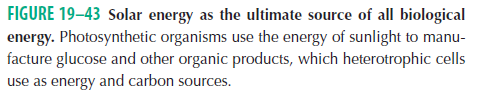
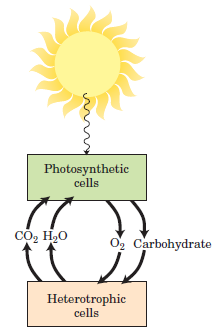
**Chapter 19 and 20**

**Photosynthesis**

* Photosynthesis is the capture of solar energy by photosynthetic organisms and its conversion to the chemical energy of reduced organic compounds.
* Photosynthetic and heterotrophic organisms live in a balanced steady state in the biosphere **(Fig. 19-43)**.

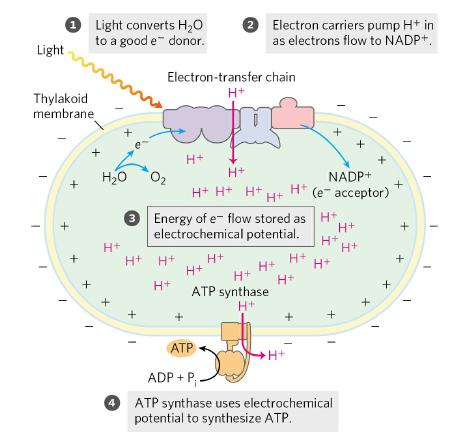


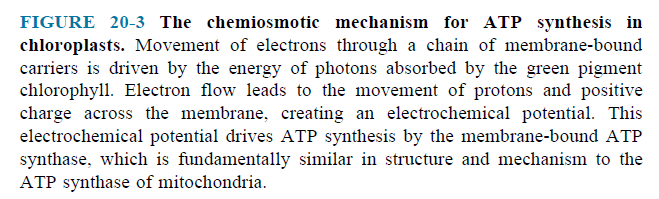
* Solar energy is the ultimate source of all biological energy.
* Photosynthetic organisms trap solar energy and form ATP and NADPH, which they use as energy sources to make carbohydrates and other organic compounds from CO2 and H2O; simultaneously, they release O2 into the atmosphere.
* Photosynthesis occurs in a variety of bacteria and in unicellular eukaryotes (algae) as well as in plants.
* The overall equation for photosynthesis in plants describes an oxidation-reduction reaction in which H2O donates electrons (as hydrogen) for the reduction of CO2 to carbohydrate (CH2O):

light

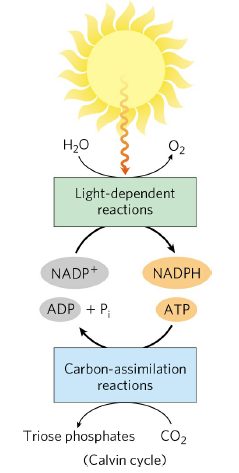
CO2 + H2O O2 + (CH2O)

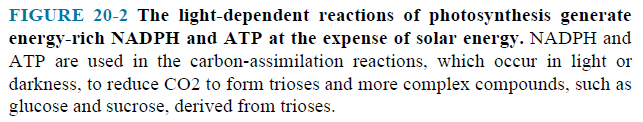
* 1. **General Features of Photophosphorylation**
* Photophosphorylation differs from oxidative phosphorylation.
* In higher plants, photophosphorylation occurs in chloroplasts **(Fig. 20-3)**.





* In photophosphorylation, electrons flow through a series of membrane-bound carriers including cytochromes, quinones, and iron-sulfur proteins, while protons are pumped across a membrane to create an electrochemical potential.
* Photosynthesis in plants encompasses two processes: **(Fig. 20-22)**.

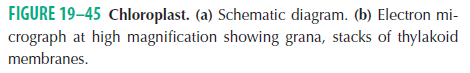
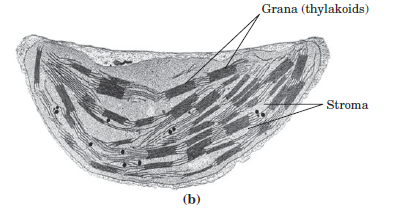
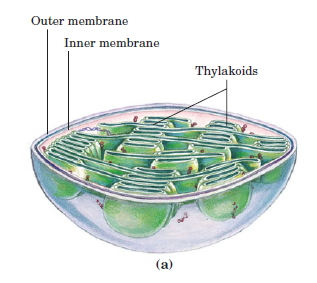




* In the **light-dependent reactions**, or **light reactions**, chlorophyll and other pigments of photosynthetic cells absorb light energy and conserve it as ATP and NADPH; simultaneously, O2 is evolved.
* In the **carbon-assimilation reactions** (or **carbon-fixation reactions**), sometimes misleadingly called the dark reactions, ATP and NADPH are used to reduce CO2 to form triose phosphates, starch, sucrose and other products.

**Photosynthesis in Plants Takes Place in Chloroplasts**

* In photosynthetic eukaryotic cells, both the light-dependent and the carbon-assimilation reactions take place in the chloroplasts **(Fig. 19–45)**.



* They are surrounded by two membranes, an outer membrane that is permeable to small molecules and ions, and an inner membrane that encloses the internal compartment.
* This compartment contains many flattened, membrane-surrounded vesicles, the **thylakoids**, usually arranged in stacks called **grana**.
* The photosynthetic pigments and the enzyme complexes that carry out the light reactions and ATP synthesis are embedded in the thylakoid membranes.
* The **stroma** (the aqueous phase enclosed by the inner membrane) contains most of the enzymes required for the carbon-assimilation reactions.

**Light Drives Electron Flow in Chloroplasts**

* NADP+ is the biological electron acceptor in chloroplasts, according to the equation

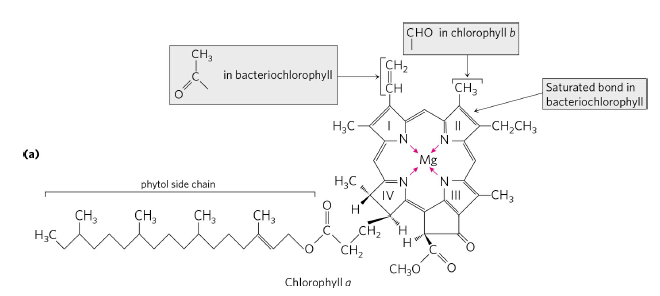
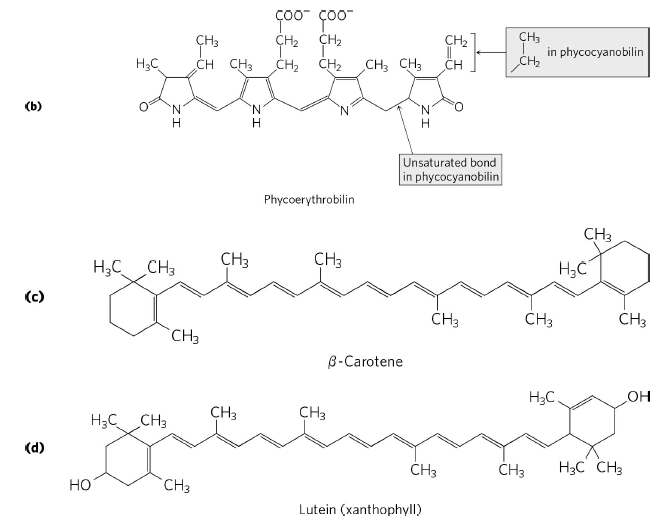
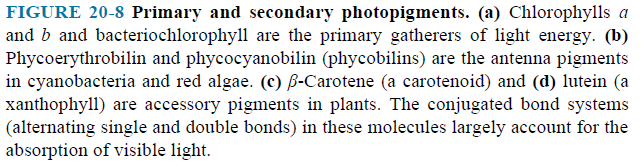
light

2H2O + 2NADP+  2NADPH + 2H+ + O2

* 1. **Light Absorption**
* The energy of a photon of visible light ranges from 150 kJ/einstein for red light to - 300 kJ/einstein for violet light. One einstein is 6.022 x 1023 photons.
* When a photon is absorbed, an electron in the absorbing molecule (chromophore) is lifted to a higher energy level.
* This molecule is in an **excited state**, which is generally unstable.

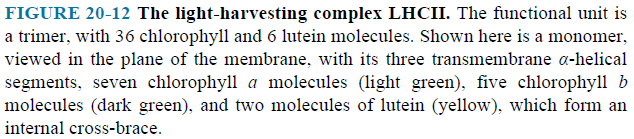
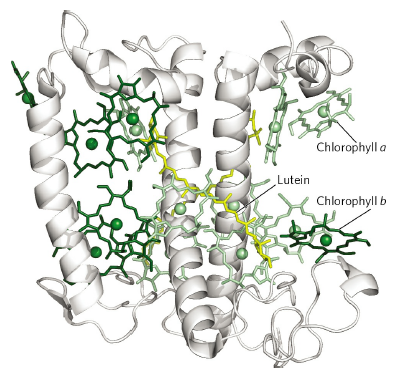
**Chlorophylls Absorb Light Energy for Photosynthesis**

* The most important light-absorbing pigments in the thylakoid membranes are the **chlorophylls**, green pigments with polycyclic, planar structures resembling the protoporphyrin of hemoglobin, except that Mg2+, not Fe2+, occupies the central position **(Fig. 20–8a)**.
* Chloroplasts always contain both chlorophyll *a* and chlorophyll *b*.
* Chlorophyll is always associated with specific binding proteins, forming **light-harvesting complexes** **(LHCs)**.

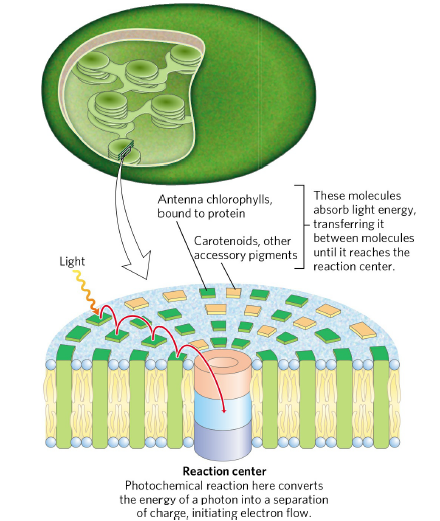
**Accessory Pigments Extend the Range of Light Absorption**

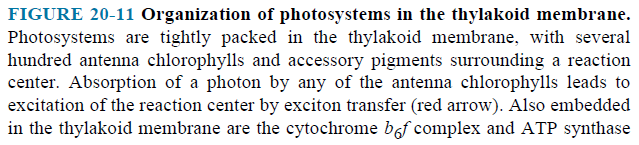
* In addition to chlorophylls, thylakoid membranes contain secondary light-absorbing pigments, or **accessory pigments**, called carotenoids.
* The most important are ****-carotene** and **lutein** **(Fig. 20–8c,d)**.
* The carotenoid pigments absorb light at wavelengths not absorbed by the chlorophylls and thus are supplementary light receptors.
* One light-harvesting complex (LHCII); contains seven molecules of chlorophyll *a*, five of chlorophyll *b*, and two of the accessory pigment lutein **(Fig. 20–12**).



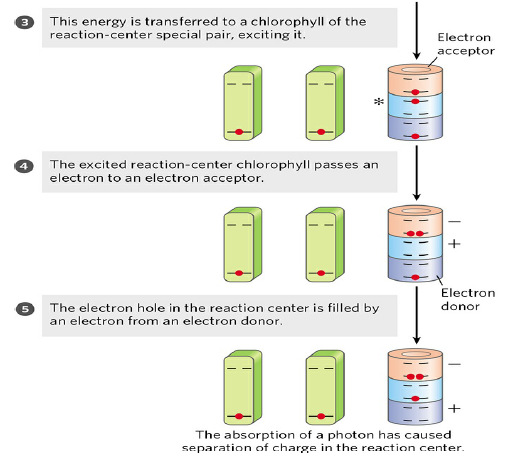
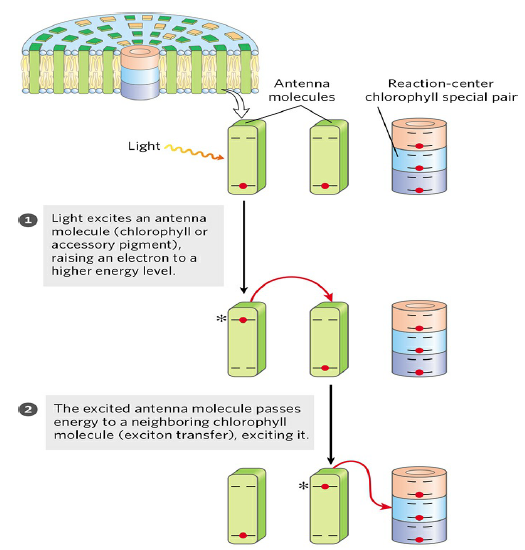
**Chlorophyll Funnels the Absorbed Energy to Reaction Centers by Exciton Transfer**

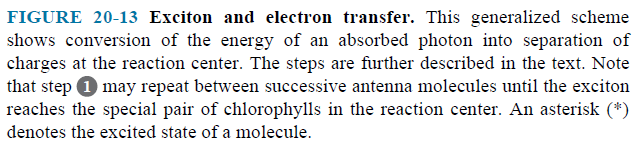
* The light-absorbing pigments of thylakoid or bacterial membranes are arranged in functional arrays called **photosystems**.
* In spinach chloroplasts, for example, each photosystem contains about 200 chlorophyll and 50 carotenoid molecules.
* All the pigment molecules in a photosystem can absorb photons, but only a few chlorophyll molecules associated with the **photochemical reaction center** are specialized to transduce light into chemical energy.
* The other pigment molecules in a photosystem are called **light-harvesting** or **antenna molecules**.
* They absorb light energy and transmit it rapidly and efficiently to the reaction center **(Fig. 20–11).**





* + Light excites an antenna molecule (chlorophyll or accessory pigment), raising an electron to a higher energy level **(Fig. 20–13).**
  + The excited antenna chlorophyll transfers energy directly to a neighboring chlorophyll molecule, which becomes excited as the first molecule returns to its ground state.
  + This energy is transferred to a reaction-center chlorophyll, exciting it.
  + The excited reaction-center chlorophyll passes an electron to an electron acceptor.
  + The electron hole in the reaction center is filled by an electron from an electron donor.
  + The absorption of a photon has caused separation of charge in the reaction center.
  + In this way, excitation by light causes electric charge separation and initiates an oxidation-reduction chain.

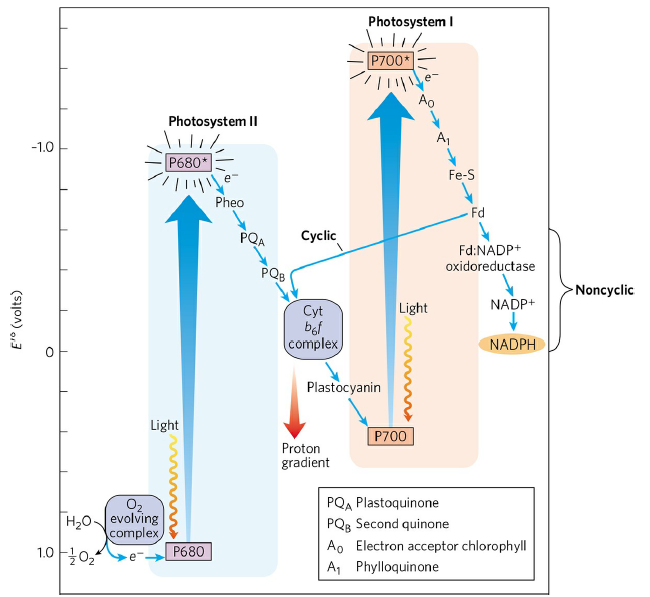
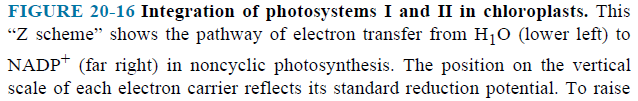
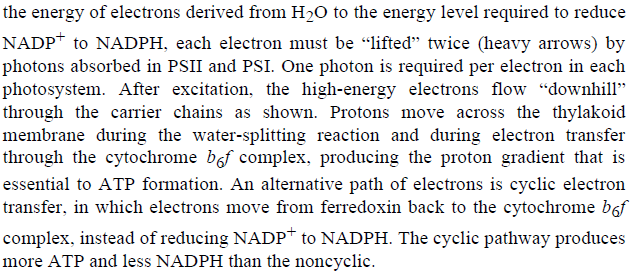




* 1. **The Central Photochemical Event : Light-Driven Electron Flow**
* Light-driven electron transfer in plant chloroplasts during photosynthesis is accomplished by multienzyme systems in the thylakoid membrane.

**In Plants, Two Reaction Centers Act in Tandem**

* The thylakoid membranes of chloroplasts have two different kinds of photosystems, each with its own type of photochemical reaction center and set of antenna molecules **(Fig. 20–16**).
* This “Z scheme” shows the pathway of electron transfer from H2O to NADP+ in noncyclic photosynthesis.
  + **Photosystem II (PSII)** is a **pheophytin** (chlorophyll lacking the central Mg2+ ion)-**quinone** type of system containingequal amounts of chlorophylls *a* and *b.* Excitation of its reaction-center P680 drives electrons through the cytochrome *b*6*f* complex with concomitant movement of protons across the thylakoid membrane.
  + **Photosystem I (PSI)** has a reaction center designated P700 and a high ratio of chlorophyll *a* to chlorophyll *b.* Excited P700 passes electrons to the Fe-S protein ferredoxin, then to NADP+, producing NADPH.
* The thylakoid membranes of a single spinach chloroplast have many hundreds of each kind of photosystem.
* These two reaction centers in plants act in tandem to catalyze the light-driven movement of electrons from H2O to NADP+.
* Electrons are carried between the two photosystems by the soluble protein **plastocyanin**.

* To replace the electrons that move from PSII through PSI to NADP+, plants oxidize H2O, producing O2. This process is called **oxygenic photosynthesis**.
* The Z scheme thus describes the complete route by which electrons flow from H2O to NADP+, according to the equation

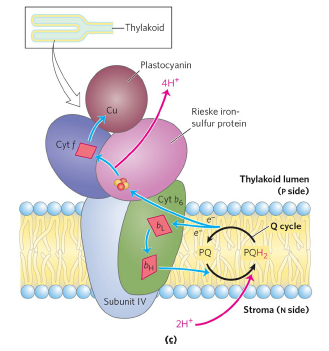
2H2O + 2NADP+ + 8 photons O2 + 2NADPH + 2H+

* A total of eight photons must be absorbed, four by each photosystem.
* In PSII, there are D1 and D2 proteins, to which all the electron-carrying cofactors are bound.
* Excitation of P680 in PSII produces P680\*, an excellent electron donor that transfers an electron to pheophytin.
* Pheo passes its extra electron to a protein-bound **plastoquinone** (**PQA**) which passes its electron to bound **plastoquinone (PQB**).
* When PQB has acquired two electrons and two protons from the solvent water, it is in its fully reduced quinol form, PQBH2.
* Eventually, the electrons in PQBH2 pass through the cytochrome *b*6 *f* complex.
* The electron initially removed from P680 is replaced with an electron obtained from the oxidation of water.
* The photochemical events of PSI at the reaction-center P700 are similar to those in PSII.
* The excited reaction-center P700\* loses an electron to an acceptor, A0 (chlorophyll).
* P700+ is a strong oxidizing agent, which quickly acquires an electron from **plastocyanin**, a soluble Cu-containing electron-transfer protein.
* First, **phylloquinone** (A1) accepts an electron and passes it to an iron-sulfur protein.
* From here, the electron moves to **ferredoxin** (Fd), another iron-sulfur protein.
* The fourth electron carrier in the chain is the flavoprotein **ferredoxin:NADP**+ **oxidoreductase**, which transfers electrons from reduced ferredoxin (Fdred) to NADP+:

2Fdred + 2H+ + NADP+  2Fdox + NADPH + H+

**The Cytochrome *b*6*f* Complex Links Photosystems II and I**

* The function of this complex involves a Q cycle **(Fig. 20–21c**).



* This cycle results in the pumping of protons across the membrane; in chloroplasts, the direction of proton movement is from the stromal compartment to the thylakoid lumen, up to four protons moving for each pair of electrons.
* The result is production of a proton gradient across the thylakoid membrane as electrons pass from PSII to PSI.
* The measured difference in pH between the stroma (pH 8) and the thylakoid lumen (pH 5) represents a 1,000-fold difference in proton concentration—a powerful driving force for ATP synthesis.

**Cyclic Electron Flow between PSI and the Cytochrome *b*6*f* Complex Increases the Production of ATP Relative to NADPH**

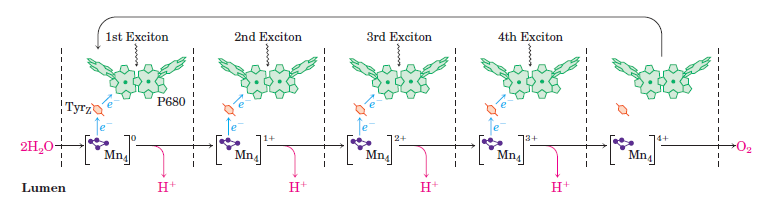
* Electron flow from PSII through the cytochrome *b*6*f* complex, then through PSI to NADP+, is sometimes called **noncyclic electron flow**, to distinguish it from **cyclic electron flow**.
* The noncyclic path produces a proton gradient, which is used to drive ATP synthesis, and NADPH, which is used in reductive biosynthetic processes.
* Electrons passing from P700 to ferredoxin do not continue to NADP+, but move back through the cytochrome *b*6*f* complex to plastocyanin.
* Plastocyanin then donates electrons to P700, which transfers them to ferredoxin.
* In this way, electrons are repeatedly recycled through the cytochrome *b*6*f* complex and the reaction center of PSI.
* Cyclic electron flow is not accompanied by net formation of NADPH or evolution of O2.
* However, it is accompanied by proton pumping by the cytochrome *b*6*f* complex and by phosphorylation of ADP to ATP, referred to as **cyclic photophosphorylation**.
* By regulating the partitioning of electrons between NADP+ reduction and cyclic photophosphorylation, a plant adjusts the ratio of ATP to NADPH produced in the light-dependent reactions to match its needs for these products in the carbon-assimilation reactions and other biosynthetic processes.

**Water Is Split by the Oxygen-Evolving Complex**

* The ultimate source of the electrons passed to NADPH in plant (oxygenic) photosynthesis is water.
* Having given up an electron to pheophytin, P680+ (of PSII) must acquire an electron to return to its ground state in preparation for capture of another photon.
* Two water molecules are split, yielding four electrons, four protons, and molecular oxygen:

1. H2O  4 H+ + 4 e- + O2

* A single photon of visible light does not have enough energy to break the bonds in water; four photons are required in this photolytic cleavage reaction.
* The four electrons abstracted from water do not pass directly to P680+, which can accept only one electron at a time **(Fig. 20–24**).



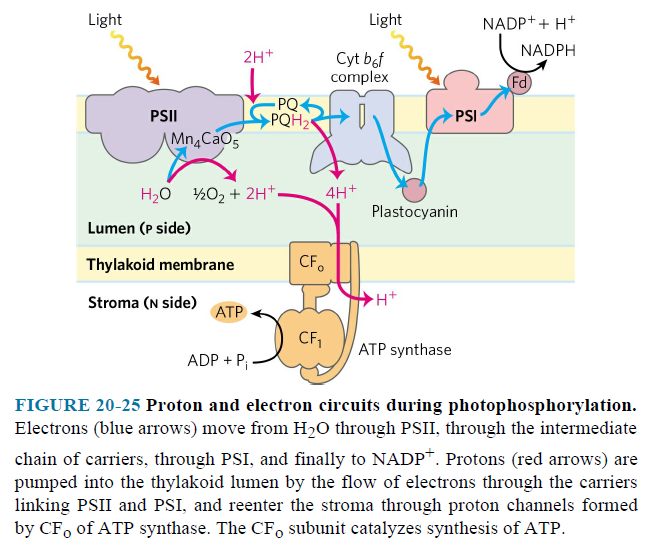
* The **oxygen-evolving complex** (also called the **water-splitting complex**) passes four electrons *one at a time* to P680+.
* In the complex, the Mn4Ca cluster can take four electrons from a pair of water molecules, releasing 4 H+ and O2:

[Mn4Ca]4+ + 2H2O  [Mn4Ca]0 + 4H+ + O2

* The electron donor to P680+ is a Tyr residue (often designated Z or Tyrz) in the PSII reaction center.
* Because the four protons produced in this reaction are released into the thylakoid lumen, the oxygen-evolving complex acts as a proton pump, driven by electron transfer.
* Electron flow through the cytochrome *b6f* complex drives protons across the plasma membrane, creating a proton-motive force that provides the energy for ATP synthesis by an ATP synthase.
  1. **ATP Synthesis by Photophosphorylation**
* The combined activities of the two plant photosystems move electrons from water to NADP+, conserving some of the energy of absorbed light as NADPH.
* Simultaneously, protons are pumped across the thylakoid membrane and energy is conserved as an electrochemical potential.
* This proton gradient drives the synthesis of ATP, the other energy conserving product of the light-dependent reactions.
* Some of the light energy captured by the photosynthetic systems of these organisms is transformed into the phosphate bond energy of ATP. This process is called **photophosphorylation**, to distinguish it from oxidative phosphorylation in respiring mitochondria.

**A Proton Gradient Couples Electron Flow and Phosphorylation**

* Several properties of photosynthetic electron transfer and photophosphorylation in chloroplasts indicate that a proton gradient plays the same role as in mitochondrial oxidative phosphorylation **(Fig. 20–25)**.
* Electron-transferring molecules in the chain of carriers connecting PSII and PSI are in the thylakoid membrane, so photoinduced electron flow results in the net movement of protons across the membrane, from the stromal side to the thylakoid lumen.
* As protons moved out of the thylakoids into the medium, ATP was generated from ADP and Pi.



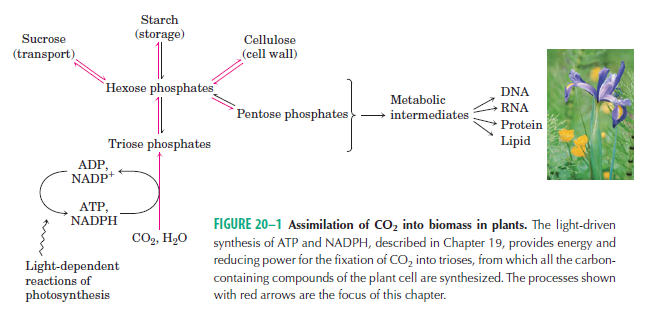
* Electrons move from H2O through PSII, through the intermediate chain of carriers, through PSI, and finally to NADP+.
* Protons are pumped into the thylakoid lumen by the flow of electrons through the carriers linking PSII and PSI, and reenter the stroma through proton channels formed by the Fo (CFo) of ATP synthase. The F1 subunit (CF1) catalyzes synthesis of ATP.

**The Approximate Stoichiometry of Photophosphorylation Has Been Established**

* As electrons move from water to NADP+ in plant chloroplasts, about 12 H+ move from the stroma to the thylakoid lumen per four electrons passed (that is, per O2 formed).
* At least eight photons must be absorbed to drive four electrons from H2O to NADPH (one photon per electron at each reaction center).
* The energy in eight photons of visible light is more than enough for the synthesis of three molecules of ATP.
* ATP synthesis is not the only energy-conserving reaction of photosynthesis in plants; the NADPH formed in the final electron transfer is also energetically rich.
* The overall equation for noncyclic photophosphorylation is

2 H2O + 8 photons + 2 NADP+ + 3 ADP + + 3 Pi  O2 + 3 ATP + 2 NADPH

* 1. **Photosynthetic Carbohydrate Synthesis**
* The synthesis of carbohydrates in animal cells always employs precursors having at least three carbons, all of which are less oxidized than the carbon in CO2.
* Plants and photosynthetic microorganisms, by contrast, can synthesize carbohydrates from CO2 and water, reducing CO2 at the expense of the energy and reducing power furnished by the ATP and NADPH that are generated by the light-dependent reactions of photosynthesis.



* Plants (and other autotrophs) can use CO2 as the sole source of the carbon atoms required for the biosynthesis of cellulose and starch, lipids and proteins, and the many other organic components of plant cells **(Fig. 20–1)**.
* Green plants contain in their chloroplasts unique enzymatic machinery that catalyzes the conversion of CO2 to simple (reduced) organic compounds, a process called **CO2 assimilation**. This process has also been called **CO2 fixation** or **carbon fixation**.
* Carbon dioxide is assimilated via a cyclic pathway and is often called the **Calvin cycle** or the **photosynthetic carbon reduction cycle**.
* **Chloroplasts** are the sites of CO2 assimilation.
* The enzymes for this process are contained in the stroma, the soluble phase bounded by the inner chloroplast membrane.

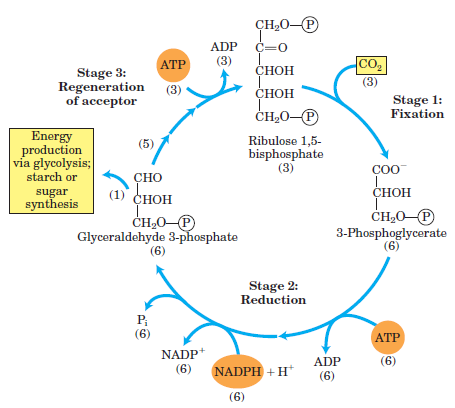
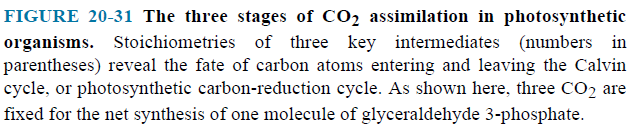
**Carbon Dioxide Assimilation Occurs in Three Stages**

*Stage 1: Fixation of CO2 into 3-Phosphoglycerate*

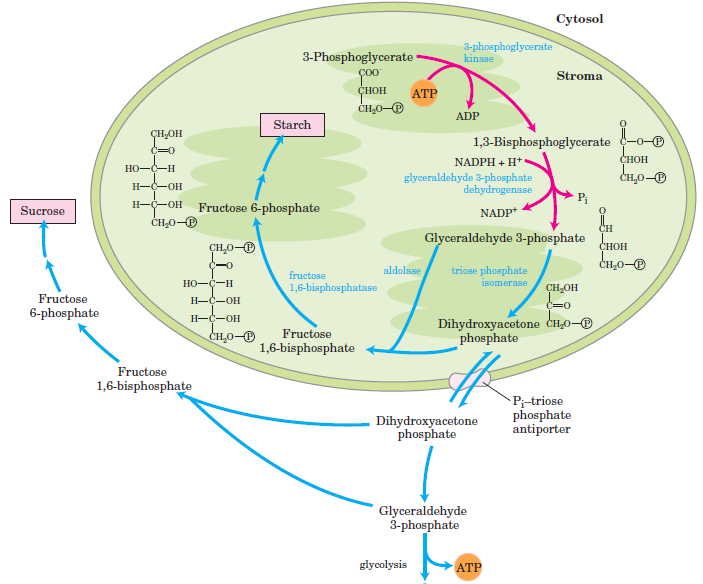
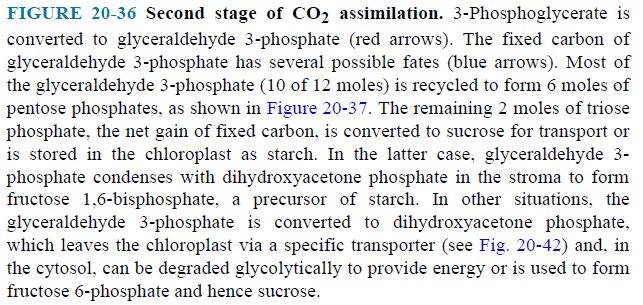
* The first stage in the assimilation of CO2 into biomolecules is the **carbon-fixation reaction**: condensation of CO2 with a five-carbon acceptor, ribulose 1,5-bisphosphate, to form two molecules of 3-phosphoglycerate **(Fig. 20–31)**.
* The enzyme is **ribulose 1,5-bisphosphate carboxylase/oxygenase**, a name mercifully shortened to **rubisco**. The enzyme’s oxygenase activity is discussed in Section 20.2.
* To achieve high rates of CO2 fixation, plants therefore need large amounts of this enzyme. In fact, rubisco makes up almost 50% of soluble protein in chloroplasts and is probably one of the most abundant enzymes in the biosphere.

*Stage 2: Conversion of 3-Phosphoglycerate to Glyceraldehyde 3-Phosphate*

* This conversion occurs in two steps **(Fig. 20–36)**.
* In the first step, ATP transfers a phosphoryl group and 3-phosphoglycerate is converted to 1,3-bisphosphoglycerate by **3-phosphoglycerate kinase**.

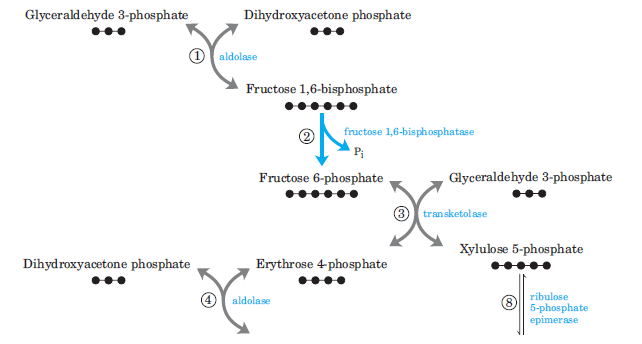
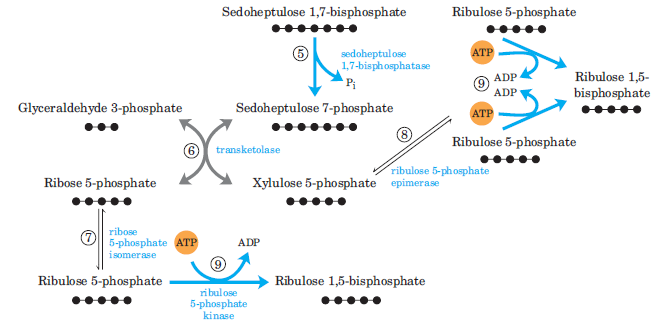
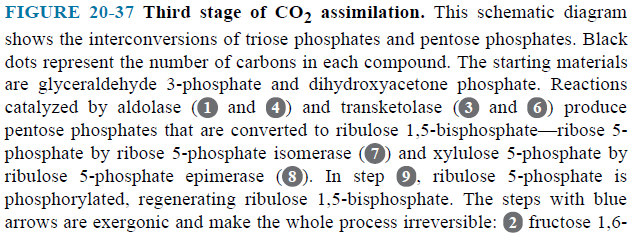
 

* In the second step, NADPH donates electrons and 1,3-bisphosphoglycerate is converted to glyceraldehyde 3-phosphate by **glyceraldehyde 3-phosphate dehydrogenase**.
* **Triose phosphate isomerase** then interconverts glyceraldehyde 3-phosphate and dihydroxyacetone phosphate.
* In the second stage, the 3-phosphoglycerate is reduced to triose phosphates. Overall, three molecules of CO2 are fixed to three molecules of ribulose 1,5-bisphosphate to form six molecules of glyceraldehyde 3-phosphate (18 carbons) in equilibrium with dihydroxyacetone phosphate.

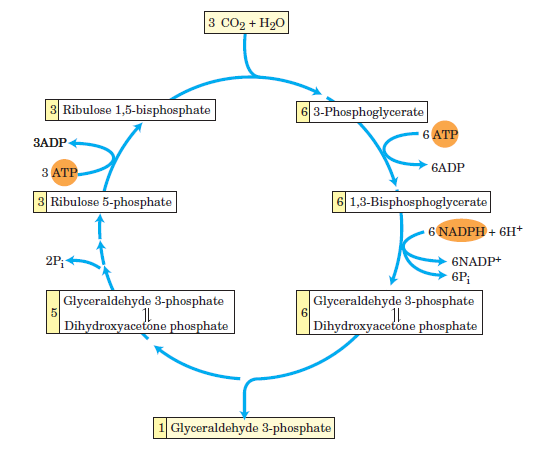
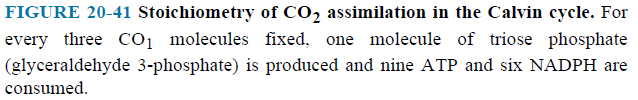
*Stage 3: Regeneration of Ribulose 1,5-Bisphosphate from Triose Phosphates*

* The first reaction in the assimilation of CO2 into triose phosphates consumes ribulose 1,5-bisphosphate and, for continuous flow of CO2 into carbohydrate, ribulose 1,5-bisphosphate must be constantly regenerated.
* In the third stage, five of the six molecules of triose phosphate (15 carbons) are used to regenerate three molecules of ribulose 1,5-bisphosphate (15 carbons), the starting material.
* This is accomplished in a series of reactions **(Fig. 20–37)**.
* The pentose phosphates (ribose 5-phosphate and xylulose 5-phosphate) are converted to ribulose 5-phosphate.
* In the final step of the cycle, ribulose 5-phosphate is phosphorylated to ribulose 1,5-bisphosphate by **ribulose 5-phosphate kinase**.

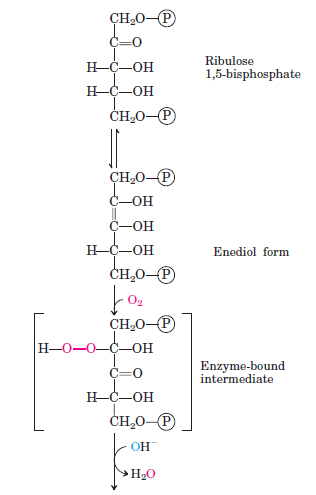
**Synthesis of Each Triose Phosphate from CO2 Requires Six NADPH and Nine ATP**

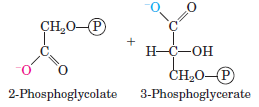
* The net result of three turns of the Calvin cycle is the conversion of three molecules of CO2 and one molecule of phosphate to a molecule of triose phosphate.
* The stoichiometry of the overall path from CO2 to triose phosphate, with regeneration of ribulose 1,5-bisphosphate, is shown in **(Fig. 20–41)**.
* One molecule of glyceraldehyde 3-phosphate is the net product of the carbon assimilation pathway.

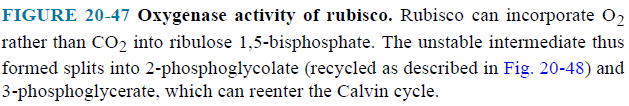
 

**20.2 Oxygenase Activity of Rubisco**

* Rubisco is not absolutely specific for CO2 as a substrate.
* Molecular oxygen (O2) competes with CO2 at the active site.
* Rubisco catalyzes the condensation of O2 with ribulose 1,5-bisphosphate to form 3-phosphoglycerate and 2-phosphoglycolate **(Fig. 20–47)**.







* The *K*m for CO2 is about 9 M, and that for O2 is about 350 M.

**20.3-4 Biosynthesis of Some Molecules**

* Plants (and other autotrophs) can use CO2 as the sole source of the carbon atoms required for the biosynthesis of sucrose, starch, cellulose, lipids, proteins and the many other organic components of plant cells **(Fig. 20–1)**.

