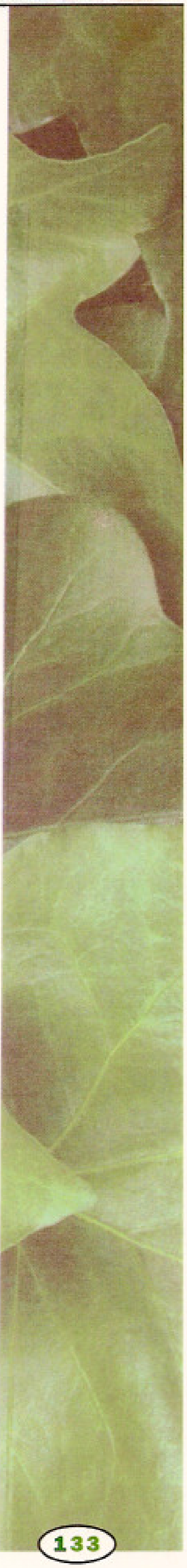

The Light Reactions of Photosynthesis

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Photosynthesis, Light Reactions and

Life requires a continuous input of energy. On Earth, the main source of energy is sunlight, which is transformed by photosynthesis into a form of chemical energy that can be used by photosynthetic and nonphotosynthetic organisms alike. Photosynthesis is the molecular process by which plants, algae, and certain bacteria use light energy to build molecules of sugar from carbon dioxide (CO_2) and water (H_2O). The sugar molecules produced by photosynthetic organisms provide the energy as well as chemical building blocks needed for their growth and reproduction. In plants and algae the photosynthetic process removes CO_2 from the atmosphere while releasing molecular oxygen (O_2) as a by-product. Some photosynthetic bacteria function like plants and algae, giving off O_2; other types of photosynthetic bacteria, however, use light energy to create organic **compounds** without producing O_2. The type of photosynthesis that releases O_2 emerged early in

compound a substance formed from two or more elements

Earth's history, more than three billion years ago, and is the source of the O_2 in our atmosphere. Thus photosynthetic organisms not only provide the food we eat, but also the air we breathe. In addition, ancient photosynthesis produced the building blocks for the oil, coal, and natural gas that we currently depend on for our survival.

The overall photosynthetic process can be written as:

Carbon Dioxide + Water + Light → Carbohydrate + Oxygen

and can be summarized by the following chemical equation:

$$6\ CO_2 + 6\ H_2O + \text{Light Energy} \rightarrow (CH_2O)_6 + 6\ O_2$$

However, this simple chemical equation does not reveal all the reactions that must occur inside a plant to produce carbohydrate. If you shine light on a mixture of CO_2 and H_2O, you end with what you started, CO_2 and H_2O. Add a plant, however, and you get sugar. Plants create this sugar in a series of molecular steps using a complicated machinery made up of proteins and other organic molecules.

This article describes the photosynthetic process in plants, focusing on the first stage of photosynthesis, known as the light reactions. The light reactions capture light energy and store it within two chemicals, **NADPH** (nicotinamide adenine dinucleotide phosphate) and **ATP** (adenosine triphosphate). These two molecules provide the energy needed to drive the second stage of photosynthesis, known as the Calvin-Benson cycle, in which carbohydrates (sugars) are made from CO_2 and H_2O.

NADPH reduced form of nicotinomide adenine dinucleotide phosphate, a small, water-soluble molecule that acts as a hydrogen carrier in biochemical reactions

ATP adenosine triphosphate, a small, water-soluble molecule that acts as an energy currency in cells

To perform photosynthesis a plant must gather light energy, transport electrons between molecules, transfer protons across a membrane, and finally rearrange chemical bonds to create carbohydrates. To understand the light reactions it is helpful to focus on the path of three critical elements: energy, electrons, and protons (hydrogen **ions**). However, before considering the series of individual reactions that make up the light reactions, the molecular machinery that does all the work must be examined.

ions charged particles

Chloroplasts

In plants and algae, photosynthesis occurs in chloroplasts, which are small **organelles** located inside cells. The chloroplast can be thought of as a factory, providing the plant with food and energy. A typical cell in a leaf contains many chloroplasts. Fortunately chloroplasts from different plants are more similar than different. This means that if you understand how photosynthesis works in one plant, you will have a general understanding of photosynthesis in all plants. The chloroplast contains a membrane system, known as the photosynthetic membrane (or thylakoid membrane), that contains most of the proteins required for the light reactions. The Calvin-Benson cycle **enzymes** that capture CO_2 and produce carbohydrate are located in the water phase of the chloroplast outside the photosynthetic membrane. The photosynthetic membrane, like other cellular membranes, is composed mainly of lipid molecules arranged in a bi-layer. As will be explained, a critical feature of the photosynthetic membrane is that it forms a **vesicle** that defines an inner and an outer water space. The photosynthetic membrane is organized into stacked membranes that are interconnected by nonstacked

organelle a membrane-bound structure within a cell

enzyme a protein that controls a reaction in a cell

vesicle a membrane-bound cell structure with specialized contents membranes. Researchers are uncertain as to why the photosynthetic membrane is organized in such a complicated structure. Fortunately, to understand the photosynthetic light reactions we can represent the shape of the photosynthetic membrane as a simple vesicle.

Gathering Sunlight: The Antenna System

Plants capture sunlight by using pigment molecules that absorb visible light (wavelengths from 400 to 700 **nanometers**). The main light-absorbing molecule is chlorophyll, which gives plants their green color. Chlorophyll is green because it is efficient at absorbing blue light and red light, but not very efficient at absorbing green light. The chlorophyll and other light-absorbing molecules (for example, **carotenoids**, which are yellow) are bound to protein complexes embedded in the photosynthetic membrane that make up an **antenna system**. This antenna system is designed to absorb light energy and funnel it to a protein complex called a **reaction center**. The reaction center can use the energy to drive an electron uphill from one site to another within the reaction center. Each reaction center is located at the center of the antenna system, which contains two hundred to three hundred chlorophyll molecules. Before the first chemical step can take place, the light energy captured by the antenna system must be transferred to the reaction center.

To understand light absorption it is best to think of light as packets of energy known as photons. The job of the antenna system is to capture photons and change the light energy into another form of energy known as excitation energy, which is a type of electronic energy. The excitation energy can be thought of as a packet of energy that jumps from antenna molecule to antenna molecule until it is trapped by a reaction center. The antenna system is very efficient. Under optimum conditions more than 90 percent of the photons gathered by the antenna system are transferred to the reaction center. The migration of excitation energy in the antenna system is also very fast. A photon is absorbed, transferred around the antenna system, and trapped by a reaction center within a few trillionths of a second (10^{-12} s).

nanometer one-billionth of a meter

carotenoid a yellow-colored molecule made by plants

antenna system a collection of protein complexes that harvests light energy and converts it to excitation energy that can migrate to a reaction center. The light is absorbed by pigment molecules (e.g., chlorophyll, carotenoids, phycobilin) that are attached to the protein

reaction center a protein complex that uses light energy to create a stable charge separation by transferring a single electron energetically uphill from a donor molecule to an acceptor molecule, both of which are located in the reaction center

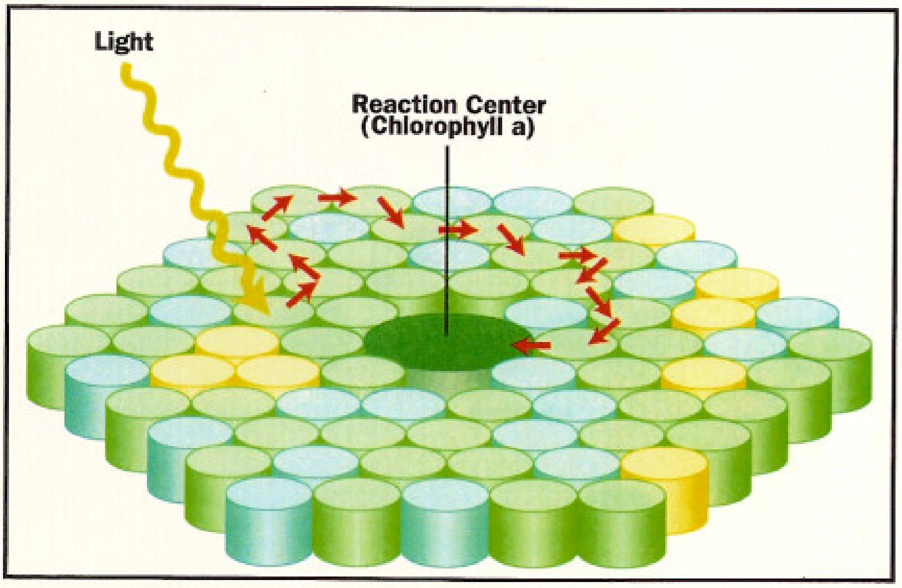


Figure 1: Antenna system with a reaction center (middle). The arrows indicate the pathway of excitation energy migration. Redrawn from Starr and Taggart, 1998, Figure 7.9.

Electron Transport

The excitation energy trapped by a reaction center provides the energy needed for electron transfer, which is the next step in the photosynthetic light reactions. During electron transfer, individual electrons are removed from water molecules and transferred, by an electron transport chain, to **$NADP^+$**. Electron transport in photosynthesis is like electron flow in an electric circuit driven by a battery. The voltage difference across the battery pushes electrons through the circuit, and the electron current can be used to do work. In photosynthesis, light energy pushes electrons up an energy hill in the reaction centers. Subsequent electron flow in the electron transport chain is energetically downhill and can be used to do work. Figure 2 shows the electron carriers that make up the photosynthetic electron transport chain in a way that reveals the relative electronic energy on the vertical scale. This is known as the Z-scheme. Note that a negative voltage corresponds to a higher energy, so that downhill electron flow is from the top to the bottom of the figure.

$NADP^+$ oxidized form of nicotinomide adenine dinucleotide phosphate

The electron transport pathway includes electron transfer from one site to another within a protein, as well as electron transfer from one molecule to another (Figure 3). Most of the electron carriers are located in the photosynthetic membrane, but a few (for example, $NADP^+$) are located in the water phase surrounding the membrane. It is important to keep in mind that the electron transport chain shown in the figure is repeated many times in each chloroplast. A typical chloroplast will contain more than a million electron transport chains.

Electron transfer from one molecule to another is possible because certain types of molecules can easily give up or receive electrons. Some electron carriers can give up and receive a single electron (e.g., plastocyanin), while others can accept or donate more than one electron (e.g., $NADP^+$

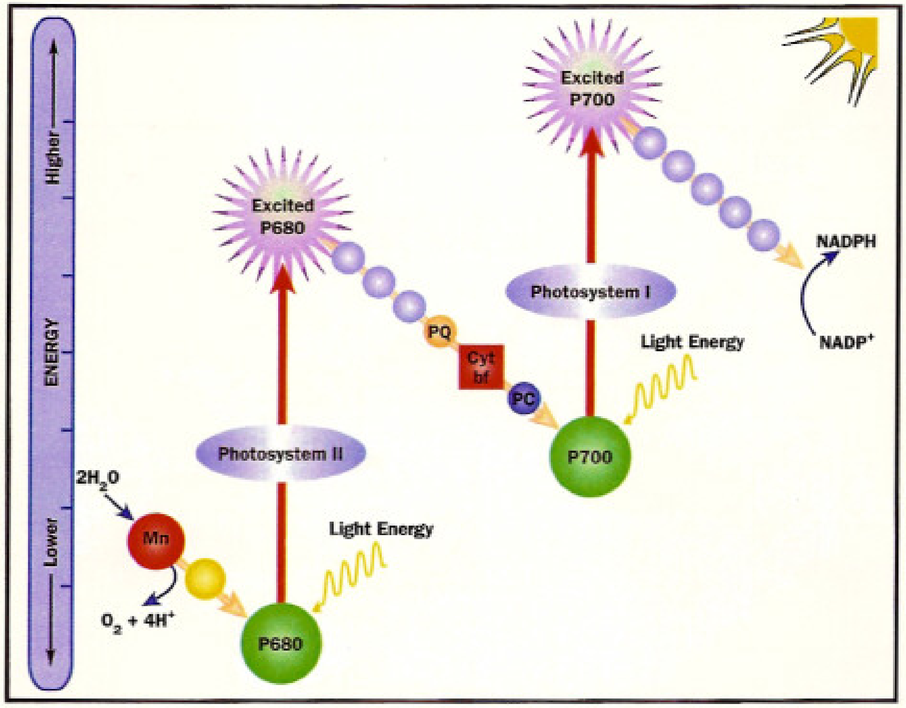


Figure 2: Z-scheme showing the pathway of electrons from water to $NADP^+$ producing oxygen and the reducing power (NADPH). Redrawn from www.life.uiuc.edu/govindjee/ZschemeG.html Mn = manganese; P680 = reaction center chlorophyll *a* of Photosystem II; PQ = plastoquinone; Cyt bf = cytochrome bf complex; PC = plastocyanin; P700 = reaction center chlorophyll of Photosystem I.

can accept two electrons). In addition, some electron carriers can take up a proton along with an electron (plastoquinone can accept two electrons and two protons), making them hydrogen (H) carriers.

When a compound gains an electron it is said to be *reduced* (**reduction**), whereas when it gives up an electron it is said to be *oxidized* (**oxidation**). In biological electron transport pathways, the electrons are always bound to a molecule (they are too reactive to hang around free), which means that an oxidation reaction is always coupled to a reduction reaction. Electrons spontaneously jump from one molecule to another because some molecules hold onto their electrons more tightly than others. This is another way of saying that energetically, electrons flow downhill. If two molecules, A and B, are close enough together, and if A is reduced and B is oxidized, an electron will jump from A to B if it is energetically downhill.

reduction the addition of one or more electrons to an atom or molecule. In the case of a molecule, protons may be involved as well, resulting in hydrogen being added

oxidation The removal of one or more electrons from an atom or molecule. In the case of a molecule, a proton may be involved as well, resulting in hydrogen being removed

NADPH Production

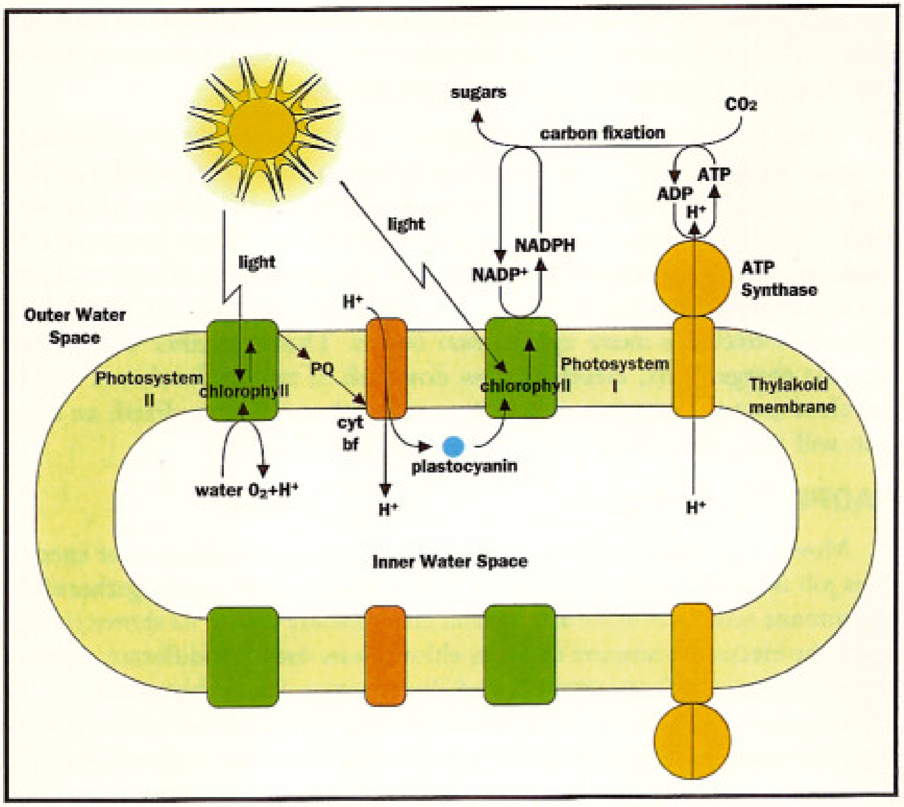
Moving an electron from water to $NADP^+$ requires an input of energy. This job is done by reaction centers, which use the light energy gathered by the antenna system to move an electron energetically uphill. As shown in Figure 3 the electron transport chain in chloroplasts uses two different types of reactions centers: Photosystem II and Photosystem I. (For historical reasons the reaction centers are not numbered according to their order in the electron transport chain, i.e., Photosystem II sends electrons to photosystem I.)

Photosystem II catalyzes two different chemical reactions. One is the oxidation of water and the other is the reduction of plastoquinone. Water oxidation is a critical reaction in photosynthesis because the electrons removed from H_2O are ultimately used to reduce CO_2 to carbohydrate. Photosystem II performs this reaction by binding two H_2O molecules and removing one electron at a time. The energy for the removal of a single electron is provided by a single photon. For Photosystem II to completely oxidize two H_2O molecules and reduce two molecules of plastoquinone, it requires four photons. (Note that electron transport from H_2O all the way to $NADP^+$ requires two light reactions: Photosystem II and Photosystem I. Thus eight photons are required for the release of one O_2 molecule.) This process creates O_2, which is released, and H^+ ions, which are used in ATP synthesis (see below).

As shown in Figure 3, electron transfer from water to $NADP^+$ requires three membrane-bound protein complexes: Photosystem II, the cytochrome *bf* complex (Cyt bf), and Photosystem I. Electrons are transferred between these large protein complexes by small mobile molecules. Because these small molecules carry electrons (or hydrogen atoms) over relatively long distances, they play a critical role in photosynthesis. This is illustrated by plastoquinone (PQ), which transfers electrons from the Photosystem II reaction center to the cytochrome *bf* complex and at the same time carries protons across the photosynthetic membrane.

Plastoquinone operates by diffusing in the photosynthetic membrane until it becomes bound to a pocket on the Photosystem II complex. The photosystem II reaction center reduces plastoquinone by adding two electrons taken from H_2O and two protons taken from the outer water phase, creating PQH_2. The reduced plastoqinone molecule unbinds from Photosystem II and diffuses in the photosynthetic membrane until it encounters a binding site on the cytochrome *bf* complex. In a reaction sequence that is

Figure 3: The electron transport chain showing the carriers in a membrane that forms a vesicle. Modified from photoscience.la.asu.edu/photosyn/education/photointro.html. See text for abbreviations used.



not completely understood, the cytochrome *bf* complex removes the electrons from reduced plastoquinone and releases protons into the inner water space of the photosynthetic vesicle. The cytochrome *bf* complex then gives up the electrons to another small molecule, plastocyanin (PC). The electrons are transferred to the Photosystem I reaction center by plastocyanin. The proton gradient, produced by water oxidation and oxidation of reduced plastoquinone, is used to create ATP (see below).

The Photosystem I reaction center is like Photosystem II in that it is served by a chlorophyll-containing antenna system and uses light energy to move an electron energetically uphill, but Photosystem I catalyzes different reactions: it oxidizes plastocyanin and reduces ferredoxin. Ferredoxin itself becomes oxidized, losing its electrons to another acceptor. The last step in the photosynthetic electron transport chain is reduction of $NADP^+$, producing NADPH.

ATP Production

In plants essentially all electron flow from water follows the pathway shown in Figure 3, at least up to ferredoxin. However, once an electron reaches ferredoxin the electron pathway becomes branched, enabling a fraction of the **redox** free energy to enter other pathways, including cycling through the Photosystem I reaction center. Photosystem I cyclic electron transport provides additional energy for ATP production, which allows plants to adjust the energy flow according to their metabolic needs.

redox oxidation and reduction

Most of the energy from the electron transfer reactions is stored as redox energy in NADPH as described above. However, some of the energy is stored across the membrane of the photosynthetic vesicle in the form of a **pH** gradient (or protein gradient) and an electric potential (positive inside). As previously noted, the electron transport chain concentrates protons in the inner water phase of the vesicle by the release of protons during the oxidation of water by Photosystem II and by transporting protons from the outer water phase to the inner water phase via plastoquinone (Figure 3). In addition, electron transport creates a net positive charge on the inner side and a net negative charge on the outer side of the vesicle, which gives rise to an electric potential across the membrane. The energy stored in the pH gradient and electric potential is known as the transmembrane proton electrochemical potential or the proton motive force.

pH a measure of acidity or alkalinity; the pH scale ranges from 0 to 14, with 7 being neutral; low pH numbers indicate high acidity; high numbers indicate alkalinity

The conversion of proton electrochemical energy into the chemical-free energy of ATP is accomplished by a single protein complex known as ATP synthase, which catalyzes the formation of ATP by the addition of inorganic phosphate (P_i) to ADP:

$$\mathrm{ADP} + \mathrm{P_i} \rightarrow \mathrm{ATP} + \mathrm{H_2O}$$

The reaction is energetically uphill and is driven by the transmembrane proton electrochemical gradient. The ATP synthase enzyme is a molecular rotary motor. Protons move through a channel in the ATP synthase pro-

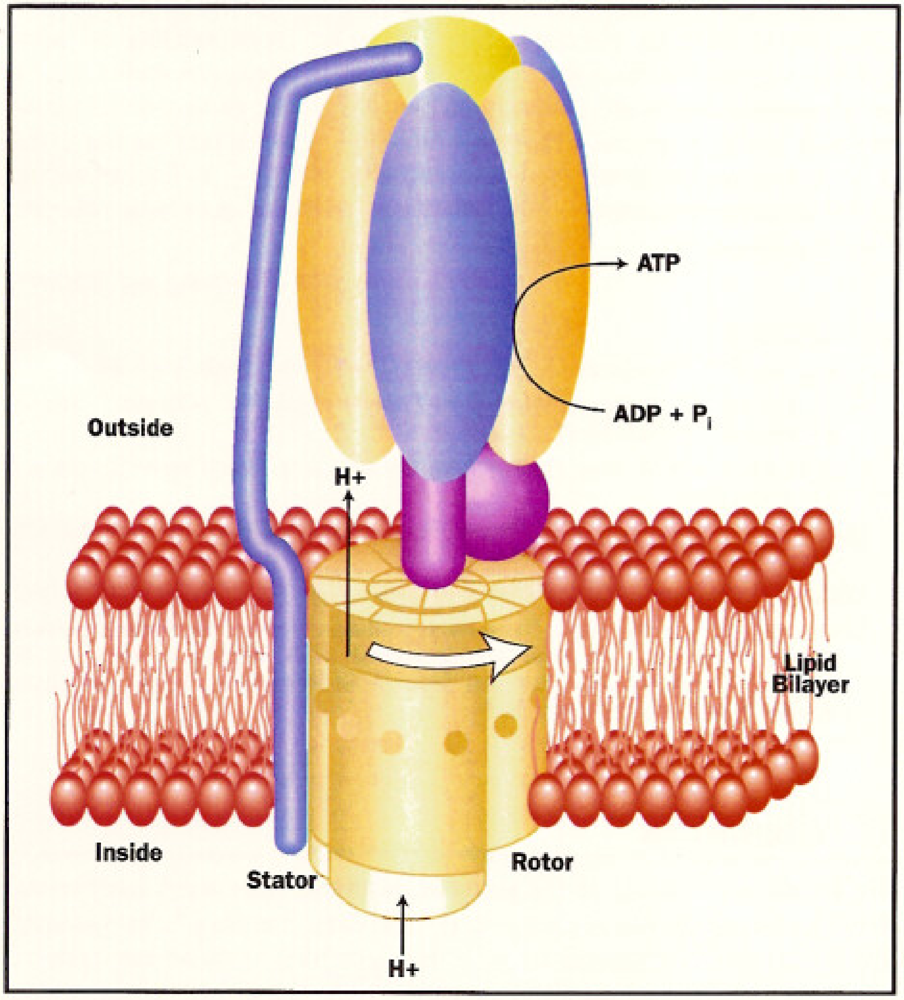


Figure 4: Rotary model of how ATP synthase catalyzes ATP. Redrawn from Fillingame, 1999, pp. 1687–88.

tein (from the inner water phase to the outer water phase of the vesicle) providing the energy for ATP synthesis. However, the protons are not involved in the chemistry of adding phosphate to ADP at the catalytic site. Although it has not been proven, it appears that proton flow drives the rotation part of the ATP synthase at rates as high as one hundred revolutions per second (Figure 4). The rotation of ATP synthase can be thought of as pushing ADP and P_i together to form ATP and water.

From the Light Reactions to the Calvin-Benson Cycle

The job of the photosynthetic light reactions is to provide energy in the form NADPH and ATP for the Calvin-Benson cycle. Although all plants depend on the Calvin-Benson cycle to make carbohydrates, the way they get the carbon dioxide to the cycle varies. The most efficient plants (soybean, for example) require two molecules of NADPH and three molecules of ATP for each molecule of CO_2 that is taken up, while some other types of plants (corn, for example) must use more energy to fix a single CO_2 molecule. During brief periods photosynthesis in plants can store nearly 30 percent of the light energy they absorb as chemical energy. However, under normal, day-to-day growing conditions the actual performance of the plant is less than one-tenth of the maximum efficiency. The factors that conspire to lower photosynthesis include limitations imposed by molecular reactions and environmental conditions that limit plant performance such as low soil moisture or high temperature. Our increasing understanding of plant **genomes** opens the door for improving plant performance under diverse environmental conditions (for example, enabling farmers to grow crops on marginal lands). A crucial step in this direction is understanding the molecular processes involved in photosynthesis. SEE ALSO CHLOROPHYLL; CHLOROPLASTS; INGENHOUSZ, JAN; PHOTOSYNTHESIS, CARBON FIXATION AND; WATER MOVEMENT.

genome the genetic material of an organism

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Phyllotaxis

Phyllotaxis is the study of the patterns on plants. The word itself comes from the Greek *phullon*, meaning "leaf," and *taxis*, meaning "arrangement." Phyllotaxis, in the restricted sense, is the study of the relative arrangement of what is called the primordia of plants. A primordium is, for example, what