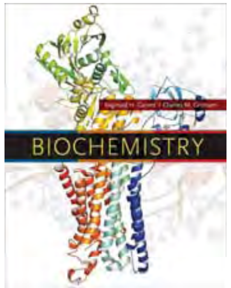
Chapter 21



Reginald H. Garrett
Charles M. Grisham

Photosynthesis

林翰佳 老師
課程網站 hanjia.km.ntou.edu.tw
hanjia@mail.ntou.edu.tw

Outline

- Part 1
  - What are the general properties of photosynthesis?
  - How is solar energy captured by chlorophyll?
- Part 2
  - What kinds of photosystems are used to capture light energy?
  - What is the molecular architecture of photosynthetic reaction centers?
  - What is the quantum yield of photosynthesis?
  - How does light drive the synthesis of ATP?
- Part 3
  - How is carbon dioxide used to make organic molecules?
  - How does photorespiration limit CO_2 fixation?

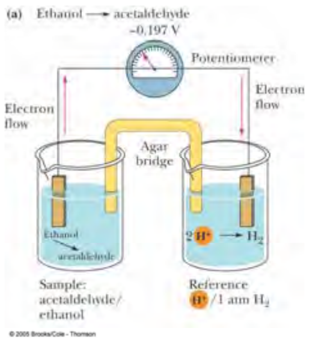
Refresh your memory

- A compound with a larger reduction potential is a:

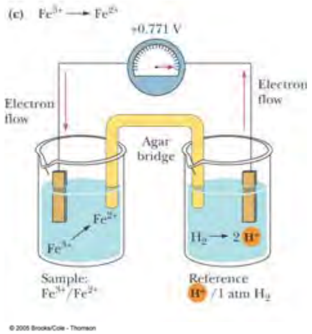
1) good e- acceptor
2) good e- donor
3) good reductant

Which sample half-cell has higher reduction potential

(1)



(2)



How electron transferred?

1) e^- will transfers to a better electron acceptor.
2) e^- will transfers to a compound with higher reduction potential.
3) e^- will transfer to O_2 as the final electron acceptor.

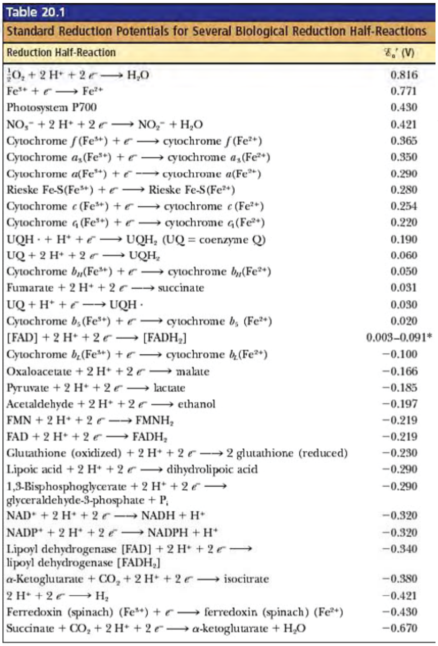


Table 20.1

Standard Reduction Potentials for Several Biological Reduction Half-Reactions

Reduction Half-Reaction	$\mathcal{E}_o'$ (V)
$\frac{1}{2}O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O$	0.816
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.771
Photosystem P700	0.430
$NO_3^- + 2\,H^+ + 2\,e^- \longrightarrow NO_2^- + H_2O$	0.421
Cytochrome f(Fe^{3+}) + e^- ⟶ cytochrome f(Fe^{2+})	0.365
Cytochrome a_3(Fe^{3+}) + e^- ⟶ cytochrome a_3(Fe^{2+})	0.350
Cytochrome a(Fe^{3+}) + e^- ⟶ cytochrome a(Fe^{2+})	0.290
Rieske Fe-S(Fe^{3+}) + e^- ⟶ Rieske Fe-S(Fe^{2+})	0.280
Cytochrome c (Fe^{3+}) + e^- ⟶ cytochrome c (Fe^{2+})	0.254
Cytochrome c_1 (Fe^{3+}) + e^- ⟶ cytochrome c_1 (Fe^{2+})	0.220
UQH · + H^+ + e^- ⟶ UQH_2 (UQ = coenzyme Q)	0.190
UQ + 2 H^+ + 2 e^- ⟶ UQH_2	0.060
Cytochrome b_H(Fe^{3+}) + e^- ⟶ cytochrome b_H(Fe^{2+})	0.050
Fumarate + 2 H^+ + 2 e^- ⟶ succinate	0.031
UQ + H^+ + e^- ⟶ UQH ·	0.030
Cytochrome b_5(Fe^{3+}) + e^- ⟶ cytochrome b_5 (Fe^{2+})	0.020
[FAD] + 2 H^+ + 2 e^- ⟶ [$FADH_2$]	0.003–0.091*
Cytochrome b_L(Fe^{3+}) + e^- ⟶ cytochrome b_L(Fe^{2+})	−0.100
Oxaloacetate + 2 H^+ + 2 e^- ⟶ malate	−0.166
Pyruvate + 2 H^+ + 2 e^- ⟶ lactate	−0.185
Acetaldehyde + 2 H^+ + 2 e^- ⟶ ethanol	−0.197
FMN + 2 H^+ + 2 e^- ⟶ $FMNH_2$	−0.219
FAD + 2 H^+ + 2 e^- ⟶ $FADH_2$	−0.219
Glutathione (oxidized) + 2 H^+ + 2 e^- ⟶ 2 glutathione (reduced)	−0.230
Lipoic acid + 2 H^+ + 2 e^- ⟶ dihydrolipoic acid	−0.290
1,3-Bisphosphoglycerate + 2 H^+ + 2 e^- ⟶ glyceraldehyde-3-phosphate + P_i	−0.290
NAD^+ + 2 H^+ + 2 e^- ⟶ NADH + H^+	−0.320
$NADP^+$ + 2 H^+ + 2 e^- ⟶ NADPH + H^+	−0.320
Lipoyl dehydrogenase [FAD] + 2 H^+ + 2 e^- ⟶ lipoyl dehydrogenase [$FADH_2$]	−0.340
α-Ketoglutarate + CO_2 + 2 H^+ + 2 e^- ⟶ isocitrate	−0.380
2 H^+ + 2 e^- ⟶ H_2	−0.421
Ferredoxin (spinach) (Fe^{3+}) + e^- ⟶ ferredoxin (spinach) (Fe^{2+})	−0.430
Succinate + CO_2 + 2 H^+ + 2 e^- ⟶ α-ketoglutarate + H_2O	−0.670

Reducing Power

(Good Oxidant, & e^- acceptor)

Reducing Power

(easy to be oxidized & Good e^- donor)

How electron transport earn energy?

- Electron transportation -> a series of oxidation reaction -> exergenic!
- The energy released from electron transport is used to pump H^+ to the P side.
- Chemiosmotic energy converts to ATP chemical energy.

---

oxidative phosphorylation and photosynthesis

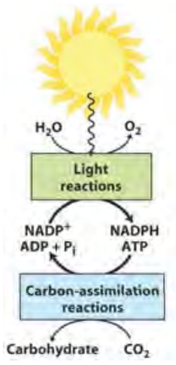
- High energy electrons from?
  - OP: NADH or $FADH_2$ from oxidative catabolism
  - PS: from the splitting of water and excited by photons at photosystem
- Energy is transformed into?
  - OP: ATP
  - PS: ATP + NADPH

The Sun - Ultimate Energy

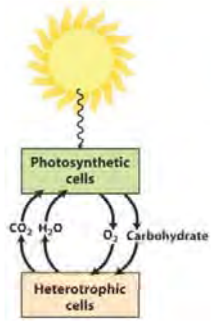
1.5 x 10^{22} kJ of sunlight energy falls on the earth each day

- 1% is absorbed by photosynthetic organisms and transformed into chemical energy
- $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
- 10^{11} tons of CO_2 are fixed globally per year
- Formation of sugar from CO_2 and water requires energy
- Sunlight is the energy source!

Solar energy as the ultimate source of all biological energy



In photosynthesis cells



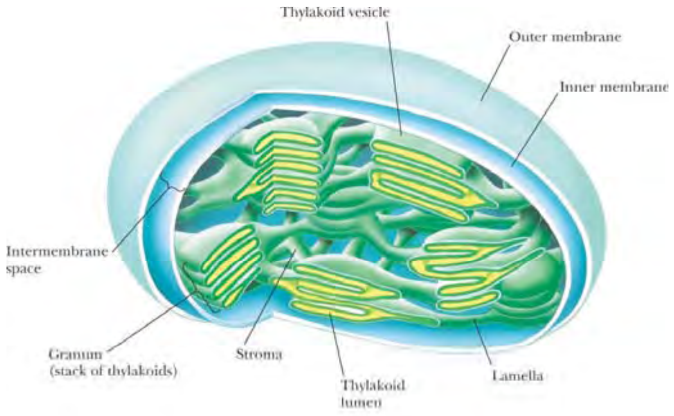
Energy flow between cells

21.1 What Are the General Properties of Photosynthesis?

General Aspects

- Photosynthesis occurs in thylakoid membranes of **chloroplasts** - structures involving paired folds (lamellae) that stack to form "**grana**"
- The soluble portion of the chloroplast is the "**stroma**"
- The interior of the thylakoid vesicles is the "**thylakoid space**" or "thylakoid lumen"
- Chloroplasts possess DNA, RNA and ribosomes

Chloroplast



© 2005 Brooks/Cole - Thomson

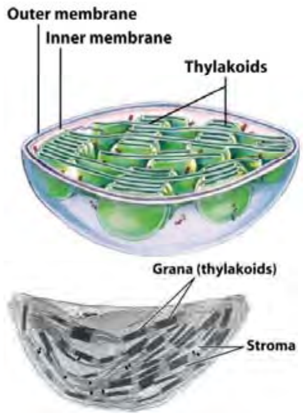
Photosynthesis

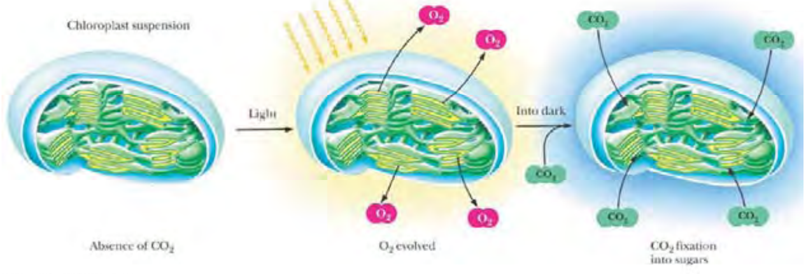
- Photosynthetic and heterotrophic organisms live in a balance steady state in biosphere.
- Solar energy provides the driving force for the continuous cycling of CO_2 and O_2 through the biosphere and provides reduced fuels. In the photosynthesis, H_2O donates electrons (as hydrogen) for the reduction of CO_2 to carbohydrate.

Two reactions in chloroplast

- Light reaction:
  - H_2O and ADP to NADPH, O_2 and ATP
  - In thylakoids
- Dark reaction:
  - Fix CO_2
  - In stroma
- Total reaction:

$$6CO_2 + 6H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2$$





© 2005 Brooks/Cole - Thomson

- The light-dependent reaction (light reactions), which occurs only when plants are illuminated
- The carbon-assimilation reactions (carbon-fixation reaction), which are driven by the products of light reaction.

General features of photophosphorylation

- H_2O is a poor donor of electron ($\Delta E`^{o}=0.816$ V comparing with -0.320 V for NADH).
- electron transfer and proton pumping are catalyzed by membrane complex similar to complex III of mitochondria.
- The electron chemical potential is the driving force for ATP synthesis by a membrane-bound ATP synthase complex closely similar to mitochondria

Water is the Ultimate e- Donor for Photosynthetic NADP+ Reduction

The reaction sequence for photosynthesis in green plants:

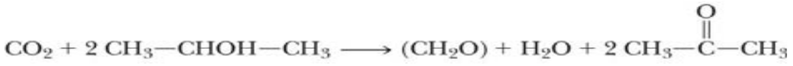
$2H_2O + 2NADP^+ + xADP + xP_i \rightarrow$

$O_2 + 2NADPH + 2H^+ + xATP + xH_2O$

A More Generalized Equation for Photosynthesis:

CO_2	+	$2H_2A$	→	(CH_2O)	+	2A	+	H_2O
Hydrogen acceptor		Hydrogen donor		Reduced acceptor		Oxidized donor		

In photosynthetic bacteria, H_2A can be H_2S or other oxidizable substrates, like isopropanol:

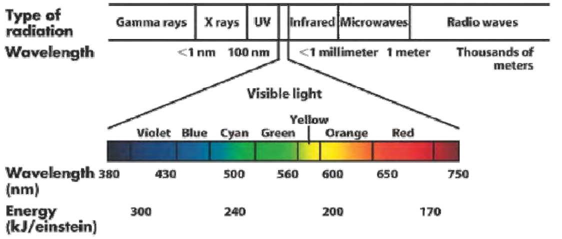


$$CO_2 + 2\,CH_3{-}CHOH{-}CH_3 \longrightarrow (CH_2O) + H_2O + 2\,CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

Photosynthesis provides the oxygen on which we depend

Energy of Light

- *E= hv*
  - the energy in a mole of photons (1 einstain, or $6x10^{23}$ photons) of visible light is 170 to 300KJ.
- Visible light: wavelengths 400 to 700 nm.



21.2 How Is Solar Energy Captured by Chlorophyll?

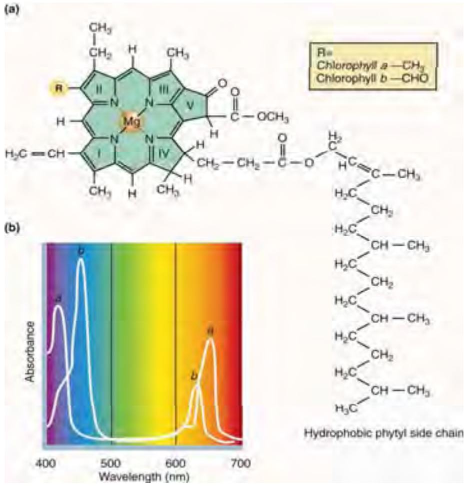
- Just as the photon is a quantum of light energy, the exciton is a quantum of energy passed from an excited molecule to another in a process called exciton transfer which is an important decay of an excitation energy in photosynthesis.

- Light absorption promotes an electron to a higher orbital, enhancing the potential for **transfer** of this electron to a suitable acceptor

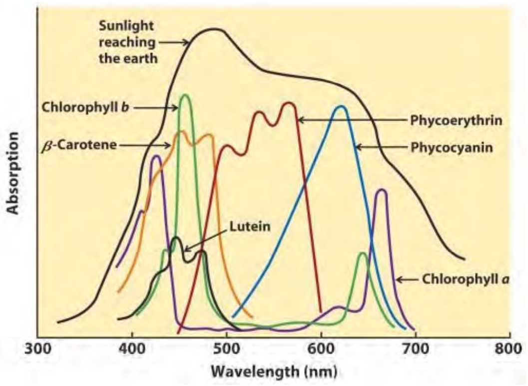
---

Photosynthesis Pigments

- **Chlorophyll** is a photoreactive, isoprene-based pigment
  - A planar, conjugated ring system - similar to porphyrins
  - **Mg^{2+}** is coordinated in the center of the planar conjugated ring structure
  - A long chain alcohol, **phytol**, group confers membrane solubility
  - Aromaticity makes chlorophyll an efficient absorber of light



How is solar energy captured?



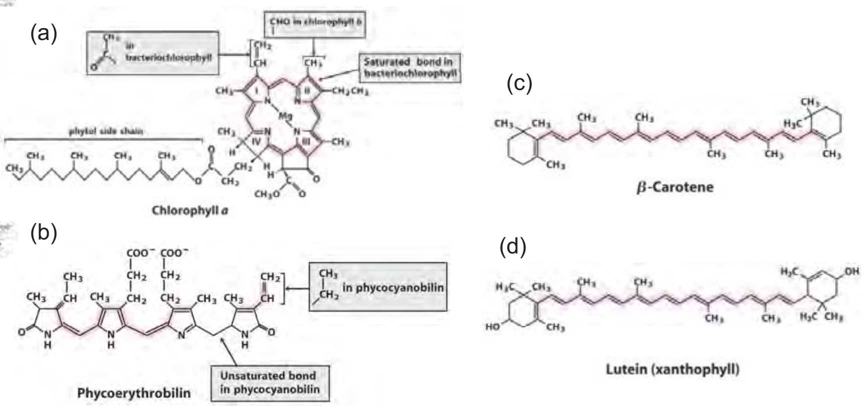
Absorption of visible light by photopigments

Accessory light harvesting pigments

- Carotenoids, lutein, phycocyanobilin..
- Functions:
  - Light harvesting
  - Photoprotection

Light harvesting complex

Photopigments



Phycocyanobilin, a blue pigment found in cyanobacteria.

Light drives electron flow in chloroplasts

- Robert Hill found that when leaf extracts contain chloroplast were illuminated, they evolved O_2 and reduced an electron acceptor (Hill reaction):

$$2H_2O + 2A \xrightarrow{light} 2AH_2 + O_2$$

- O_2 evolution could be dissociated from CO_2 reduction: CO_2 was neither required nor reduced to stable form when O_2 evolved.

- AH_2 will become hydrogen donors to reduce CO_2 to carbohydrate.

$$CO_2 + 2H_2A \rightarrow (CH_2O) + 2A + H_2O$$

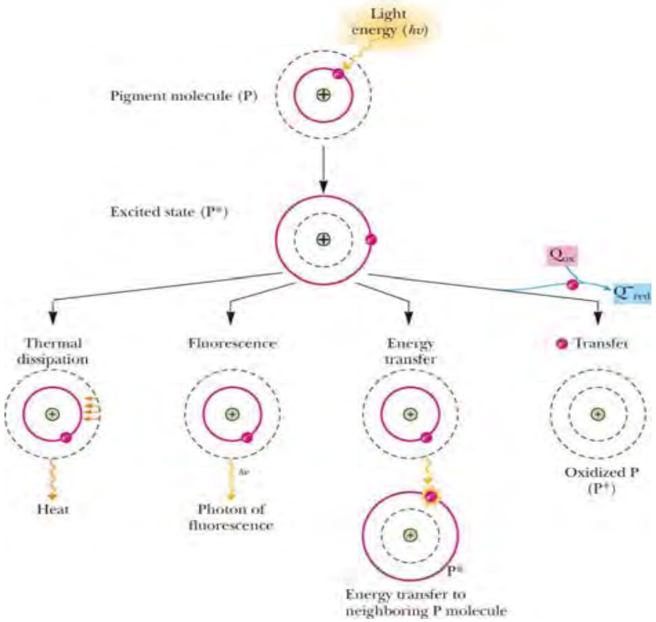
- In photosynthetic bacteria (purple sulfur bacteria), H_2S is used instead of H_2O.

Chlorophylls absorb light energy for photosynthesis

- Chlorophylls in thylakoid are coordinated with Mg2+. All chlorophylls have a long phytyl side chain, esterified to a carboxy-group substitution in ring IV
- The heterocyclic five-member ring system that surrounds the Mg2+ has the extended conjugated double bonds, showing the strong absorption in the visible region of spectrum.
- Chloroplasts always contain both chlorophyll a and chlorophyll b. their absorption spectra are sufficient different and their complement each other range's of light absorption in the visible light. Most plants contain about twice as much chlorophyll a as chlorophyll b.
- The pigments in algae and photosynthetic bacteria include chlorophylls that differ only slightly from plant pigments (Bacteriochlorophyll).
- Chlorophyll is always associated with specific binding proteins in the light-harvesting complexes (LHCS) in such a way that chlorophyll molecules are fixed in relation to each other, to other protein complexes, and to membrane.

The Light Energy Absorbed by Photosynthetic Pigments Has Several Possible Fates

- Each photon represents a quantum of energy
- Each quantum of light energy has 4 possible fates:
  1. **Loss as heat.** Energy can be dissipated as heat through redistribution into atomic vibrations within the pigment molecule.
  2. **Loss as light.** A light-excited electron can return to a lower orbital, emitting a photon of fluorescence.
  3. **Resonance energy transfer.** Excitation energy can be transferred to a neighboring molecule.
  4. **Energy transduction.** The excitation energy changes the reduction potential of the pigment, making it an effective electron donor.



Quiz time

- Which is not the special feature of chlorophyll comparing with heme.

1) Containing Mn2+ instead of Fe2+
2) Hydrophobic phytol side chain
3) An extra ring V

One more quiz

- After a photon exciting a photosysthetic reaction center, what is the most possible fate of the energy from the photon?

1) Loss as heat
2) Loss of light
3) Resonance energy transfer
4) Energy transduction

Last quiz, for now…..

- After a photon exciting a beta-carotene molecule, what is the most possible fate of the energy from the photon?

1)Loss as heat
2)Loss of light
3)Resonance energy transfer
4)Energy transduction

End of Part 1

Ask yourself…

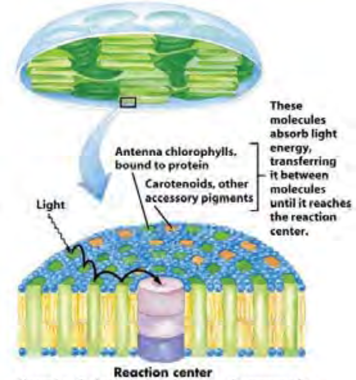
- Where do the light reaction and dark reaction take place in chloroplast?
- What are photopigments? How many kinds of them have you learned?
- What is the quantum of light? What are the fate of light where it hit to a molecule?
- Compare the electron donor in oxidative phosphorylation and photosynthesis!

Photosynthetic Units Consist of Many Chlorophyll Molecules but Only a Single Reaction Center

- The **photosynthetic unit** consists of several hundred light-capturing chlorophylls plus a pair of special chlorophylls in the **reaction center**
- Light is captured by one of the "antenna chlorophylls" and routed from one to the other until it reaches the reaction center chlorophyll dimer that is photochemically active
- Oxidation of chlorophyll leaves a cationic free radical, Chl•$^{+}$, whose properties as an electron acceptor are important to photosynthesis

Chlorophyll funnels the absorbed energy to reaction centers by exciton transfer.

- The light-absorbing pigments of thylakoid or bacterial membrane are arranged in functional arrays (photosystems).
- All the pigment molecules in a photosystem can absorb photons, but only a few chlorophyll molecules associated with the photochemical reaction center are specialized to transude light into chemical energy.
- The other pigment molecules in a photosystem are light-harvesting or antenna molecules.



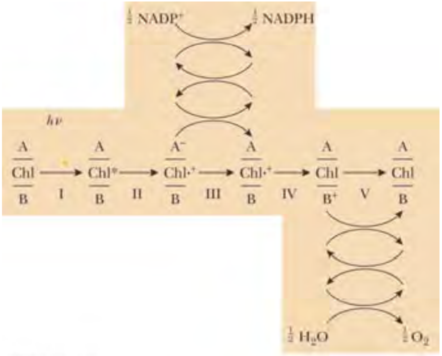
Photochemical reaction here converts the energy of a photon into a separation of charge, initiating electron flow.

Transduction of Light Energy into Chemical Energy Involves Oxidation-Reduction

- The basis of photosynthesis is transduction of light energy into chemical energy (of oxidation-reduction).
- Photon absorption raises chlorophyll (Chl) to Chl*
- Electron transfer from Chl* to an adjacent molecule A, producing oxidized Chl ($Chl^{\bullet +}$) and reduced A (A^-)
- Oxidation of A^- eventually culminates in reduction of $NADP^+$ to NADPH
- The system is restored to its original state once NADPH is formed and water is oxidized

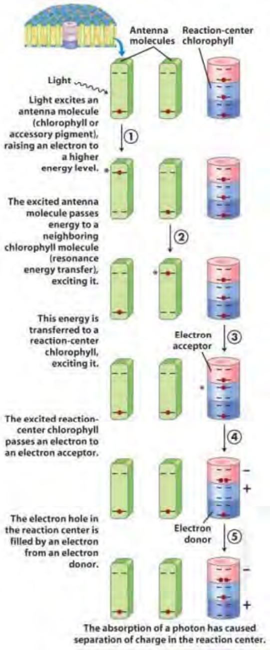
---

Excitation and electron transfer



© 2005 Brooks/Cole - Thomson

A, B are electron transfer molecules



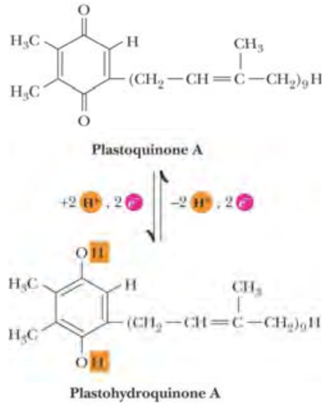
The absorption of a photon has caused separation of charge in the reaction center.

Special electron carriers in chloroplast

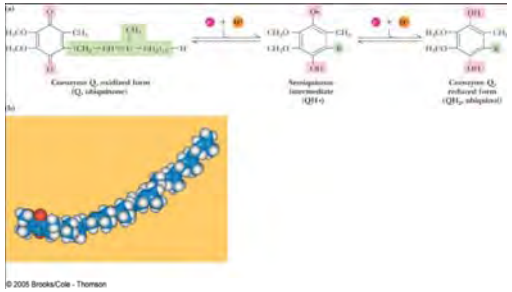
- Plastoquinone: similar to CoQ
- Plastocyanim: shuttle between cyt b6/f complex and PSI, one electron carrier, similar to cyt C, but use copper as cofactor
- Ferredoxin: $NADP^+$ reductase
- Pheophytin: similar to *chlorophyll a*

Plastoquinone vs. CoQ

- Please find out where are the differences?



© 2005 Brooks/Cole - Thomson



© 2005 Brooks/Cole - Thomson

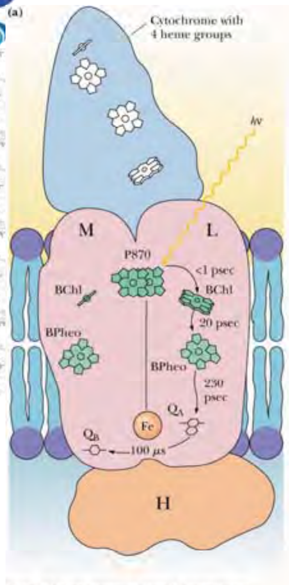
The simplest photosystem

Use Bacteria as an example: have one of two types of single photochemical reaction centers.

- The photosynthetic machinery in purple bacteria (*R. viridis*) consists of 3 basic modules:
- reaction center (P870),
- cytochrome bc$_1$ electron transfer complex,
- ATP synthase.

Purple bacteria

- Membrane proteins (as always) are resistant to crystallization (and X-ray diffraction studies)
  - Johann Deisenhofer, Hartmut Michel and Robert Huber solved the *R.viridis* structure in 1984 (and received the Nobel Prize in Chemistry just four years later, underscoring the impact of this achievement)
- Pigments: Bacteriochlorophyll *a* or *b*, together with various carotenoids
- The light-driven → flow of electron → provides the energy for proton pumping by cyt bc1 complex → Powered by the proton gradient, ATP synthase provides ATP.



Note: The cytochrome subunit is membrane associated via a diacylglycerol moiety on its N-terminal Cys residue.

- Photoreaction center of the purple bacterium:
  - Two pair of bacteria chlorophyll molecules (one special pair, chl2, and one accessory pigment pair)
  - A pair of pheophytin a (pheo a) molecules
  - Two quinones (QA and QB)
  - A single non-heme Fe located approximately on the axis of symmetry between the quinones.

The *R. viridis* Photosynthetic Reaction Center is an Integral Membrane Protein

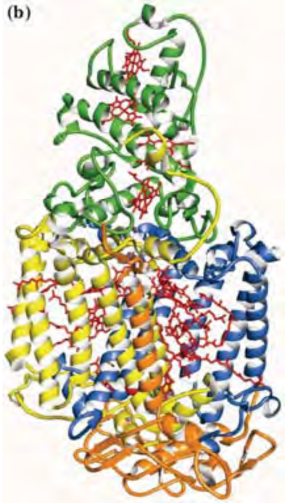


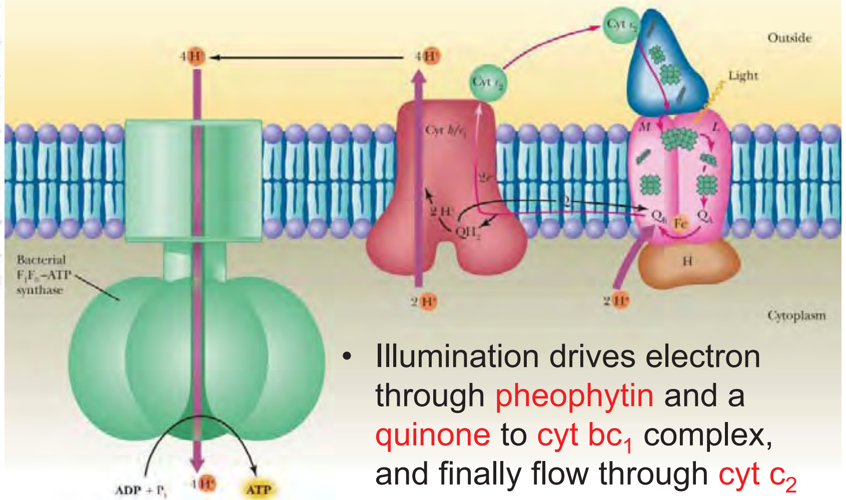
Figure 21.14 (b) Molecular graphic of the *R. viridis* reaction center. M and L are yellow and blue; H is orange; the cytochrome is green.

Photosynthetic Electron Transfer by the *R. viridis* Center Leads to ATP Synthesis

- The prosthetic groups of the *R. viridis* reaction center are arranged spatially to facilitate photosynthetic e^- transfer
- Pheophytin is like chlorophyll a, except $2H^+$ replace Mg^{2+}
- Photoexcitation of P870 leads to e^- loss via electron transfer to the nearby bacteriochlorophyll (BChl)
- The e^- is then transferred via the L protein to Q_A (on L) and then to Q_B (on M)
- The reduced quinone formed at Q_B diffuses to a neighboring cytochrome bc_1 membrane complex
- Oxidation of the quinone at bc_1 is coupled to proton transport, and thus eventually to ATP synthesis

---

Photosynthetic electron transfer in the R. viridis reaction center



- Illumination drives electron through pheophytin and a quinone to cyt bc_1 complex, and finally flow through cyt c_2 back to the reaction center.

Kinetic and thermodynamic factors prevent the dissipation of energy by internal conversion.

- The proteins of reaction center are fixed in an orientation relative to each other, allowing the photochemical reactions to take place in a virtually solid state and nothing is left to chance collision or random diffusion. This accounts for the high efficiency and rapidity of the reactions.
- The electron-transfer reactions not only are fast but are thermodynamically downhill the excited special pair:

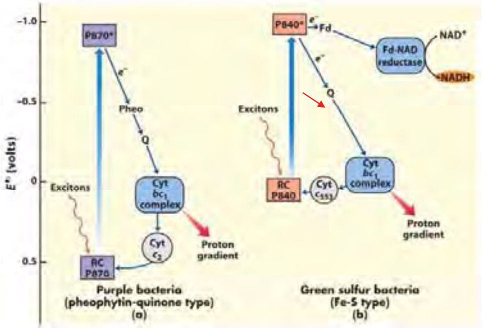
$$(Chl)_2^* \rightarrow {}^{\bullet}(Chl)_2^+ + e^- \qquad \Delta E'^o = -1.0V$$

$$Q + 2H^+ + 2e^- \rightarrow QH_2 \qquad \Delta E'^o = -0.045V$$

$$\Delta G'^o = -nF\Delta E'^o = -2(96.5KJ/mol)[-0.045V - (-1.0V)] = -180KJ/mol$$

- The percentage of the photoenergy conserved in QH_2 is >30% with the remainder of the energy dissipitated as heat.

The energy of light is not only used in ATP synthesis but also in…

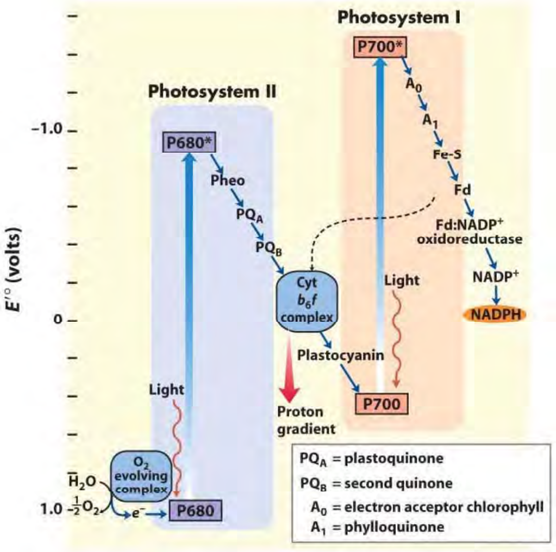


- Green sulfur bacteria have two routes for electrons driven by excitation of P840 (a cyclic and non-cyclic electron transfer. The latter yields NADH). The electrons takes from the reaction center to reduce NAD^+ are replaced by the oxidation of H_2S to elemental S, then to SO_4^{2-} in the reaction that defines the green sulfur bacteria.

Noncyclic photosynthesis system

- The photosynthetic apparatus of modern cyanobacteria algae and vascular plants appears to have evolved through the combination of two simpler bacteria photocenters.
- Two photosystems (PS I and PS II) in the thylakoid membranes of chloroplasts are integrated to show the 2 scheme pathway of electron transfer from H_2O (lower left) to $NADP^+$ in noncyclic photosynthesis.

The Z scheme of photosynthesis.



PSI and PSII Participate in the Overall Process of Photosynthesis

- What do PSI and PSII do?
- **PSI** provides reducing power in the form of NADPH
- **PSII** splits water, producing O_2, and feeds the electrons released into an electron transport chain that couples PSII to PSI
- Electron transfer between PSII and PSI pumps protons for **chemiosmotic ATP synthesis**
- Essentially, *electrons flow from H_2O to $NADP^+$,* driven by light energy absorbed at the reaction centers
- Light-driven phosphorylation of ADP to make ATP is termed **photophosphorylation**

PSI and PSII Participate in the Overall Process of Photosynthesis

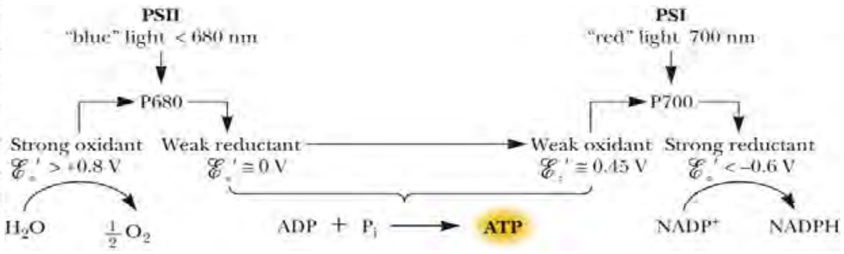


Figure 21.10 Roles of the two photosystems, PSI and PSII.

21.3 What Kinds of Photosystems Are Used to Capture Light Energy?

Oxygenic phototrophs have two distinct photosystems: PSI (P700) and PSII (P680)

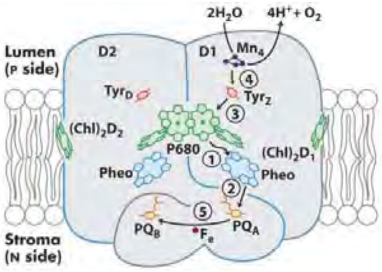
- PSI systems have a maximal red light absorption at 700 nm and use ferredoxins as terminal electron acceptors
- PSII have a maximal red absorption at 680 nm and use quinones as terminal electron acceptors
- Chloroplasts given light at 680 and 700 nm simultaneously yield more O_2 than the sum of amounts when each is used alone
- All chlorophyll is protein-bound – as part of either PSI or PSII or light-harvesting complexes (LHCs)

Photosystem II

- PS II is pheophytin-quinone type of system like the single photosystem of purple bacteria.
- Excitation of its reaction center P680 drives electrons through the cytochrome b_6f complex with concomitant movement of protons across the thylakoid membrane.

Oxygen evolving photosystem

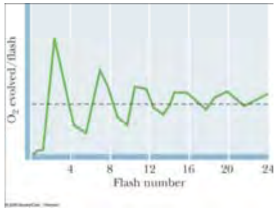
- Cyanobacteria and plant oxidize H_2O to release electrons which replace the electron that move from PS II through PS I to $NADP^+$. This process is called oxygenic photosynthesis.
- All O_2-evolving photosynthetic cells contain both PS I and PS II
- Organisms with only one photosystem do not evolve O_2.

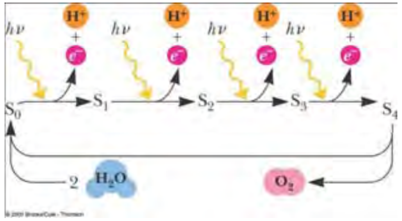


PS II of cyanobacteria

Water is split by the oxygen-evolving complex.

- PS II must acquire an electron to return to its ground state in the preparation for capture of another photon.
  - Photosynthetic bacteria use a variety of electron donors (succinate, malate, or sulfide), depending on which is available in a particular ecological niche.
- Evolution of primitive photosynthetic bacteria 3 billions year ago produced a photosystem capable of taking electrons from water: $2H_2O \rightarrow 4H^+ + 4e^- + O_2$, four photons are required in this photolytic cleavage reaction.



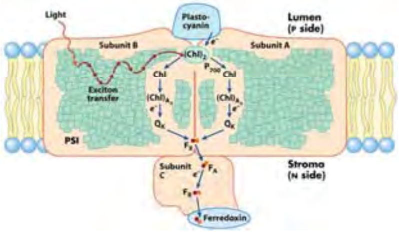


Photosystem I

- PS I similar to the type I reaction center of green sulfur bacteria has a reaction center P700.
- Excitation of P700 passes electrons to the Fe-S protein ferredoxin, then to $NADP^+$, producing NADPH.
- Electrons are carried between two photosystems by the soluble protein plastocyanin, a one-electron carrier functionally similar to cyt c of mitochondria.

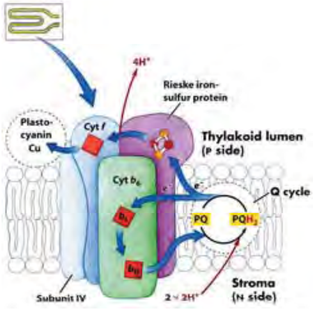
Antenna chlorophylls are tightly integrated with electron carriers

- PS I is a supramolecular complex with many antenna chlorophylls and carotenoid molecules are precisely arrayed around the reaction center.
- The reaction center's electron carrying factors are tightly integrated with antenna chlorophylls. The electron flow initiated by absorption of a photon is believed to occur through both branches of carriers in PS I.



The cytochrome b6f complex linked PS II and PS I.

- cyt b_6f complex contains a b-type cytochrome with two heme group (b_H and b_L), a Rieske iron-sulfur protein, and cyt f.
- Electrons flow through cyt b_6f complex from PQ_BH_2 to cyt f, then to plastocyanin and finally to P700, thereby reducing it.
- The function of this complex involves a Q cycle in which electrons pass, one at a time, from PQH_2 to cyt b_6. The result is proton gradient across thylakoid membrane as electrons pass from PS II to PS I with the direction of proton movement from stroma compartment to thykaloid lumen. This has a relatively large effect on luminal pH. The pH difference between the stroma (pH8.0) and the thykaloid lumen (pH5.0) gives a powerful driving force for ATP synthesis.



How Do Green Plants Carry Out Photosynthesis?

- The structure of a **light-harvesting complex (LHC)** has been determined
- LHC1 is a supercomplex of 16 distinct protein subunits and 200 prosthetic groups
- Four LHC1 subunits form an arc around one side of the PSI reaction center
- A second LHC (LHC2) binds to another side
- The many Chl molecules and other light-harvesting molecules of the supercomplex form an integrated network for highly efficient transfer of light energy into P700

Overall reaction of PS

- Overall reaction of the 2-scheme.
  $2H_2O+2NADP^{+}+8\ \text{photons}\rightarrow O_2+2NADPH+H^{+}$
- The electron transport of PS II:
  $4\ P680+4\ H^{+}+2\ PQ_B+4\ \text{photon}\rightarrow 4\ P680^{+}+2\ PQ_BH_2$
- The binding site or plastoquinone is point of action of many herbicides that kills plant by blocking electron transport through cyt b_6f complex.
- The electron transport of PS I:
  Ferredoxin: $NADP^{+}$ oxidoredutase transfers electrons from reduced ferredoxin to $NADP^{+}$
  $4\ P700+2\ NADP^{+}+4\ \text{photon}\rightarrow 4\ P700^{+}+2\ NADPH$

21.5 What Is the Quantum Yield of Photosynthesis?

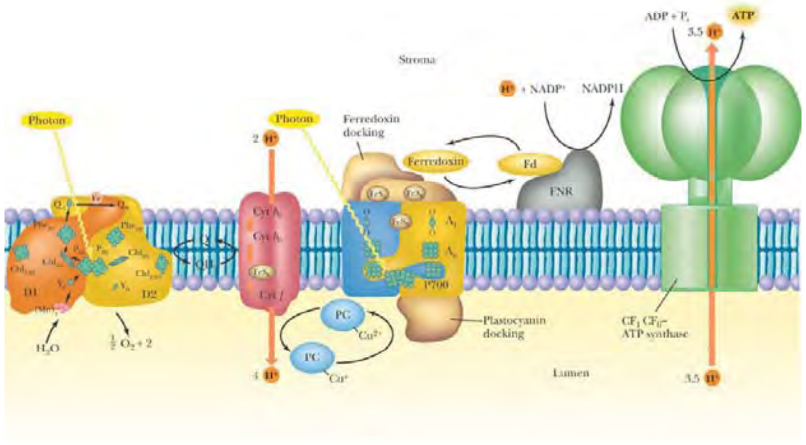
- The **quantum** yield of photosynthesis is defined as the amount of product formed per equivalent of light input
- Each electron passing from H_2O to $NADP^{+}$: 3 H^{+} pump out.
- Two photons per center: allow a pair of electrons to flow from H_2O to $NADP^{+}$.
- 8 quanta: evolution an O_2, reduction of 2 $NADP^{+}$ and translocation of 12 H^{+}.
- 14 H^{+} = 3 ATP
- (12/14)3 =2.57 ATP/8 quanta

21.6 How Does Light Drive the Synthesis of ATP?

Photophosphorylation

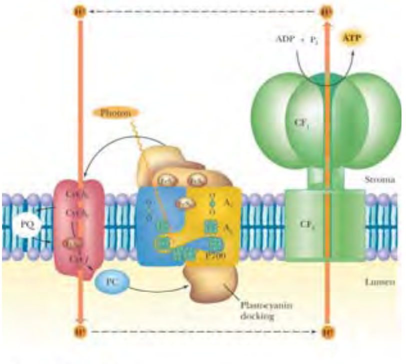
- The transduction of the electrochemical gradient into the chemical energy of ATP is carried out by the chloroplast ATP synthase, more properly called the **CF_1CF_0-ATP synthase**
- Electron transfer through the proteins of the Z scheme drives the generation of a proton gradient across the thylakoid membrane
- Protons pumped into the lumen of the thylakoids flow back out, driving the synthesis of ATP
- CF_1-CF_o ATP synthase is similar to the mitochondrial ATP synthase

Noncyclic photophosphorylation



Cyclic Photophosphorylation Generates ATP but Not NADPH or O_2

- Use PSI but not PSII
- Electrons passing from P700 to ferredoxin do not continue to NADP$^+$, but move back through cyt b_6f complex to plastocyanin which donates electrons to P700 cyclic electron flow
- Overcome the ATP deficit for CO_2 fixation, adjusts the ratio of ATP to NADPH produced.
- 5% rate of noncyclic pathway!



Bio-Fuel application

- In some algae

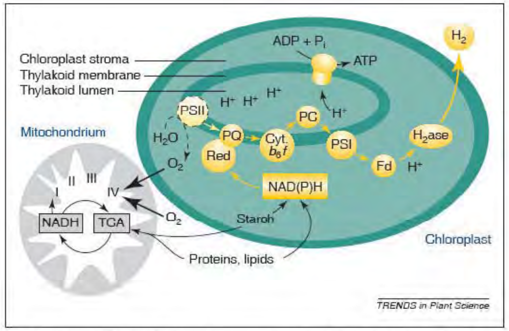
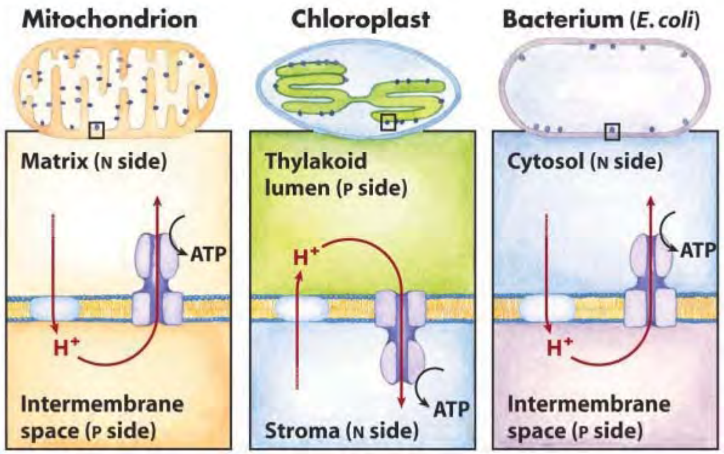


Fig. 2. Hydrogen metabolism in *Chlamydomonas reinhardtii* under sulfur deprivation. Yellow arrows indicate the main electron transport during hydrogen evolution; grey arrows show the oxidation of reducing equivalents during respiration. Photosystem II is depicted in broken lines because it is almost completely inactivated under sulfur deprivation. Red indicates NAD(P)H–plastoquinone oxidoreductase. Abbreviations: Cyt. b_6f, cytochrome b_6f complex; Fd, ferredoxin; H_2ase, hydrogenase; I–IV, complexes of respiratory electron transport chain; PC, plastocyanin; PQ, plastoquinone; PS, photosystem; TCA, tricarboxylic acid cycle.

Comparison of different ATP synthase systems



Quiz

- Reaction center of PS II is:

1) P700
2) P680
3) P840
4) P800

End of Part 2

Ask yourself….

- What is a photochemical reaction center?
- Can you tell the differences between the electron transport chains in mitochondria and chloroplast
- Why plants need two photosystems?

21.7 How Is Carbon Dioxide Used to Make Organic Molecules?

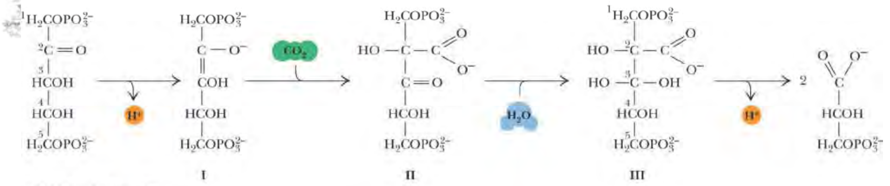
Fixation of CO_2 is a unique ability of plants, algae, etc.

- Melvin Calvin at Berkeley in 1945 showed that *Chlorella* could take up $^{14}CO_2$ and produce 3-phosphoglycerate
- What was actually happening was that CO_2 was combining with a 5-C sugar to form a 6-C intermediate
- This breaks down to two 3-P-glycerates
- Ribulose-1,5-bisphosphate is the CO_2 acceptor in CO_2 Fixation

---

How is carbon dioxide used to make organic molecules?

- Ribulose-1,5-bisphosphate is the CO_2 acceptor
- Ribulose bisphosphate carboxylase/oxygenase (rubisco)



© 2005 Brooks/Cole - Thomson

2-carboxy-3-keto-arabinitol

Regulation of rubisco

- Carbamylation (at Lys201)
- Active form (carbamylation + Mg2+)
- Rubisco activase helps RuBP release from rubisco (20 nM → 20 uM) and promote it carbamylation.
- Rubisco activase activated by light indirectly.

Calvin-Benson cycle

- Produce carbohydrate and regenerate RuBP.
- 6(1) + 6 (5) → 12 (3)

  12 (3) → 1(6) + 6 (5)

  Net: 6 (1) → 1 (6)

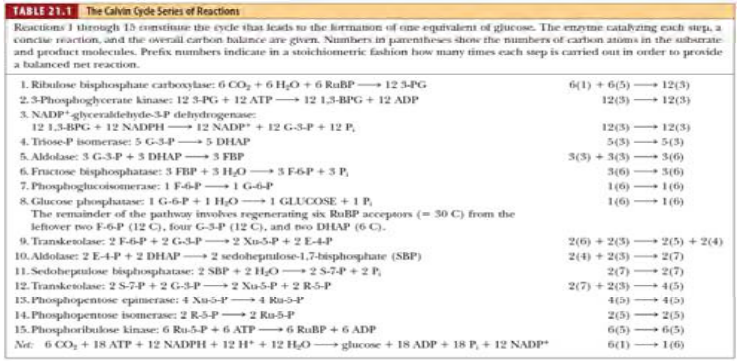
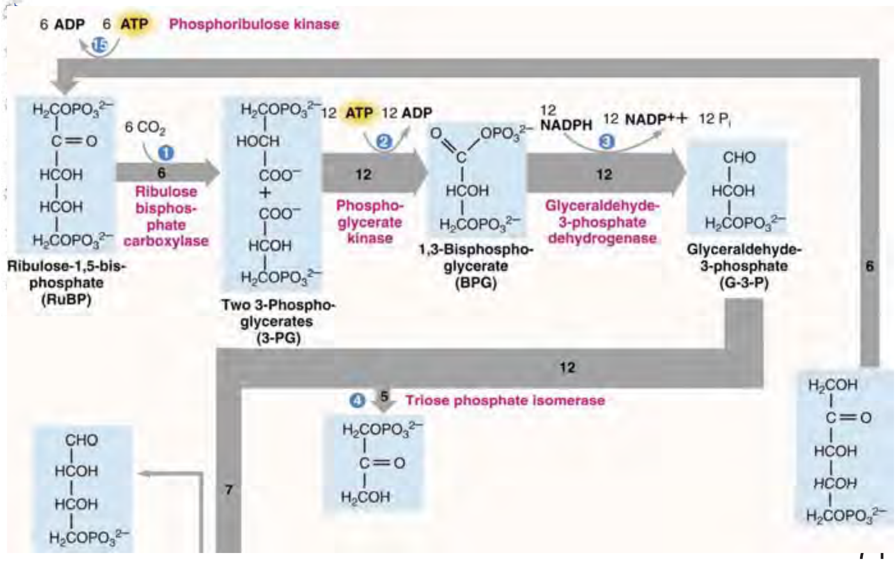


TABLE 21.1 The Calvin Cycle Series of Reactions

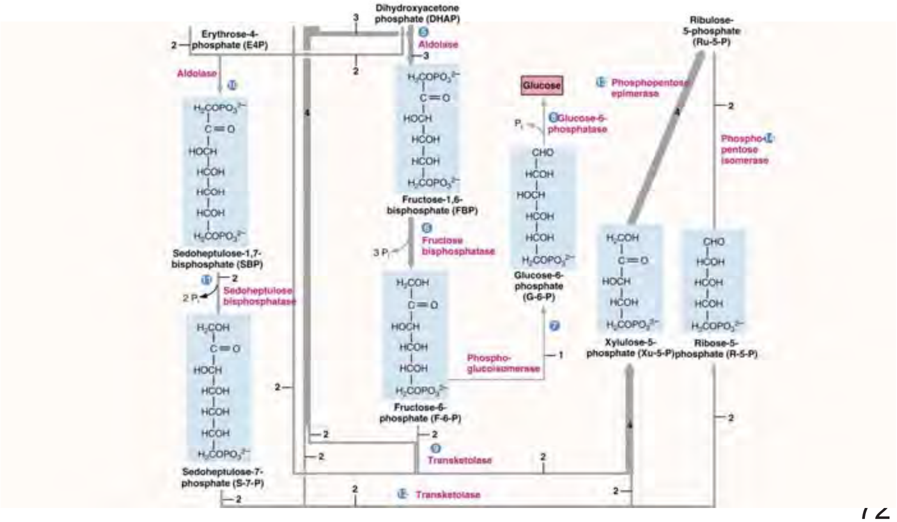
Reactions 1 through 15 constitute the cycle that leads to the formation of one equivalent of glucose. The enzyme catalyzing each step, a concise reaction, and the overall carbon balance are given. Numbers in parentheses show the numbers of carbon atoms in the substrate and product molecules. Prefix numbers indicate in a stoichiometric fashion how many times each step is carried out in order to provide a balanced net reaction.

1. Ribulose bisphosphate carboxylase: 6 CO_2 + 6 H_2O + 6 RuBP ⟶ 12 3-PG	6(1) + 6(5) ⟶ 12(3)
2. 3-Phosphoglycerate kinase: 12 3-PG + 12 ATP ⟶ 12 1,3-BPG + 12 ADP	12(3) ⟶ 12(3)
3. NADP⁺-glyceraldehyde-3-P dehydrogenase: 12 1,3-BPG + 12 NADPH ⟶ 12 NADP⁺ + 12 G-3-P + 12 P_i	12(3) ⟶ 12(3)
4. Triose-P isomerase: 5 G-3-P ⟶ 5 DHAP	5(3) ⟶ 5(3)
5. Aldolase: 3 G-3-P + 3 DHAP ⟶ 3 FBP	3(3) + 3(3) ⟶ 3(6)
6. Fructose bisphosphatase: 3 FBP + 3 H_2O ⟶ 3 F-6-P + 3 P_i	3(6) ⟶ 3(6)
7. Phosphoglucoisomerase: 1 F-6-P ⟶ 1 G-6-P	1(6) ⟶ 1(6)
8. Glucose phosphatase: 1 G-6-P + 1 H_2O ⟶ 1 GLUCOSE + 1 P_i	1(6) ⟶ 1(6)
The remainder of the pathway involves regenerating six RuBP acceptors (= 30 C) from the leftover two F-6-P (12 C), four G-3-P (12 C), and two DHAP (6 C).	
9. Transketolase: 2 F-6-P + 2 G-3-P ⟶ 2 Xu-5-P + 2 E-4-P	2(6) + 2(3) ⟶ 2(5) + 2(4)
10. Aldolase: 2 E-4-P + 2 DHAP ⟶ 2 sedoheptulose-1,7-bisphosphate (SBP)	2(4) + 2(3) ⟶ 2(7)
11. Sedoheptulose bisphosphatase: 2 SBP + 2 H_2O ⟶ 2 S-7-P + 2 P_i	2(7) ⟶ 2(7)
12. Transketolase: 2 S-7-P + 2 G-3-P ⟶ 2 Xu-5-P + 2 R-5-P	2(7) + 2(3) ⟶ 4(5)
13. Phosphopentose epimerase: 4 Xu-5-P ⟶ 4 Ru-5-P	4(5) ⟶ 4(5)
14. Phosphopentose isomerase: 2 R-5-P ⟶ 2 Ru-5-P	2(5) ⟶ 2(5)
15. Phosphoribulose kinase: 6 Ru-5-P + 6 ATP ⟶ 6 RuBP + 6 ADP	6(5) ⟶ 6(5)
Net: 6 CO_2 + 18 ATP + 12 NADPH + 12 H⁺ + 12 H_2O ⟶ glucose + 18 ADP + 18 P_i + 12 NADP⁺	6(1) ⟶ 1(6)

CO_2 Fixation into Carbohydrate Proceeds Via the Calvin-Benson Cycle



CO_2 Fixation into Carbohydrate Proceeds Via the Calvin-Benson Cycle



The Carbon Dioxide Fixation Pathway Is Indirectly Activated by Light

- The activities of key Calvin cycle enzymes are coordinated with the output of photosynthesis
- In effect, these enzymes respond indirectly to **light activation**
- Light induces pH changes in chloroplast compartments
  - Rubisco, rubisco activase, and several Calvin cycle enzymes are more active at alkaline pH
- Light energy generates reducing power
  - Reduced ferredoxin and NADPH
- Light induces movement of Mg^{2+} ions from the thylakoid vesicles into the stroma

---

The Carbon Dioxide Fixation Pathway Is Indirectly Activated by Light

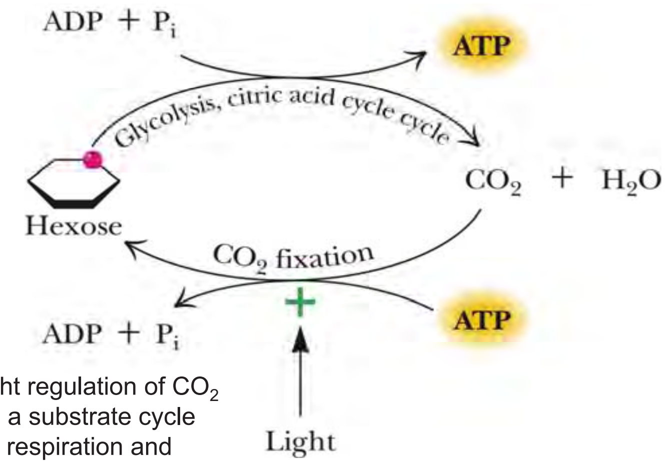
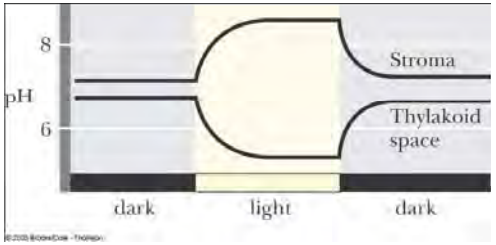


Figure 21.25 Light regulation of CO_2 fixation prevents a substrate cycle between cellular respiration and hexose synthesis by CO_2 fixation.

Regulation of CO_2 fixation

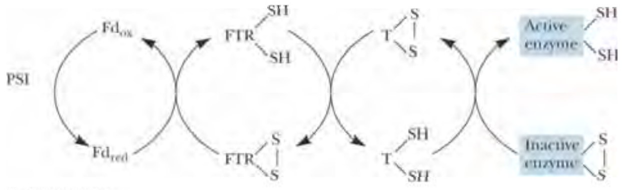
- Light activation
  - Change in stromal pH
    - Alkaline optimization (fructose-1,6-bisphosphatase, ribulose-5-phophate kinase, glyceraldehyde-3-phosphate dehydrogenase)



© 2005 Brooks/Cole - Thomson

Regulation of CO_2 fixation

- Generation of reducing power



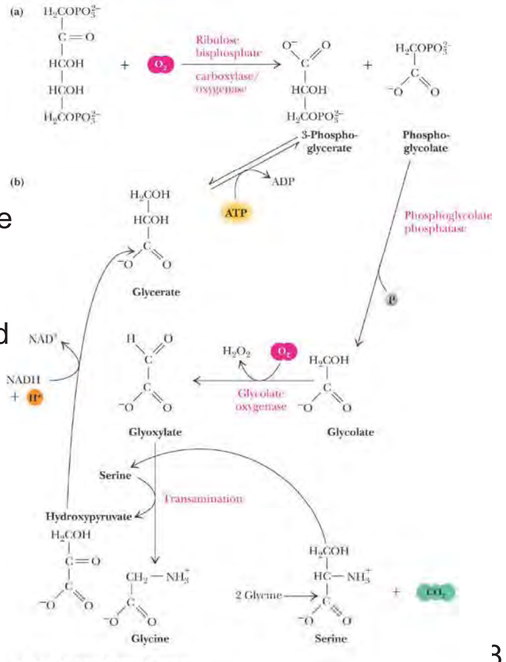
© 2005 Brooks/Cole - Thomson

- Mg^{2+} efflux
  - Ribulose bisphophate carboxylase, fructose-1,6-bisphosphatase are Mg^{2+}-activated enzymes.

21.9 How Does Photorespiration Limit CO_2 Fixation?

- Ribisco has a dual role: carboxylase/oxygenase
- When O_2 excess/CO_2 deficiency, oxygenase activity will increase.
- Net effect: CO_2 fixation decreased, plant productivity diminished (because it leads to loss of RuBP, the CO_2 acceptor)

- The products of the oxygenase reaction are 3-phosphoglycolate and phosphoglycolate
- Dephosphorylation and oxidation convert phosphoglycolate to glyoxylate
- Transamination yields glycine



© 2005 Brooks/Cole - Thomson

Hatch-Slack pathway

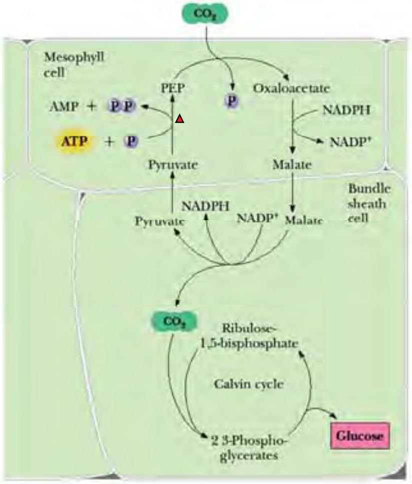
- Function:

  transport CO_2, avoid photorespiration

▲

Cost 2 ATP

Pyruvate-Pi dikinase



© 2005 Brooks/Cole - Thomson

Regulation of Pyruvate-Pi dikinase

E-His + AMP-P-P +Pi → E-His-P + AMP + PPi

E-His-P + pyruvate → PEP + E-His

Net : ATP + Pi + pyruvate → AMP + PEP + PPi

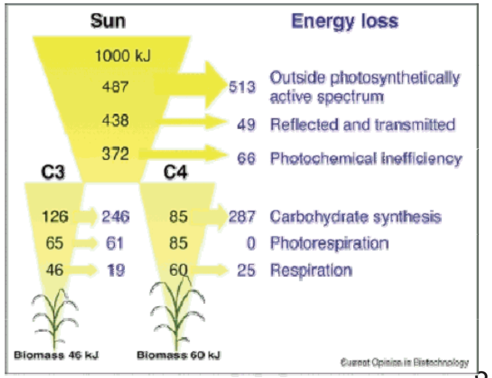
- Threonine phosphorylation: inhibition
- ADP provides phospho-group for such regulation. Why?

C4 plants are more efficient!

- C4 and C3 plants
- Tropical grass (1% of 230,000 plants)

Sugarcane

maize



Current Opinion in Biotechnology

End of Part 3

Ask yourself….

- How CO_2 is fixed in the dark reaction?
- What is Calvin cycle?
- How the dark reaction is regulated?
- What is photorespiration?
- What is a C4 plant?

End of the class

You should have learned….

- How the solar energy was used in plant!
- What are photosystems? How electrons are transferred in photosystems? How the energy of electron comes from? Where is the energy applied to?
- The relationship between light and dark reactions!