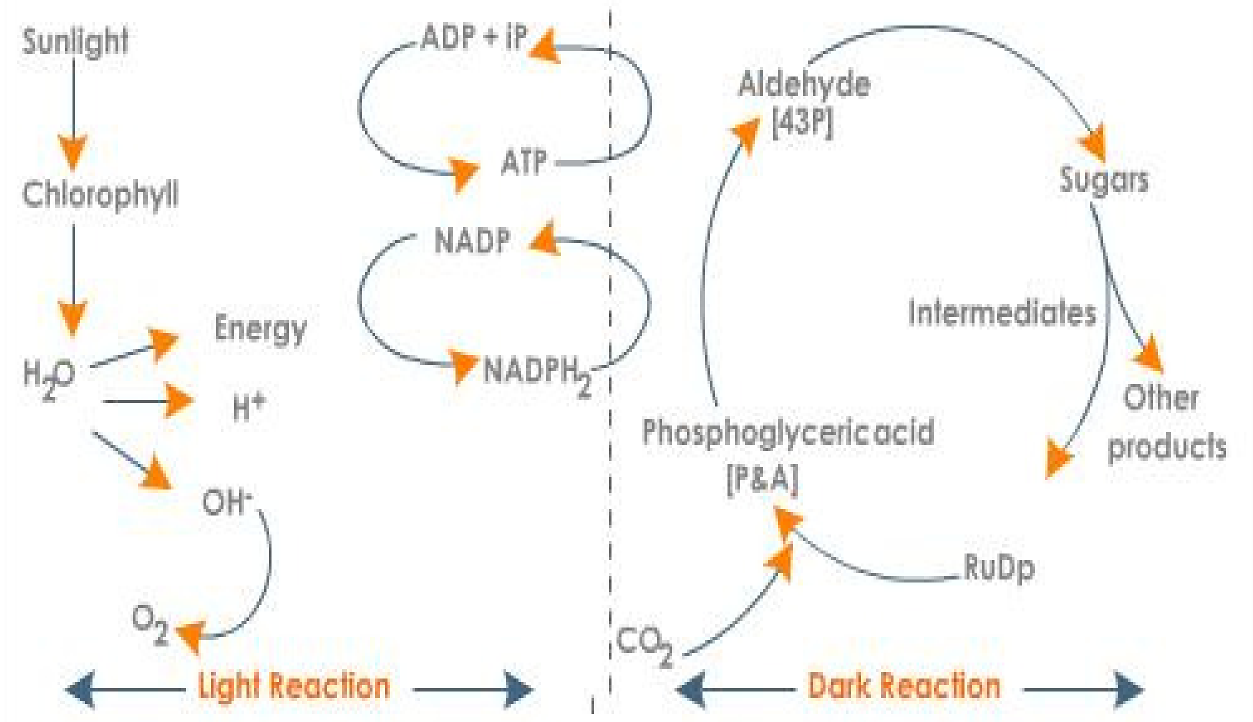
❖ 3) One molecule of this triose phosphate [glyceraldehydes-3-phosphate ] can either be used for energy production via glycolysis and citric acid cycle , or condensed to hexose phosphate to be used in the synthesis of starch or sucrose .

- In the 3 rd stage5 of the 6 molecules of glyceraldehydes -3-P are used to regenerate 3 molecules of ribulose -1.5 diphosphate .

- The plants in which the first step in CO2 fixation is reaction of CO2 with ribulose -1, 5 diphosphate to form 3- phosphoglycerate are called C3 plants.


Phosphoglyceric Acid
ATP
NADPH
ADP + iP
NADP
Phosphoglyceraldehyde
$CO_2$
Ribulose 1, -5 Diphosphate
ADP
ATP
Fructose 1, -6 Diphosphate
Ribulose phosphate
Intermediate sugar phosphates
Other carbohydrates

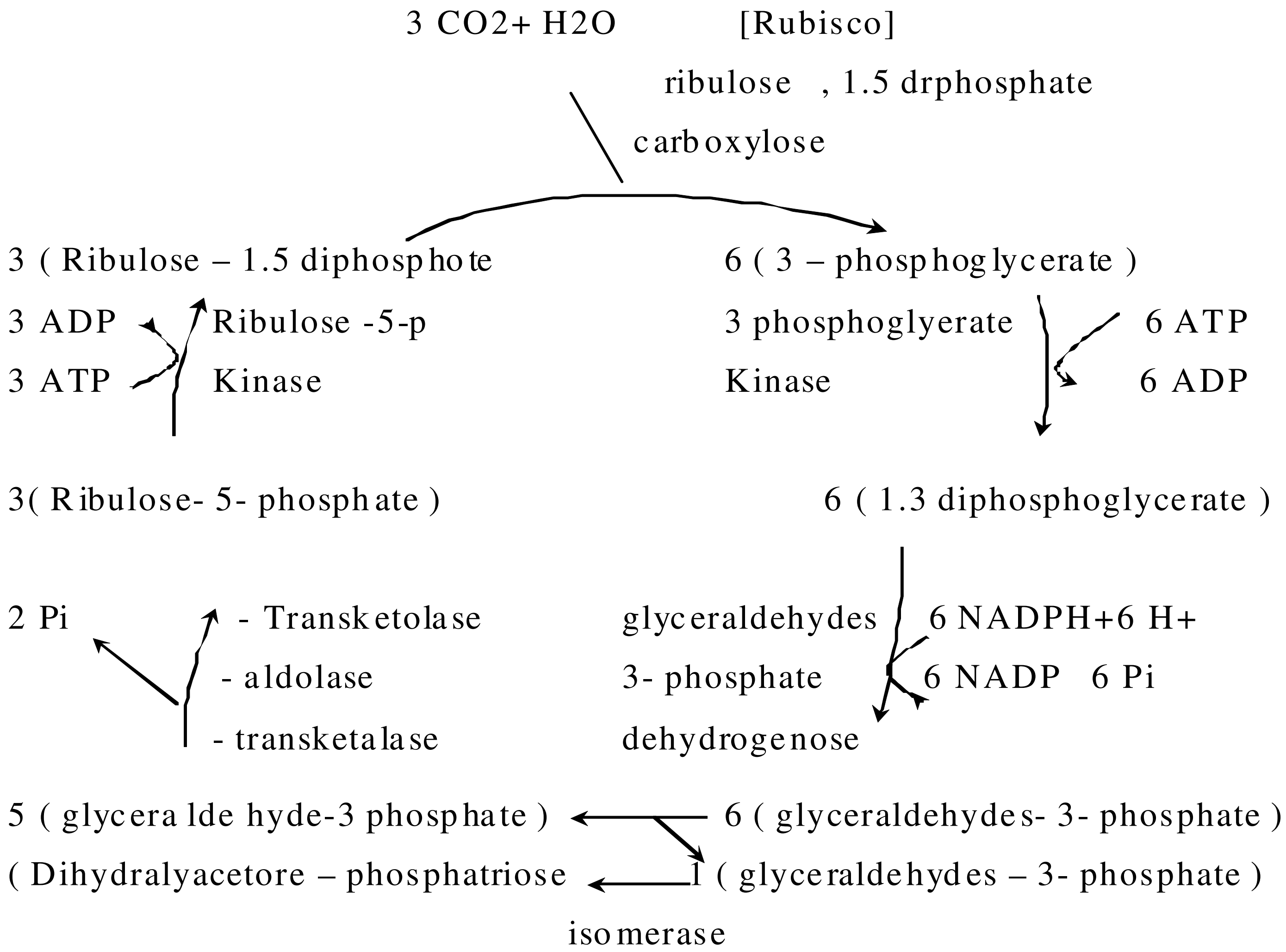

3 molecules
$CO_2$ 1C
3 molecules
ribulose 1,5-bisphosphate 5C
6 molecules
3-phosphoglycerate 3C
3 ADP
3 ATP
6 ATP
6 ADP
3 molecules
ribulose 5-phosphate 5C
6 molecules
1,3-bisphosphoglycerate 3C
2 $P_i$
6 NADPH
6 $NADP^+$
6 $P_i$
5 molecules
glyceraldehyde 3-phosphate 3C
6 molecules
glyceraldehyde 3-phosphate 3C
3 molecules of $CO_2$ fixed give a net yield of 1 molecule of glyceraldehyde 3-phosphate at a net cost of 9 molecules of ATP and 6 molecules of NADPH
1 molecule
glyceraldehyde 3-phosphate 3C
SUGARS, FATTY ACIDS, AMINO ACIDS




**Summary of photosynthesis**

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Water}}{6H_2O}$$

## **Calvin cycle :**



- Regeneration of ribulose 1.5 diphosphate ; involves rearrangement of carbon skeleton of glyceraldehydes-3- phosphate and dihydroxyacetone phosphate produced in the first two stages of carbon fixation.

- The intermediates in the pathway include 3.4.5.6.7 carbon sugars .

- The balanced equation for the net reactions of Calvin cycle is:

- $6\ CO_2 + 18\ ATP + 12\ NADPH + 12H^+ + 12\ H_2O$

$$\longrightarrow C_6H_{12}O_6 + 18\ ADP + 18\ P_i + 12\ NADP + 6\ H^+$$

3 molecules of ATP & 2 molecules of NADPH are consumed in converting $CO_2$ into hexose e.g. glucose or fructose.

Glyceraldehyde – 3-P+ Fructose -6- P  Transketolase  xylose -5-p +
thiamin P 2- $Mg^{2+}$  Erythrose -4- P

* Erythrose -4- P +Dihydroxyacetone – P aldolase ⟷ sedoheptulose, 1,7 di P

* Sedoheptulose 1.7 di P  sedoheptulose 1,7 diphosphtase ⟹ sedoheptulose -7-p

* sedoheptulose -7 –P + gluceraldehyd, -3-P  Transketolase ⟹
thiamin-P2- $Mg^{2+}$

↓

Ribose – 5- P + xylulose -5-p

Isomerase  phosphopentose
Epimerase

Ribulose – 5 –P  Ribulose – 5- P

C6+ C3  Transketolase  C4+ C5
C4+ C3  aldolase  C7
C7 + C3  transketolase  C5+C5

Glyceraldehyde – 3-P+ Fructose -6- P  Transketolase  xylose -5-p +

thiamin P 2- $Mg^{2+}$  Erythrose -4- P

* Erythrose -4- P +Dihydroxyacetone – P aldolase ⟷ sedoheptulose, 1,7 di P

* Sedoheptulose 1.7 di P  sedoheptulose 1,7 diphosphtase ⟹ sedoheptulose -7-p

* sedoheptulose -7 –P + gluceraldehyd, -3-P  Transketolase ⟹

thiamin-P2- $Mg^{2+}$

↓

- Within the chloroplast stroma are present all the enzymes necessary to convent the triose phosphate which is produced by CO2 fixation [ glyceraldehydes -3- phosphate and dihydroxyacentone – phosphate ] into starch , that is stored in the chloroplast as in soluble granules.

- Aldolase condenses the triases to fructose -1.6- diphosphate fructose 1.6 diphosphate produces fructose - 6 phosphate, phosphor hexoisomerase yields glucose -6- phosphate, and phosphglycomutase produces glucose -1- phosphate, the starting material for starch synthesis .

# Inside the chloroplast :

Glyceraldehyde -3- p triose phosphate → dihydroxyacetone- p
Isomenase

Glyceroldehyde – 3- p + dihydroryacetone – P aldolase → fructose -1.6 –
diphosphate

↓ Fructose 1.6
– diphosphatase

Phosphogluco - ← Glucose -6-P phosphohexose ← fructose -6- P
Mutase isomerase

↓

Glucose -1- p …………………… starch

# Outside the chloroplast .

Glyceraldehyde – 3- P —Triose – P isomerase→ Dihydroxyacetone – p

↓ Gets to the cytosol via specific transporter

Starch ← F-6- P ← F-1-6-P ← Dihydroxyactone – P

To produce energy ← glycolysis ← glyceraldehyde -3- p