allow a plant to manufacture sugars only when it is appropriate to do so. Several of the enzymes required for carbon fixation, for example, are inactivated in the dark and reactivated by light-stimulated electron transport.

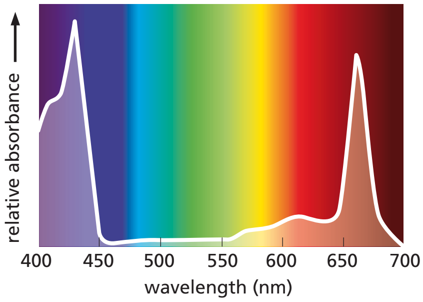


Figure 14–30 Chlorophylls absorb light of blue and red wavelengths. As shown in this absorption spectrum, one form of chlorophyll preferentially absorbs light around wavelengths of 430 nm (*blue*) and 660 nm (*red*). Green light, in contrast, is absorbed poorly by this pigment. Other chlorophylls can absorb light of slightly different wavelengths.

Chlorophyll Molecules Absorb the Energy of Sunlight

Visible light is a form of electromagnetic radiation composed of many wavelengths, ranging from violet (wavelength 400 nm) to deep red (700 nm). Most chlorophylls best absorb light in the blue and red wavelengths (**Figure 14–30**). Because these pigments absorb green light poorly, plants look green to us: the green light is reflected back to our eyes.

Chlorophyll's ability to harness energy derived from sunlight stems from its unique structure. The electrons in a chlorophyll molecule are distributed in a decentralized cloud around the molecule's light-absorbing porphyrin ring (**Figure 14–31**). When light of an appropriate wavelength hits a molecule of chlorophyll, it excites electrons in this diffuse network, perturbing the way the electrons are distributed. This perturbed high-energy state is unstable, and an excited chlorophyll molecule will seek to get rid of this excess energy so it can return to its more stable, unexcited state.

A molecule of chlorophyll, on its own in solution, would simply release its absorbed energy in the form of light or heat—accomplishing nothing useful. However, chlorophyll molecules in a chloroplast are able to convert light energy into a form of energy useful to the cell because they are associated with a special set of photosynthetic proteins in the thylakoid membrane, as we see next.

Excited Chlorophyll Molecules Funnel Energy into a Reaction Center

In the thylakoid membrane of plants and the plasma membrane of photosynthetic bacteria, chlorophyll molecules are held in large multiprotein complexes called **photosystems**. Each photosystem consists of a set of *antenna complexes*, which capture light energy, and a *reaction center*, which converts that light energy into chemical energy.

In each **antenna complex**, hundreds of chlorophyll molecules are arranged so that the light energy captured by one chlorophyll molecule can be transferred to a neighboring chlorophyll molecule in the network. In this way, energy jumps randomly from one chlorophyll molecule to the next—either within the same antenna or in an adjacent antenna. At some point, this wandering energy will encounter a chlorophyll dimer called the *special pair*, which holds its electrons at a lower energy than do the other chlorophyll molecules. Thus when energy is accepted by this special pair, it becomes effectively trapped there.

The chlorophyll special pair is not located in an antenna complex. Instead, it is part of the **reaction center**—a transmembrane complex of proteins and pigments that is thought to have first evolved more than 3 billion years ago in primitive photosynthetic bacteria (**Movie 14.6**). Within the reaction center, the special pair is positioned directly next to a set of electron carriers that are poised to accept a high-energy electron

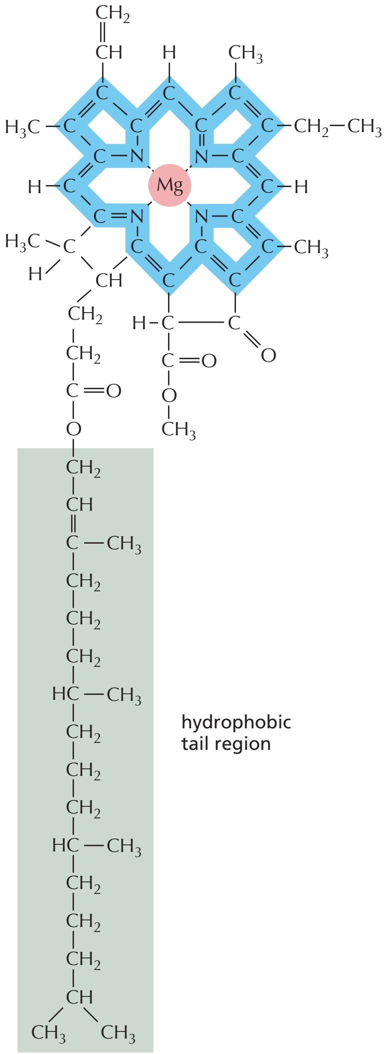


Figure 14–31 Chlorophyll's structure allows it to absorb energy from light. Each chlorophyll molecule contains a porphyrin ring with a magnesium atom (*pink*) at its center. This porphyrin ring is structurally similar to the one that binds iron in heme (see Figure 14–25). Light is absorbed by electrons within the bond network shown in *blue*, while the long, hydrophobic tail (*gray*) helps hold the chlorophyll in the thylakoid membrane.

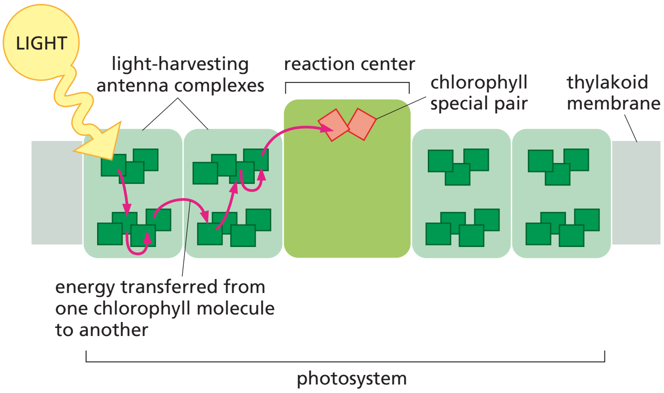


Figure 14–32 A photosystem consists of a reaction center surrounded by chlorophyll-containing antenna complexes. Once light energy has been captured by a chlorophyll molecule in an antenna complex, it will pass randomly from one chlorophyll molecule to another (*red lines*), until it gets trapped by a chlorophyll dimer called the *special pair*, located in the reaction center. The chlorophyll special pair holds its electrons at a lower energy than the antenna chlorophylls, so the energy transferred to it from the antenna gets trapped there. Note that in the antenna complex only energy moves from one chlorophyll molecule to another, not electrons.

from the excited chlorophyll special pair (**Figure 14–32**). This electron transfer lies at the heart of photosynthesis, because it converts the light energy that came into the special pair into chemical energy in the form of a transferable electron. As soon as the high-energy electron is handed off, the chlorophyll special pair becomes positively charged, and the electron carrier that accepts the electron becomes negatively charged. The rapid movement of this electron along a set of electron carriers in the reaction center then creates a *charge separation* that sets in motion the flow of electrons from the reaction center to an electron-transport chain (**Figure 14–33**).

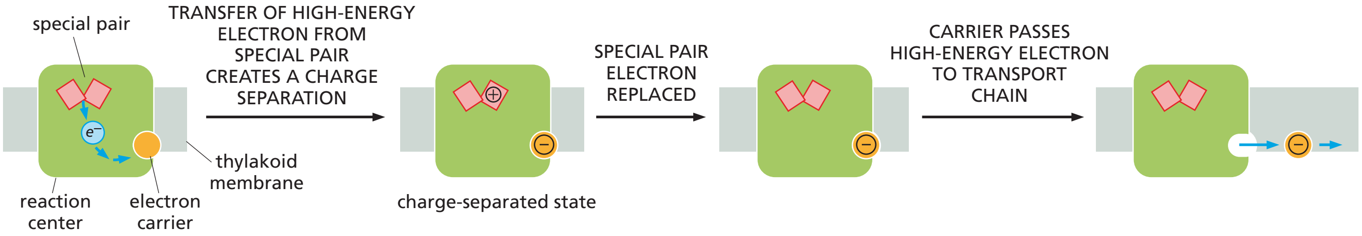
A Pair of Photosystems Cooperate to Generate Both ATP and NADPH

Photosynthesis is ultimately a biosynthetic process, and to build organic molecules from CO_2, a plant cell requires a huge input of energy, in the form of ATP, and a very large amount of reducing power, in the form of the activated carrier NADPH (see Figure 3–34). To generate both ATP and NADPH, plant cells—and free-living photosynthetic organisms such as cyanobacteria—use a pair of photosystems that are similar in structure, but that do different things with the high-energy electrons that leave their reaction center chlorophylls.

When the first photosystem (which, paradoxically, is called photosystem II for historical reasons) absorbs light energy, its reaction center passes electrons to a mobile electron carrier called *plastoquinone*, which is part of the photosynthetic electron-transport chain. This carrier transfers the high-energy electrons to a proton pump, which—like the proton pumps in the mitochondrial inner membrane—uses the movement of electrons to generate an electrochemical proton gradient. The electrochemical proton gradient then drives the production of ATP by an ATP synthase located in the thylakoid membrane (**Figure 14–34**).

At the same time, a second nearby photosystem—called photosystem I—has been also busy capturing the energy from sunlight. The reaction center of this photosystem passes its high-energy electrons to a different mobile electron carrier, which brings them to an enzyme that uses them to reduce $NADP^+$ to NADPH (**Figure 14–35**). The combined action of these

Figure 14–33 In a reaction center, a high-energy electron is transferred from the special pair to a carrier that becomes part of an electron-transport chain. Not shown is a set of intermediary carriers embedded in the reaction center that provide the path from the special pair to this carrier (*orange*). As illustrated, the transfer of the high-energy electron from the excited chlorophyll special pair leaves behind a positive charge that creates a charge-separated state, thereby converting light energy to chemical energy. Once the electron in the special pair has been replaced (an event we will discuss in detail shortly), the carrier diffuses away from the reaction center, transferring the high-energy electron to the transport chain.



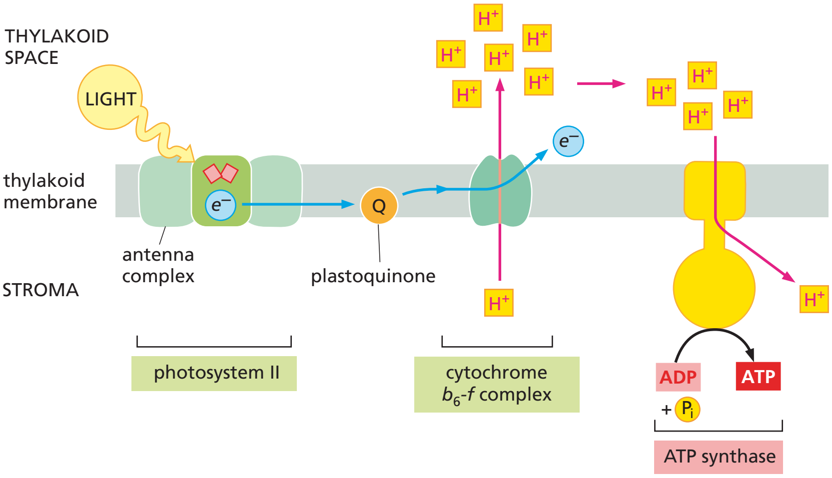


Figure 14–34 Photosystem II feeds electrons to a photosynthetic proton pump, leading to ATP synthesis by ATP synthase. When light energy is captured by photosystem II, a high-energy electron is transferred to a mobile electron carrier called plastoquinone (Q), which closely resembles the ubiquinone of mitochondria. This carrier transfers its electrons to a proton pump called the cytochrome b_6-*f* complex, which resembles the cytochrome *c* reductase complex of mitochondria and is the sole site of active proton pumping in the chloroplast electron-transport chain. As in mitochondria, an ATP synthase embedded in the membrane then uses the energy of the electrochemical proton gradient to produce ATP.

two photosystems thus produces both the ATP (photosystem II) and the NADPH (photosystem I) that will be used in stage 2 of photosynthesis (see Figure 14–29).

QUESTION 14–9

Both NADPH and the related carrier molecule NADH are strong electron donors. Why might plant cells have evolved to rely on NADPH, rather than NADH, to provide the reducing power for photosynthesis?

Oxygen Is Generated by a Water-Splitting Complex Associated with Photosystem II

The scheme that we have thus far described for photosynthesis has ignored a major chemical conundrum. When a mobile electron carrier removes an electron from a reaction center (whether in photosystem I or photosystem II), it leaves behind a positively charged chlorophyll special pair (see Figure 14–33). To reset the system and allow photosynthesis to proceed, this missing electron must be replaced.

For photosystem II, the missing electron is replaced by a special protein complex that removes the electrons from water. This *water-splitting enzyme* contains a cluster of manganese atoms that holds onto two water molecules from which electrons are extracted one at a time. Once four electrons have been removed from these two water molecules—and used to replace the electrons lost by four excited chlorophyll special pairs—O_2 is released (**Figure 14–36**).

This "waiting for four electrons" maneuver ensures that no partly oxidized water molecules are released as dangerous highly reactive chemicals. The same trick is used by the cytochrome *c* oxidase that catalyzes the reverse reaction—the transfer of electrons to O_2 to produce water—during oxidative phosphorylation (see Figure 14–26).

It is astounding to realize that essentially all of the oxygen in the Earth's atmosphere has been produced by the water-splitting enzyme of photosystem II.

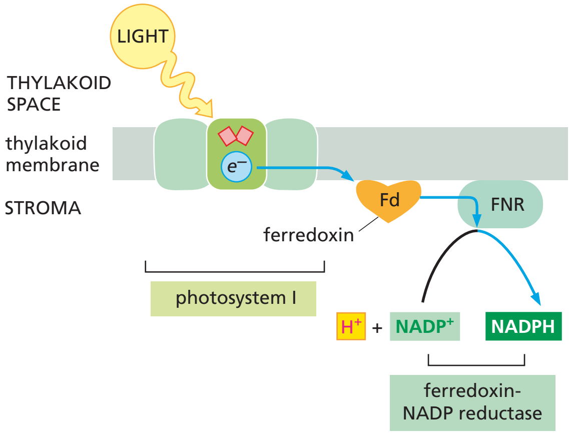


Figure 14–35 Photosystem I transfers high-energy electrons to an enzyme that produces NADPH. When light energy is captured by photosystem I, a high-energy electron is passed to a mobile electron carrier called ferredoxin (Fd), a small protein that contains an iron–sulfur center. Ferredoxin carries its electrons to ferredoxin-NADP reductase (FNR), the final protein in the electron-transport chain that generates NADPH.

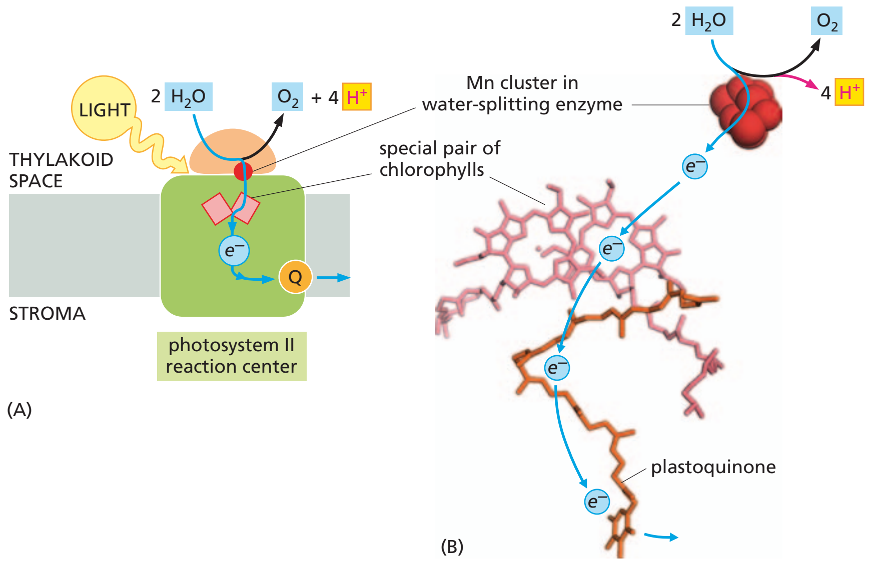


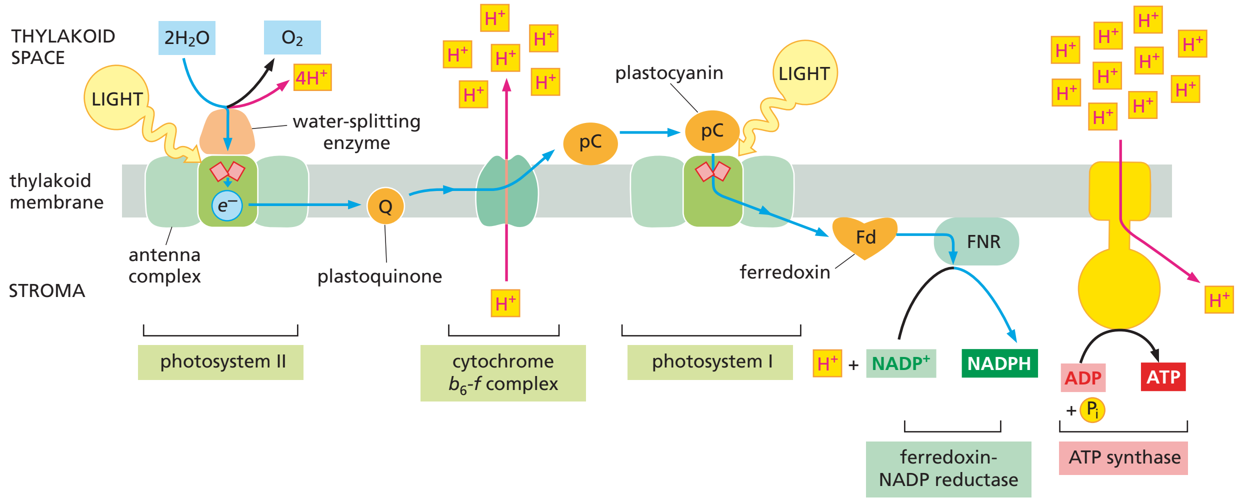
Figure 14–36 The reaction center of photosystem II includes an enzyme that catalyzes the extraction of electrons from water. (A) Schematic diagram shows the flow of electrons through the reaction center of photosystem II. When light energy excites the chlorophyll special pair, an electron is passed to the mobile electron carrier plastoquinone (Q). An electron is then returned to the special pair by a water-splitting enzyme that extracts electrons from water. The Mn cluster that participates in the electron extraction is shown as a *red spot*. Once four electrons have been withdrawn from two water molecules, O_2 is released into the atmosphere. (B) The structure and position of some of the electron carriers involved.

The Special Pair in Photosystem I Receives its Electrons from Photosystem II

We have seen that photosystem II receives electrons from water. But where does photosystem I get the electrons it needs to reset its special pair? It gets them from photosystem II: the chlorophyll special pair in photosystem I serves as the final electron acceptor for the electron-transport chain that carries electrons from photosystem II. The overall flow of electrons is shown in **Figure 14–37**. Electrons removed from water by photosystem II are passed, through a proton pump (the cytochrome b_6-f complex), to a mobile electron carrier called plastocyanin. Plastocyanin then carries these electrons to photosystem I, to replace the electrons lost by its excited chlorophyll special pair. When light is again absorbed by this photosystem, this electron will be boosted to the very high-energy level needed to reduce $NADP^+$ to NADPH.

Having these two photosystems operating in tandem effectively couples their two electron-energizing steps. This extra boost of energy—provided by the light harvested by both photosystems—allows an electron to be moved from water, which normally holds onto its electrons very tightly (redox potential = +820 mV), to NADPH, which normally holds onto its electrons loosely (redox potential = –320 mV). There is even enough energy left over to enable the electron-transport chain that links the two photosystems to pump H^+ across the thylakoid membrane, so that ATP

Figure 14–37 The movement of electrons along the photosynthetic electron-transport chain powers the production of both ATP and NADPH. Electrons are supplied to photosystem II by a water-splitting complex that extracts four electrons from two molecules of water, producing O_2 as a by-product. After their energy is raised by the absorption of light, these electrons power the pumping of protons by the cytochrome b_6-f complex. Electrons that pass through this complex are then donated to a copper-containing protein, the mobile electron carrier plastocyanin (pC), which ferries them to the reaction center of photosystem I. After an additional energy boost from light, these electrons are used to generate NADPH. An overview of these reactions is shown in Movie 14.7.



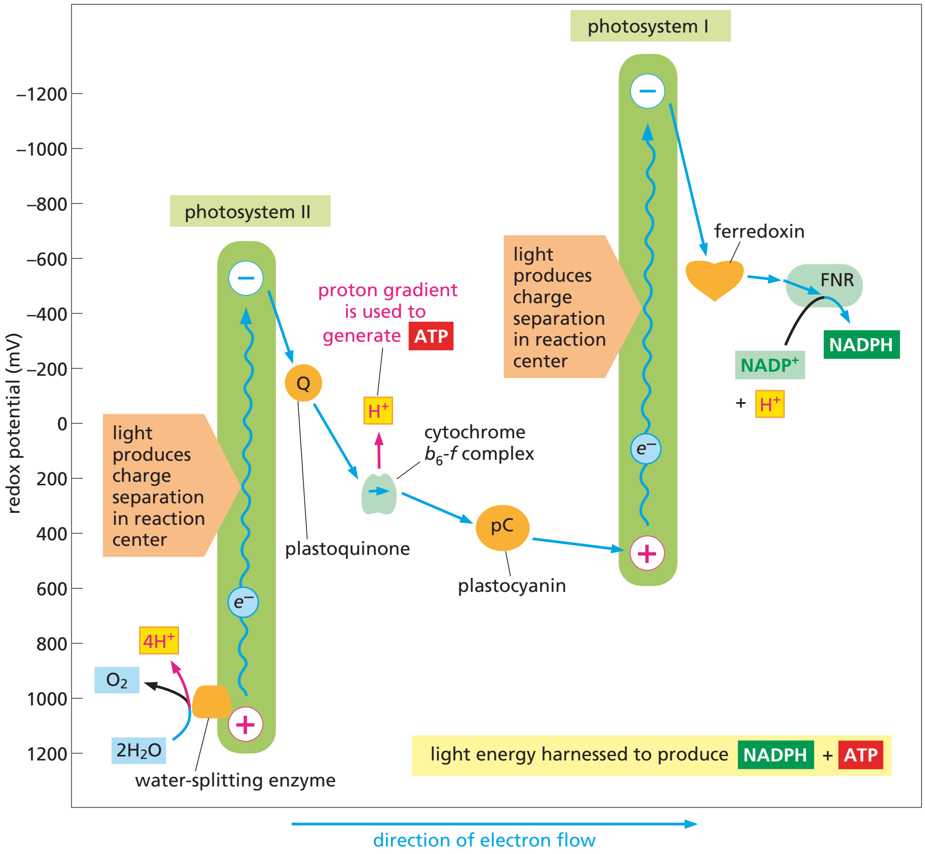


Figure 14–38 The combined actions of photosystems I and II boost electrons to the energy level needed to produce both ATP and NADPH. The redox potential for each molecule is indicated by its position on the vertical axis. Electron transfers are shown with non-wavy *blue arrows*. Photosystem II passes electrons from its excited chlorophyll special pair to an electron-transport chain in the thylakoid membrane that leads to photosystem I (see Figure 14–37). The net electron flow through the two photosystems linked in series is from water to $NADP^+$, to form NADPH.

synthase can harness some of the light-derived energy for ATP production (**Figure 14–38**).

Carbon Fixation Uses ATP and NADPH to Convert CO_2 into Sugars

The light reactions of photosynthesis generate ATP and NADPH in the chloroplast stroma, as we have just seen. But the inner membrane of the chloroplast is impermeable to both of these compounds, which means that they cannot be exported directly to the cytosol. To provide energy and reducing power for the rest of the cell, the ATP and NADPH are instead used within the chloroplast stroma to produce sugars, which can be exported by specific carrier proteins in the chloroplast inner membrane. This production of sugar from CO_2 and water, which occurs during the dark reactions (stage 2) of photosynthesis, is called **carbon fixation**.

In the central reaction of photosynthetic carbon fixation, CO_2 from the atmosphere is attached to a five-carbon sugar derivative, ribulose 1,5-bisphosphate, to yield two molecules of the three-carbon compound *3-phosphoglycerate*. This carbon-fixing reaction, which was discovered in 1948, is catalyzed in the chloroplast stroma by a large enzyme called ribulose bisphosphate carboxylase or *Rubisco* (**Figure 14–39**). Rubisco works much more slowly than most other enzymes: it processes about three molecules of substrate per second—compared with 1000 molecules per second for a typical enzyme. To compensate for this sluggish behavior, plants maintain a surplus of Rubisco to ensure the efficient production of sugars. The enzyme often represents more than 50% of the total chloroplast protein, and it is widely claimed to be the most abundant protein on Earth.

Although the production of carbohydrates from CO_2 and H_2O is energetically unfavorable, the fixation of CO_2 catalyzed by Rubisco is an

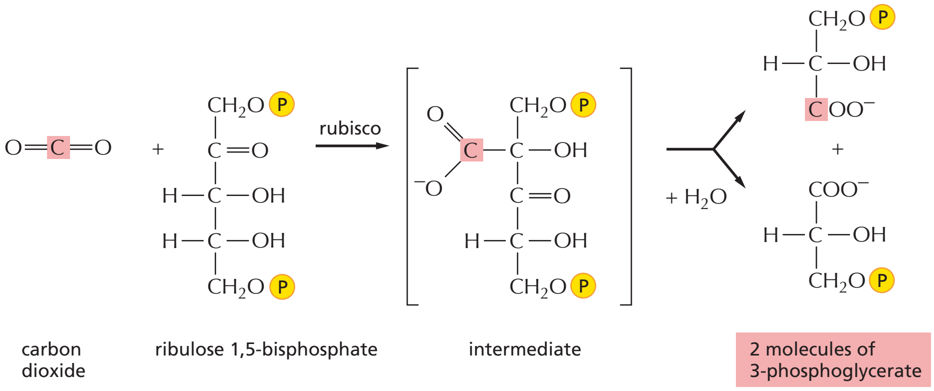


Figure 14–39 Carbon fixation involves the formation of a covalent bond that attaches carbon dioxide to ribulose 1,5-bisphosphate. The reaction is catalyzed in the chloroplast stroma by the abundant enzyme ribulose bisphosphate carboxylase, or Rubisco. As shown, the product is two molecules of 3-phosphoglycerate.

energetically favorable reaction. Carbon fixation is energetically favorable because a continuous supply of the energy-rich ribulose 1,5-bisphosphate is fed into it. As this compound is consumed—by the addition of CO_2 (see Figure 14–39)—it must be replenished. The energy and reducing power needed to regenerate ribulose 1,5-bisphosphate come from the ATP and NADPH produced by the photosynthetic light reactions.

The elaborate series of reactions in which CO_2 combines with ribulose 1,5-bisphosphate to produce a simple sugar—a portion of which is used to regenerate ribulose 1,5-bisphosphate—forms a cycle, called the *carbon-fixation cycle*, or the Calvin cycle (**Figure 14–40**). For every three

QUESTION 14–10

A. How do cells in plant roots survive, since they contain no chloroplasts and are not exposed to light?

B. Unlike mitochondria, chloroplasts do not have a transporter that allows them to export ATP to the cytosol. How, then, do plant cells obtain the ATP that they need to carry out energy-requiring metabolic reactions in the cytosol?

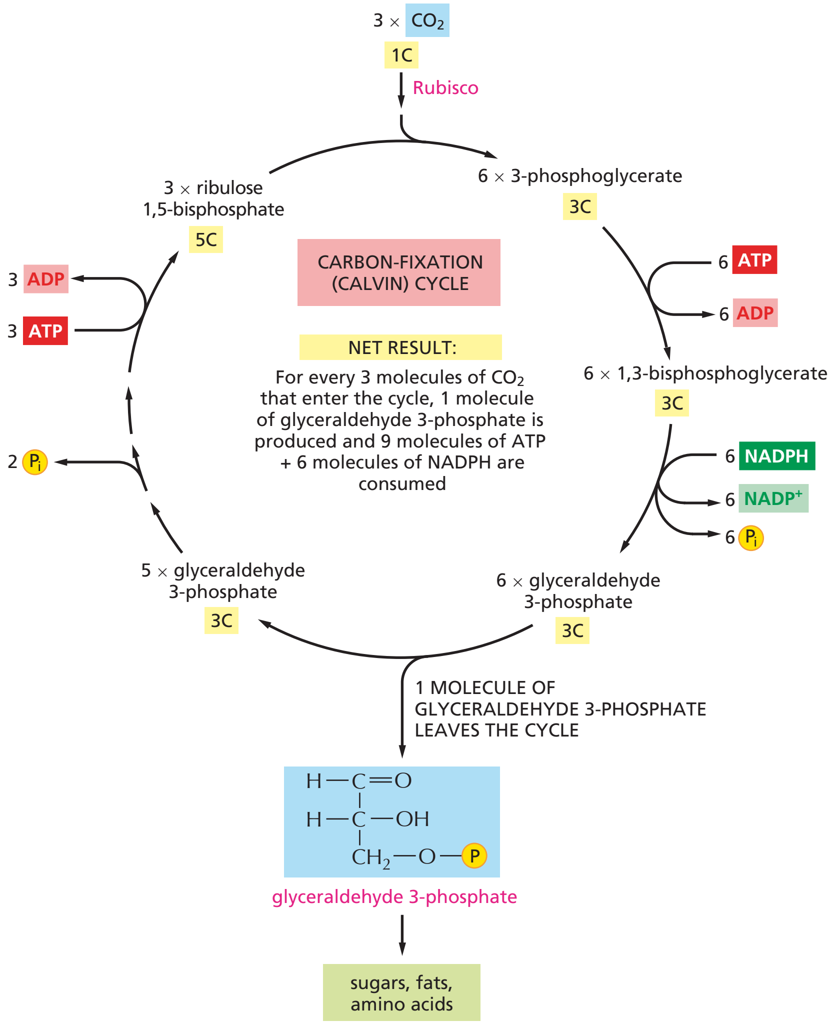


Figure 14–40 The carbon-fixation cycle consumes ATP and NADPH to form glyceraldehyde 3-phosphate from CO_2 and H_2O. In the first stage of the cycle, CO_2 is added to ribulose 1,5-bisphosphate (as shown in Figure 14–39). In the second stage, ATP and NADPH are consumed to produce glyceraldehyde 3-phosphate. In the final stage, some of the glyceraldehyde 3-phosphate produced is used to regenerate ribulose 1,5-bisphosphate; the rest is transported out of the chloroplast stroma into the cytosol. The number of carbon atoms in each type of molecule is indicated in *yellow*. There are many intermediates between glyceraldehyde 3-phosphate and ribulose 5-phosphate, but they have been omitted here for clarity. The entry of water into the cycle is also not shown.

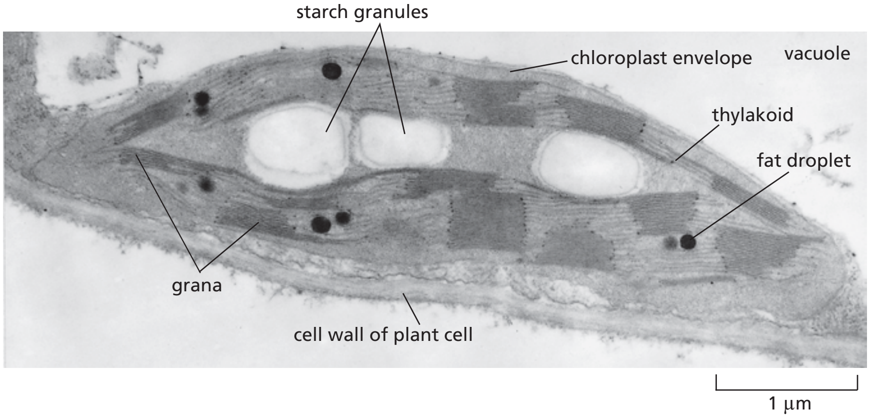


Figure 14–41 Chloroplasts often contain large stores of carbohydrates and fatty acids. A thin section of a single chloroplast shows the chloroplast envelope, starch granules, and fat droplets that have accumulated in the stroma as a result of the biosynthetic processes that occur there.

molecules of CO_2 that enter the cycle, one molecule of glyceraldehyde 3-phosphate is produced, and nine molecules of ATP and six molecules of NADPH are consumed. *Glyceraldehyde 3-phosphate*, the three-carbon sugar that is the final product of the cycle, then provides the starting material for the synthesis of many other sugars and other organic molecules.

Sugars Generated by Carbon Fixation Can Be Stored As Starch or Consumed to Produce ATP

The glyceraldehyde 3-phosphate generated by carbon fixation in the chloroplast stroma can be used in a number of ways, depending on the needs of the plant. During periods of excess photosynthetic activity, much of it is retained in the chloroplast stroma and converted to *starch*. Like glycogen in animal cells, starch is a large polymer of glucose that serves as a carbohydrate reserve, and it is stored as large granules in the chloroplast stroma. Starch forms an important part of the diet of all animals that eat plants. Other glyceraldehyde 3-phosphate molecules are converted to fat in the stroma. This material, which accumulates as fat droplets, likewise serves as an energy reserve (**Figure 14–41**).

At night, this stored starch and fat can be broken down to sugars and fatty acids, which are exported to the cytosol to help support the metabolic needs of the plant. Some of the exported sugar enters the glycolytic pathway (see Figure 13–5), where it is converted to pyruvate. That pyruvate, along with the fatty acids, can enter the plant cell mitochondria and be fed into the citric acid cycle, ultimately leading to the production of ATP by oxidative phosphorylation (**Figure 14–42**). Plants use this ATP in the same way that animal cells and other nonphotosynthetic organisms do to power a variety of metabolic reactions.

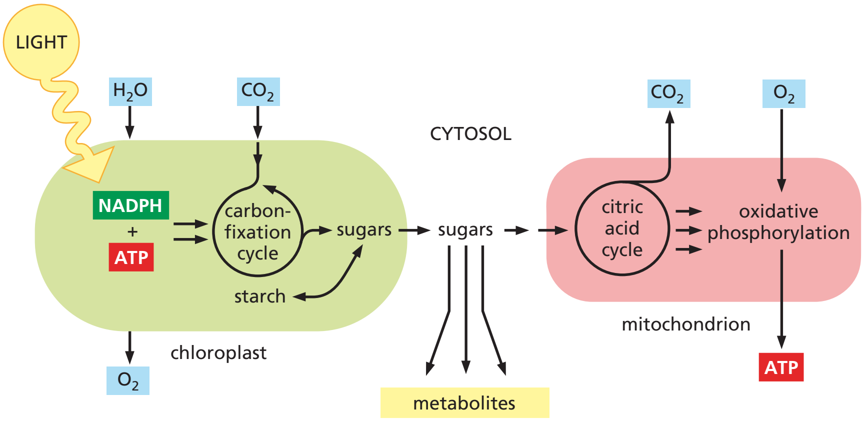


Figure 14–42 In plants, the chloroplasts and mitochondria collaborate to supply cells with metabolites and ATP. The chloroplast's inner membrane is impermeable to the ATP and NADPH that are produced in the stroma during the light reactions of photosynthesis. These molecules are therefore funneled into the carbon-fixation cycle, where they are used to make sugars. The resulting sugars and their metabolites are either stored within the chloroplast—in the form of starch or fat—or exported to the rest of the plant cell. There, they can enter the energy-generating pathway that ends in ATP synthesis in the mitochondria. Mitochondrial membranes are permeable to ATP, as indicated. Note that the O_2 released to the atmosphere by photosynthesis in chloroplasts is used for oxidative phosphorylation in mitochondria; similarly, the CO_2 released by the citric acid cycle in mitochondria is used for carbon fixation in chloroplasts.