Chapter 18   Photosynthesis

In the preceding chapters, you learned that free energy is derived from reduced foodstuffs such as glucose and that the energy produced from catabolic pathways is used to generate both ATP and NAD(P)H. Photosynthesis, an ancient and important process, allows energy to be harvested directly form the most abundant and renewable source, the sun. Photosynthesis is a light-driven process in which carbon dioxide is "fixed" to produce carbohydrates. This occurs in two phases: (1) The light reactions (requiring light) produce ATP and NADPH, and (2) the dark reactions (not requiring light) use ATP and NADPH to synthesize carbohydrates. This chapter describes how different pigments (e.g., chlorophylls in plants and bacteria) efficiently capture light energy and redistribute it to specific reaction centers. Purple photosynthetic bacteria contain one photosystem that recycles its electrons, whereas higher plants have two photosystems that use water as a source of electrons to reduce NADPH. The oxidation of water in higher plants generates O_2 as a by-product of photosynthesis. As in mitochondria, the topology of chloroplasts is central to the biochemistry of photosynthesis, starting with the light-driven reactions in the thylakoid membrane and finishing with the dark reactions in the stroma. The dark reactions occur via the Calvin cycle, a set of reactions that synthesize glyceraldehyde-3-phosphate from 3 CO_2. The chapter also discusses the control of the Calvin cycle along with a variant called the C_4 pathway.

Essential Concepts

1. Photosynthesis is divided into two processes:
    (a) In the light reactions, organisms capture light energy to synthesize ATP and generate reducing equivalents in the form of NADPH.
    (b) In the dark reactions, carbon dioxide is converted to carbohydrates using the ATP and NADPH generated in the light reactions. Although the dark reactions are not light-driven, they only occur when it is light and hence are better described as light-independent.

Chloroplasts

2. Plants differ from bacteria by providing a separate organelle for the photosynthetic machinery, the chloroplast. A chloroplast is enveloped by a highly permeable outer membrane and a nearly impermeable inner membrane. The inner membrane encloses the stroma, which contains the soluble enzymes of carbohydrate synthesis, and the thylakoid membrane, which is organized in stacks of pancake-like disks (grana) that enclose the thylakoid compartment and that are linked by unstacked stromal lamellae. The proteins that capture light energy and mediate electron-transport processes are embedded in the thylakoid membrane.

3. Various pigment molecules absorb light of different wavelengths. The principal photosynthetic pigment is chlorophyll, a cyclic tetrapyrrole that ligands a central Mg^{2+} ion. Photosynthetic organisms also contain other pigments, such as carotenoids, phycoerythrin,

and phycocyanin, which together with chlorophyll absorb most of the visible light in the solar spectrum.

4. Multiple pigment molecules are arranged in light-harvesting complexes (LHCs), which are proteins that act as antennae to gather light energy and redirect it to photosynthetic reaction centers, where the light energy is converted to chemical energy in the form of ATP and NADPH. The accessory pigments in the LHCs boost light absorption at wavelengths at which chlorophyll does not absorb strongly.

The Light Reactions

5. Photons propagate as discrete energy packets called quanta, whose energy, E, is given by Planck's law: $E = hv = hc/\lambda$, where h is Planck's constant (6.626×10^{-34} J·s) c is the speed of light (2.998×10^8 m·s^{-1}), λ is the wavelength of light, and v is the frequency of the radiation.

6. When a molecule absorbs a photon, one of its electrons is promoted to a higher energy orbital. The excited electron can return to the ground state in several ways:
   (a) In internal conversion, electronic energy is converted to kinetic energy (heat).
   (b) Fluorescence results when the molecule emits a photon at a lower wavelength.
   (c) The excitation energy can be transferred to another molecule by exciton transfer (resonance energy transfer). This occurs in the transfer of light energy from LHCs to the photosynthetic reaction center.
   (d) The molecule may undergo photooxidation by transfer of an electron to another molecule. The excited chlorophyll at the reaction center transfers electrons in this manner.

7. The bacterial photosynthetic reaction center of *Rps. viridis* consists of a series of prosthetic groups arranged with nearly twofold symmetry: 2 closely associated bacteriochlorophyll *a* (BChl *a*) molecules known as the special pair, 2 bacteriopheophytin *a* (BPheo *a*; BChl *a* that lacks an Mg^{2+} ion), 2 additional BChl *a* molecules, a menaquinone, a ubiquinone, and an Fe(II) ion.

8. In purple photosynthetic bacteria, the special pair undergoes photooxidation virtually every time it absorbs a photon. The transferred electron is first passed to the BPheo *a* on the "right" side of the photosynthetic reaction center and then to the menaquinone and then the ubiquinone to yield a semiquinone radical anion (Q_B^-). A second photon absorption then transfers a second electron to yield Q_B^{2-}, which picks up two protons from the cytoplasm to form QH$_2$ and then exchanges with the membrane-bound pool of ubiquinone.

9. The electrons ejected from the special pair return to the photosynthetic reaction center via an electron-transport chain consisting of a cytochrome bc_1 complex and cytochrome c_2. Electrons flow follows a Q cycle in cytochrome bc_1, which translocates four protons to the periplasmic space for every two electrons transferred. The free energy of the resulting transmembrane proton gradient drives ATP synthesis.

10. In plants and cyanobacteria, photooxidation occurs at two reaction centers, and electron transport is noncyclical. The path of electrons from water to NADPH is described by the Z-scheme, in which photosystem II (PSII) passes its electrons to the cytochrome b_6f complex via the mobile electron carrier ubiquinol (QH_2), and cytochrome b_6f then transfers these electrons to photosystem I (PSI) via the mobile Cu-containing protein plastocyanin. Since PSII and PSI are thereby "connected in series," the energy of each electron is boosted by two photon absorptions.

11. PSII includes the Mn-containing oxygen-evolving center (OEC), which cycles through five electronic states (S_0–S_4) in the conversion of H_2O to O_2 and is driven by four consecutive excitations of the PSII reaction center (called P680). The four electrons released from H_2O follow a path similar to that of the bacterial photosynthetic reaction center, eventually reaching the membrane plastoquinone pool.

12. Electron transport through the cytochrome b_6f complex (which resembles the mitochondrial Complex III) generates a transmembrane proton gradient via a Q cycle. Eight protons are translocated to the thylakoid lumen for the four electrons released from each H_2O. Plastocyanin, a peripheral membrane protein, has a Cu redox center than ferries one electron at a time from cytochrome b_6f to PSI.

13. PSI contains multiple pigments and redox groups, including chlorophylls, carotenoids, [4Fe–4S] clusters, and phylloquinone. Photooxidation of the PSI special pair (called P700) allows the electron received from plastocyanin to pass through a series a electron carriers in one of two routes:
    (a) In the noncyclic pathway, electrons flow through PSI to the [2Fe–2S]-containing one-electron carrier ferredoxin (Fd), which is a soluble stromal protein. Two Fd's deliver their electrons to ferredoxin–$NADP^+$ reductase, which thereupon carries out the two-electron reduction of $NADP^+$ to NADPH.
    (b) In the cyclic pathway, electrons return from PSI through cytochrome b_6f to the plastoquinone pool and thereby participate in the Q cycle. This pathway augments the proton gradient across the thylakoid membrane and hence contributes additional free energy for the synthesis of ATP but does not yield NADPH.

14. The free energy of the proton gradient is tapped by chloroplast CF_1CF_0 ATP synthase, which closely resembles the mitochondrial F_1F_0-ATPase. Approximately 12 protons enter the thylakoid lumen for each O_2 generated in noncyclic electron transport (4 H^+ from the OEC reaction and 8 H^+ from the Q cycle). The synthesis of ATP requires the transport of ~3 protons from the thylakoid lumen to the stroma.

The Dark Reactions

15. CO_2 is incorporated into carbohydrates by carboxylation of a 5-carbon sugar, ribulose-5-phosphate (R5P). The resulting 6-carbon compound is split into two molecules of 3-phosphoglycerate (3PG), which is then converted to glyceraldehyde-3-phosphate (GAP). Some of the GAP is diverted to carbohydrate synthesis, and the rest is converted back to Ru5P. This set of 13 reactions, called the Calvin cycle, has two stages:

(a) In the production phase, 3 Ru5P react with 3 CO_2 to yield 6 GAP (for a net yield of 1 GAP from 3 CO_2), at a cost of 9 ATP and 6 NADPH.

(b) In the recovery phase, the carbons of 5 GAP are shuffled via aldolase- and transketolase-catalyzed reactions to reform 3 Ru5P, without consuming ATP or NADPH.

The GAP product of the cycle is then converted to glucose-1-phosphate, a precursor of sucrose and starch.

16. Ribulose bisphosphate carboxylase, which accounts for up to 50% of leaf proteins, catalyzes the carboxylation of ribulose-1,5-bisphosphate (RuBP). Enzymatic abstraction of a proton from RuBP generates an enediolate that attacks CO_2. H_2O then attacks the resulting β-keto acid to yield two 3PG.

17. The activity of RuBP carboxylase is controlled in several ways so that the dark reactions proceed only when the light reactions are able to provide the ATP and NADPH necessary to drive them:

(a) RuBP carboxylase is most active at pH 8.0, which occurs when protons are pumped out of the stroma during the light reactions.

(b) The Mg^{2+} that enters the stroma to compensate for the efflux of H^+ stimulates RuBP carboxylase.

(c) Plants synthesize 2-carboxyarabinitol-1-phosphate, an inhibitor of RuBP carboxylase, only in the dark.

18. The Calvin cycle enzymes fructose bisphosphatase and sedoheptulose bisphosphatase are also activated by increases in pH, $[Mg^{2+}]$, and [NADPH]. The redox state of ferredoxin is sensed by a thiol-exchange cascade involving ferredoxin–thioredoxin reductase, thioredoxin, and disulfide groups on the bisphosphatases, so that the Calvin cycle enzymes are stimulated when Fd is reduced (i.e., when the light reactions are occurring).

19. RuBP carboxylase can also react with oxygen, which competes with CO_2 at the carboxylase active site. This process, called photorespiration, converts RuBP into 3PG and 2-phosphoglycolate, a two-carbon compound. A series of reactions in the chloroplast and peroxisome convert two 2-phosphoglycolate to two glycine, which are converted in the mitochondria to serine + CO_2. The serine is converted back to the Calvin cycle intermediate 3PG by reactions that require NADH and ATP. Thus, photorespiration consumes O_2 and produces CO_2, at the expense of ATP and NADH, thereby reversing the results of photosynthesis. All known RuBP carboxylases have this activity, which may protect chloroplasts from photoinactivation when high light intensity has greatly reduced the local CO_2 concentration..

20. The rate of photorespiration becomes significant on hot bright days when photosynthesis has depleted the level of CO_2 at the chloroplast and raised the concentration of O_2. However, C_4 plants such as corn and sugar cane prevent photorespiration by concentrating CO_2 at the chloroplast. They do so by using phosphoenolpyruvate (PEP) carboxylase to make oxaloacetate. Oxaloacetate is converted to malate in the mesophyll cells (which lack RuBP carboxylase) and transported to the bundle-sheath cells, where the Calvin cycle operates. There, malic enzyme cleaves malate into pyruvate and CO_2. The CO_2 is thereby delivered to

RuBP carboxylase at a high enough concentration to essentially eliminate photorespiration. The pyruvate is transported back to the mesophyll cells and converted to PEP at the expense of two "high-energy" bonds. In the tropics, C_4 plants grow faster than so-called C_3 plants. In more temperate climates, where the rate of photorespiration is reduced, C_3 plants have an advantage because they require less energy to fix CO_2.

21. Many desert succulent plants conserve water by opening their stomata only at night to acquire CO_2. The CO_2 is converted to PEP at night and is released as CO_2 in the day, to be fixed by RuBP carboxylase. This process is called Crassulacean acid metabolism (CAM) because it was discovered in the family Crassulaceae.

Key equation

$$E = h\nu = \frac{hc}{\lambda}$$

Guide to Study Exercises (text p. 560)

1. The light reactions and dark reactions are the two stages of photosynthesis. In the light reactions, specialized pigment molecules capture light energy and are thereby photooxidized. The transfer of their electrons through a series of electron carriers results in the reduction of $NADP^+$ to NADPH and the generation of a transmembrane proton concentration gradient whose free energy is harnessed by CF_1CF_0-ATPase to phosphorylate ADP. In the dark reactions, the NADPH and ATP produced in the light reactions are used to reduce CO_2 and incorporate it into carbohydrates. The light reactions occur only in the presence of light energy. In contrast, the dark reactions do not strictly require light, but they are regulated so that they proceed when the light reactions are active and hence producing the NADPH and ATP required for the dark reactions. (Chapter introduction and Section 18-3B)

2. Light-harvesting complexes (LHCs) are complexes of pigment molecules that function as light-absorbing antennae that gather the energy of photons and pass it to a photosynthetic reaction center. LHCs are transmembrane proteins that typically contain a variety of pigment molecules whose number and arrangement have been optimized for efficient light absorption and energy transfer. Without the LHCs, the photosynthetic reaction centers would intercept too few photons to support life. (Section 18-1B)

3. A molecule that has absorbed light energy becomes electronically excited. This energy can be dissipated by the following processes:
   (a) Internal conversion, which is the conversion of electronic energy to kinetic energy (heat).
   (b) Fluorescence, which is the emission of a photon whose energy is lower (of longer wavelength) than that of the photon absorbed by the molecule.
   (c) Exciton transfer (resonance energy transfer),which is the transfer of absorbed energy to an unexcited molecule with similar electronic properties.

(d) Photooxidation, which occurs when an electron held by the excited molecule is transferred to another molecule. (Section 18-2A)

4. The purple bacterial reaction center is a transmembrane protein containing 4 bacteriochlorophyll (BChl), 2 bacteriopheophytin (BPheo), a Fe(II) ion, and 2 ubiquinone (or a ubiquinone and a menaquinone). When the so-called special pair of BChl absorbs a photon, it becomes energized (has a more negative reduction potential) and transfers an electron to a BPheo group on its "right" side, possibly via the intervening accessory BChl. The electron then migrates to the adjacent quinone and then to the other quinone. Another such electron transfer, resulting from the absorption of a second photon, is required to completely reduce the terminal quinone acceptor to a quinol. The electrons lost by the special pair are returned to it via a series of electron transfers involving membrane-bound ubiquinol, a cytochrome bc_1 complex, and cytochrome c_2. Electron flow through the cytochrome bc_1 complex follows the Q cycle pathway, which transfers the two electrons from ubiquinol to two molecules of cytochrome c_2, each of which returns an electron to the special pair. The overall pathway of electron transfer is cyclic, with no net oxidation or reduction of its components. (Section 18-2B)

5. The Z-scheme describes the noncyclic path of electrons through the photosynthetic machinery of green plants and cyanobacteria. The zig-zag appearance of the Z-scheme on a reduction potential diagram reflects the shifts in reduction potential that occur when its two photosynthetic reaction centers absorb light energy. Overall, electrons flow from groups with lower reduction potentials to groups with higher reduction potentials, so that the net result of the pathway is the reduction of $NADP^+$ by electrons derived from H_2O. The Z-scheme links three membrane-bound protein complexes with mobile electron carriers. The oxygen-evolving complex (OEC) of photosystem II (PSII) catalyzes the conversion of 2 H_2O to $O_2 + 4\ H^+$ in a catalytic cycle driven by the excitation of the PSII reaction center. The four electrons released from H_2O are transferred by the excited reaction center through the redox groups of PSII to a membrane-bound pool of plastoquinone. From there, electrons pass to the cytochrome b_6f complex, where they follow a cyclic pathway (the Q cycle) that results in the reduction of the mobile electron carrier plastocyanin. This peripheral membrane protein shuttles one electron at a time to the reaction center of photosystem I (PSI). The absorption of a photon decreases the reduction potential of the PSI reaction center so that it can transfer the electron through a series of redox groups. The electron eventually reaches the soluble one-electron carrier ferredoxin. Two reduced ferredoxin proteins carry their electrons to the stromal enzyme ferredoxin–$NADP^+$ reductase, which carries out the two-electron reduction of $NADP^+$. (Section 18-2C)

6. Noncyclic electron transport in PSI results in the net transfer of electrons to ferredoxin and then to $NADP^+$. In cyclic electron flow, electrons ejected from PSI return to the cytochrome b_6f complex, where they participate in the Q cycle. This results in the translocation of two protons from the stroma to the thylakoid lumen for each electron. Therefore, cyclic electron flow augments the transmembrane proton concentration gradient and results in the synthesis of more ATP. The balance between cyclic and noncyclic electron transfer determines the relative amounts of NADPH and ATP produced by the light reactions. (Section 18-2C)

7. In both photophosphorylation and oxidative phosphorylation, the free energy of a transmembrane proton concentration gradient drives the synthesis of ATP from ADP + P_i as catalyzed by a membrane protein consisting of a pseudo-threefold symmetric ATP synthase in complex with a transmembrane proton channel. In both cases, ATP synthesis requires an intact membrane and can be uncoupled from electron transport by agents that dissipate the proton gradient.

    Photophosphorylation differs from oxidative phosphorylation in that the proton gradient involves the chloroplast stroma (which is analogous to the mitochondrial matrix) and the thylakoid space, which is not in contact with the cytoplasm (as is the mitochondrial intermembrane space). Another difference is that the thylakoid membrane is permeable to Mg^{2+} and Cl^- so that the membrane potential ($\Delta\Psi$) does not contribute significantly to the electrochemical gradient in the chloroplast. Finally, the stoichiometry of ATP molecules synthesized per electron transferred is relatively constant in mitochondria, but it varies in chloroplasts depending on the proportion of cyclic to noncyclic electron flow. (Section 18-2D)

8. In the first stage of the Calvin cycle, three molecules of ribulose-5-phosphate (Ru5P) react with three CO_2 to yield six molecules of glyceraldehyde-3-phosphate (GAP) at the expense of 9 ATP and 6 NADPH. This process is equivalent to the conversion of 3 CO_2 to 1 GAP.

    In the second stage of the Calvin cycle, the carbon skeletons of 5 GAP are rearranged to yield 3 Ru5P. The reactions in this stage, most of which are reversible, do not require ATP or NADPH. (Section 18-3A)

9. Photosynthesis is regulated so that the dark reactions occur only when the free energy they require (in the form of ATP and NADPH) is available from the light reactions. This is accomplished through several mechanisms:

    (a) Ribulose bisphosphate (RuBP) carboxylase activity increases in response to light by the increase in stromal pH and the influx of Mg^{2+} ions that occur when protons are pumped across the thylakoid membrane. The increase in pH and [Mg^{2+}] also activates the Calvin cycle enzymes FBPase and SBPase.

    (b) Plants synthesize 2-carboxyarabinitol-1-phosphate (CA1P), which inhibits RuBP carboxylase, only in the dark.

    (c) The productivity of the light reactions, represented by the redox state of ferredoxin, is communicated to thioredoxin. This small protein activates FBPase and SBPase by a disulfide interchange reaction. (Section 18-3B)

10. Photorespiration, a pathway that consumes NADH and ATP, may occur when there is insufficient CO_2. So-called C_4 plants minimize photorespiration by a mechanism that increases the availability of CO_2 at the chloroplast. These plants take up CO_2 in mesophyll cells (which lack RuBP carboxylase) by condensing it with phosphoenolpyruvate to yield the C_4 compound oxaloacetate. The oxaloacetate is reduced to malate, which enters the bundle-sheath cells (which contain RuBP carboxylase) and is decarboxylated to produce pyruvate and CO_2 at a higher concentration than that directly available from the atmosphere.

Questions

1. Define the terms light reactions and dark reactions. Do the dark reactions occur in the dark? Explain.

Chloroplasts

2. Draw a cross-section of a chloroplast and indicate the locations of the following proteins and other structural features:

   Outer membrane   Thylakoid lumen
   Stromal lamella   Photosystem I
   Inner membrane   Photosystem II
   Intermembrane space   Cytochrome b_6f
   Grana CF_1CF_0-ATP synthase
   Stroma   Direction of proton pumping

The Light Reactions

3. Calculate the energy of a mole of photons with wavelengths of (a) 400 nm, (b) 500 nm, (c) 600 nm, and (d) 700 nm.

4. Purple photosynthetic bacteria have different pigments than higher plants. Why is this an advantage for these bacteria?

5. What distinguishes the chlorophyll in a reaction center from the antennae chlorophyll?

6. The initial electron transfers in the bacterial photosynthetic reaction center are extremely rapid, but the lifetime of the terminal semiquinone is relatively long. (a) Why is it essential for the electrons to quickly leave the vicinity of the special pair? (b) Why does the terminal semiquinone persist?

7. Compare the electron flow in purple photosynthetic bacteria to that in higher plant chloroplasts. What is the origin of the electrons and their eventual fates? How many protons are translocated?

8. What is the standard reduction potential for the oxidation of H_2O (see Table 13-3)? Can this value be obtained from purple bacterial photosynthesis? Compare this to two-center photosynthesis.

9. The number of O_2 molecules released per photon absorbed by a suspension of algae can be measured at different wavelengths. When algae are illuminated by 700 nm light, very little O_2 is produced. However, when they are also illuminated by 500 nm light, the O_2 production is well in excess of that produced with only the 500 nm light. Explain.

10. What is the fate of water-derived electrons in chloroplasts treated with DCMU? What simple screening method could be used to identify plants that had been exposed to DCMU?

11. What do the S states represent in the oxygen-evolving center (OEC)? What S state predominates in dark-adapted chloroplasts?

12. What chloroplast component generates the majority of the proton gradient used for ATP production? Does it have a mitochondrial counterpart?

13. Why does the Cu atom of plastocyanin have an unusually high standard reduction potential?

14. What are the similarities and differences between photosystem I and photosystem II?

15. Estimate the minimum reduction potential for P680. Estimate the maximum reduction potential for ferredoxin. Explain your answers.

16. Describe the distribution of LHCs between grana (stacked membranes) and stromal lamellae (unstacked membranes) in chloroplasts under a bright sun and in shady light.

The Dark Reactions

17. What is the first stable radioactive sugar intermediate seen when $^{14}CO_2$ is added to algae such as *Chlorella*? When the supply of $^{14}CO_2$ is cut off, what compound accumulates? What do these results suggest about the pathway of CO_2 incorporation into carbohydrates?

18. Using Figure 18-20, write out the 13 reactions of the Calvin cycle. What is the main difference between Stage I and Stage II reactions? Write a net equation for each stage.

19. Glycolysis and the Calvin cycle are opposing pathways. Which reactions form a potential futile cycle? How are these reactions controlled in plant chloroplasts?

20. What is photorespiration? What is the ultimate result of this process?

21. The concentration of atmospheric CO_2 has been increasing for many decades. If this trend continues, how might it affect the relative abundance of C_3 and C_4 plants?

Answers to Questions

1. The light reactions depend on light for activity and include the reactions of the photosystems and the electron transport chain. The dark reactions are those of the Calvin cycle, which convert CO_2 to GAP.

    The dark reactions do not require light for their mechanisms. However, the light reactions regulate the dark reactions to ensure that the cell maintains adequate levels of ATP and NADPH. Thus the dark reactions do not actually occur in the dark.

2.
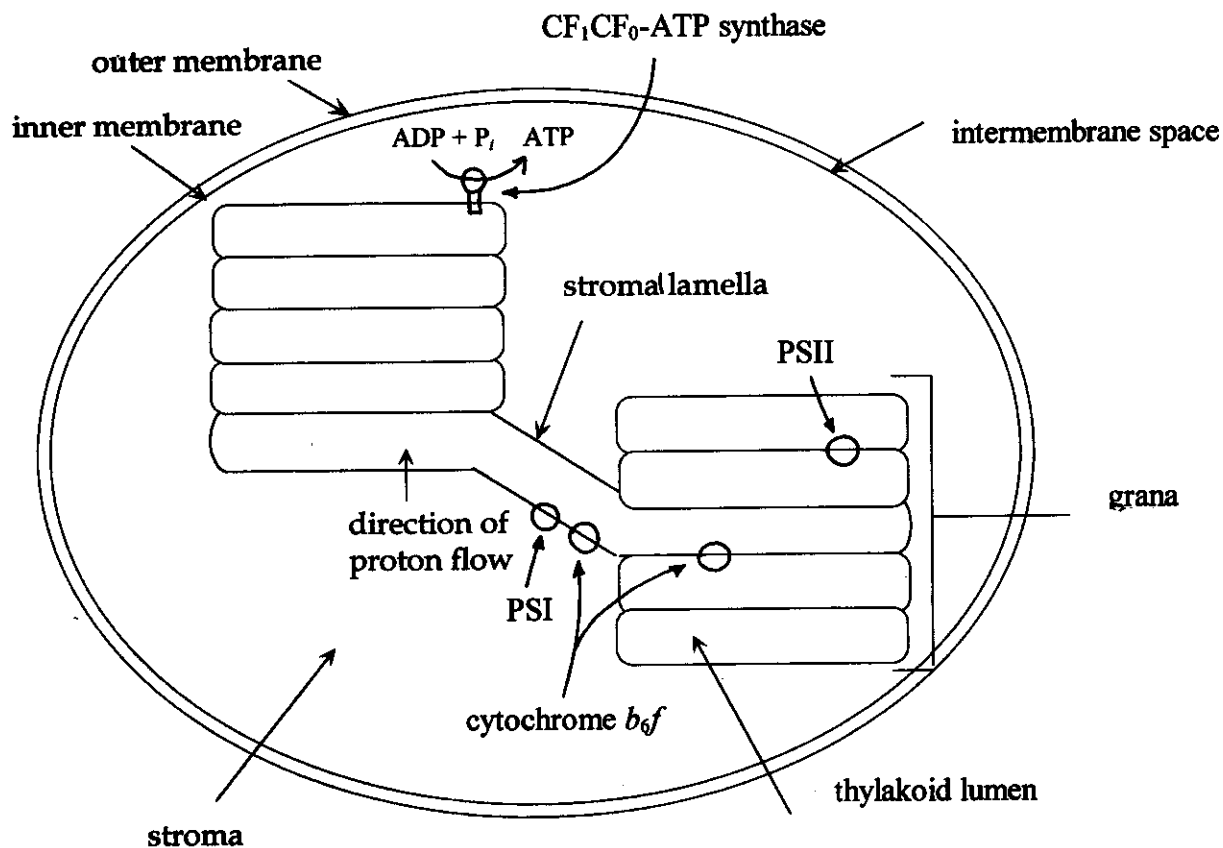
3. Use Planck's law multiplied by Avogadro's number:

$$E = \frac{hc}{\lambda} N$$

$$= (6.626 \times 10^{-34} \text{ J·s}) (2.998 \times 10^8 \text{ m·s}^{-1}) (6.0221 \times 10^{23} \text{ mol}^{-1}) / \lambda$$
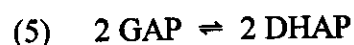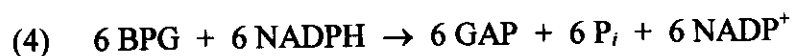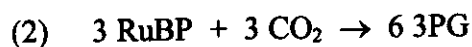$$= (0.1196 \text{ J·m·mol}^{-1}) / \lambda$$

(a) $E = (0.1196 \text{ J·m·mol}^{-1}) / (4 \times 10^{-7} \text{ m}) = 3.0 \times 10^5 \text{ J·mol}^{-1} = 300 \text{ kJ·mol}^{-1}$

(b) $E = (0.1196 \text{ J·m·mol}^{-1}) / (5 \times 10^{-7} \text{ m}) = 2.4 \times 10^5 \text{ J·mol}^{-1} = 240 \text{ kJ·mol}^{-1}$

(c) $E = (0.1196 \text{ J·m·mol}^{-1}) / (6 \times 10^{-7} \text{ m}) = 2.0 \times 10^5 \text{ J·mol}^{-1} = 200 \text{ kJ·mol}^{-1}$

(d) $E = (0.1196 \text{ J·m·mol}^{-1}) / (7 \times 10^{-7} \text{ m}) = 1.7 \times 10^5 \text{ J·mol}^{-1} = 170 \text{ kJ·mol}^{-1}$

4. The pigments in purple photosynthetic bacteria absorb radiation with longer wavelengths than visible light. This is the most intense radiation in the environments that they inhabit, the murky bottoms of stagnant ponds.

5. The chlorophyll molecules in a reaction center have a slightly lower-energy excited state than that of the antenna chlorophyll molecules. This allows excitation energy to be transferred from the antennae molecules to the reaction center, where photooxidation occurs.

6. (a) The electron ejected from the excited special pair must be transferred away so that it cannot return immediately to the special pair, which would allow the excitation energy to be released as heat (or possibly in a way that would damage the reaction center).
    (b) After its reduction by an electron, the quinone (now a semiquinone) must await a second excitation event and electron transfer to become fully reduced to a quinol so that it can transfer both electrons to the membrane-bound quinol pool.

7. Electrons from the bacterial reaction center flow to ubiquinone and then to cytochrome bc_1 and cytochrome c_2 before returning to the special pair. This cyclic electron flow does not yield reduced $NADP^+$, but it translocates four protons per electron pair to the periplasmic space.
    In the chloroplast, electrons flow in a linear fashion (the Z-scheme) from water to $NADP^+$, so that 2 NADPH are produced for every 2 H_2O oxidized to O_2. The 4 electrons pass from PSII to cytochrome b_6f and then to PSI before they reach ferredoxin–$NADP^+$ reductase. This results in the transmembrane movement of 12 protons. In noncyclic electron flow, electrons cycle from PSI back to cytochrome b_6f and hence no NADPH is produced. Instead, this increases the number of protons translocated without affecting the stoichiometry of the $H_2O \rightarrow O_2$ reaction.

8. The standard reduction potential for the reaction $O_2 + 4\,e^- + 4\,H^+ \rightarrow 2\,H_2O$ is 0.815 V. The reduction potential of the P870 bacterial reaction center is ~0.500 V (Figure 18-10), which is not sufficient to oxidize water (electrons spontaneously flow to centers with more positive reduction potentials). The two-reaction center Z-scheme (Figure 18-12) spans a redox range that allows both the oxidation of water and the reduction of $NADP^+$.

9. The longer wavelength activates only PSI (which contains P700), whereas the shorter wavelength activates both PSI and PSII (which contains P680). Since PSII feeds electrons to PSI, both photosystems must operate together for the redox reactions to proceed most efficiently. When only 700 nm light is available, PSII is unable to extract the electrons from H_2O necessary to form O_2. However, in the presence of 700 nm and 500 nm light, PSII can supply electrons to PSI, which can energize them with 700 nm light, thereby driving O_2 production.

10. DCMU blocks electron flow between PSII and PSI. This would cause the excitation energy of PSII to be dissipated by a mechanism other than photooxidation (since the electrons have nowhere to go). Some of the absorbed energy is released as fluorescence. Plants in which electron flow was blocked by DCMU can be detected by their fluorescence.

11. The S states in the OEC are chemical intermediates in the five-step reaction in which H_2O is oxidized to O_2. Dark-adapted chloroplasts are in the S_1 state, since O_2 is generated on the third flash of light (Figure 18-13).

12. The cytochrome b_6f complex, via the Q cycle, pumps the majority of the protons that make up the proton gradient required for ATP synthesis. Eight protons are translocated for every 2 H_2O oxidized; more during cyclic electron flow. The membrane-bound cytochrome b_6f complex resembles mitochondrial Complex III (cytochrome bc_1).

13. The Cu(II)/C(I) half-reaction normally has a redox potential of 0.158 V, but plastocyanin's redox potential is 0.370 V. In the protein, the Cu(II) atom is strained toward the tetrahedral coordination geometry of Cu(I), which promotes its reduction.

14. Both photosystems are membrane-bound protein complexes, contain special pairs of chlorophyll where photooxidation occurs, and have near-symmetrical arrangements of pigment molecules at the reaction center.

    The photosystems differ in overall structure, their redox groups, and the pathway of electron transfer.

15. The reduction potential for P680 should be greater than that of the O_2/H_2O half-reaction (0.815 V; Table 13-3) since electrons flow from H_2O to P680. The standard reduction potential of ferredoxin should be less than that for the $NADP^+/NADPH$ half-reaction (−0.320 V) since electrons flow from ferredoxin to $NADP^+$.

16. Under bright sun (high proportion of short-wavelength light), PSII is more active than PSI. As a result, reduced plastoquinone accumulates. This activates a protein kinase to phosphorylate the LHCs, which then move to the stromal lamellae, where they associate with and funnel more light energy to PSI.

    Under shady light (high proportion of long-wavelength light), PSI is more active than PSII. Oxidized plastoquinone therefore accumulates. This leads to dephosphorylation of the LHCs, which move to the grana to associate with and funnel light energy to PSII.

17. 3-Phosphoglycerate is the first stable sugar that incorporates the $^{14}CO_2$. This suggests that $^{14}CO_2$ is added to a 2-carbon compound. Ribulose-5-phosphate levels increase after the removal of $^{14}CO_2$, which instead suggests that ribulose-5-phosphate is the $^{14}CO_2$ acceptor.

18. Shown below are the 13 reactions of the Calvin cycle:

    (1) $3\,Ru5P\ +\ 3\,ATP\ \rightarrow\ 3\,RuBP\ +\ 3\,ADP$

    (2) $3\,RuBP\ +\ 3\,CO_2\ \rightarrow\ 6\,3PG$

    (3) $6\,3PG\ +\ 6\,ATP\ \rightarrow\ 6\,BPG\ +\ 6\,ADP$

    (4) $6\,BPG\ +\ 6\,NADPH\ \rightarrow\ 6\,GAP\ +\ 6\,P_i\ +\ 6\,NADP^+$

    (5) $2\,GAP\ \rightleftharpoons\ 2\,DHAP$

(6)   GAP + DHAP $\rightleftharpoons$ FBP

(7)   FBP $\rightarrow$ F6P + P_i

(8)   F6P + GAP $\rightleftharpoons$ Xu5P + E4P

(9)   E4P + DHAP $\rightleftharpoons$ SBP

(10) SBP $\rightarrow$ S7P + P_i

(11) S7P + GAP $\rightleftharpoons$ Xu5P + R5P

(12) 2 Xu5P $\rightleftharpoons$ 2Ru5P

(13) R5P $\rightleftharpoons$ Ru5P

Stage I (Reactions 1–4) is the production phase or energy-requiring phase and consists of carboxylation, phosphorylation, and reduction steps. Stage II (Reactions 5–13) is the rearrangement or recovery phase, which regenerates ribulose-5-phosphate.
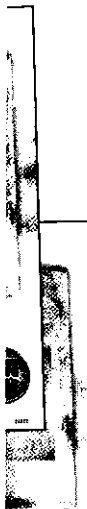
Stage I:
$3\,Ru5P + 3\,CO_2 + 9\,ATP + 6\,NADPH \rightarrow 6\,GAP + 9\,ADP + 6\,P_i + 6\,NADP^+$
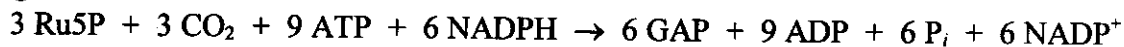
Stage II:
$5\,GAP \rightarrow 3\,Ru5P + 2\,P_i$

19. The interconversion of fructose-1,6-bisphosphate (FBP) and fructose-6-phosphate (F6P) is a potential futile cycle. The relevant enzymes are phosphofructokinase (PFK, for glycolysis) and fructose bisphosphatase (FBPase, for the Calvin cycle). To control these enzymes, a redox-sensing protein, thioredoxin, activates FBPase and deactivates PFK in the light, and activates PFK and deactivates FBPase in the dark.

20. Photorespiration is a side reaction of ribulose bisphosphate carboxylase in which O_2 (which competes with CO_2 for binding to the active site) reacts with RuBP to form 3PG and 2-phosphoglycolate. The 2-phosphoglycolate is eventually converted back to 3PG by a multistep pathway that consumes NADH and ATP and yields CO_2. Photorespiration therefore wastes some of the free energy captured in the photosynthetic light reactions as well as "unfixing" some of the CO_2 fixed by photosynthesis.

21. C_4 plants have an advantage when CO_2 is relatively scarce, since they concentrate CO_2 in mesophyll cells. However, this process consumes 2 ATP equivalents. The more energy-efficient C_3 plants therefore have an advantage when CO_2 is not limiting. Thus, a higher atmospheric concentration of CO_2 would favor C_3 plants over C_4 plants.