The light-dependent reactions

How light energy is used to make ATP and NADPH. Photosystems I and II. Reaction centre chlorophylls P700 and P680.

Introduction

Plants and other photosynthetic organisms are experts at collecting solar energy, thanks to the light-absorbing pigment molecules in their leaves. But what happens to the light energy that is absorbed? We don't see plant leaves glowing like light bulbs, but we also know that energy can't just disappear (thanks to the First Law of Thermodynamics).

As it turns out, some of the light energy absorbed by pigments in leaves is converted to a different form: chemical energy. Light energy is converted to chemical energy during the first stage of photosynthesis, which involves a series of chemical reactions known as the light-dependent reactions.

In this article, we'll explore the light-dependent reactions as they take place during photosynthesis in plants. We'll trace how light energy is absorbed by pigment molecules, how reaction centre pigments pass excited electrons to an electron transport chain, and how the energetically "downhill" flow of electrons leads to synthesis of ATP and NADPH. These molecules store energy for use in the next stage of photosynthesis: the Calvin cycle.

Photosynthesis takes place differently in different organisms, and the form of photosynthesis we'll discuss in this article is the one that occurs in plants. Other photosynthetic organisms, such as purple sulphur bacteria, can use different molecules and metabolic pathways to carry out photosynthesis. For example:

- Plants carry out a form of photosynthesis called **oxygenic photosynthesis**. In oxygenic photosynthesis, water molecules are split to provide a source of electrons for the electron transport chain, and oxygen gas is released as a by-product. Plants organize their photosynthetic pigments into two separate complexes called photosystems (photosystems I and II), and they use chlorophylls as their reaction centre pigments.
- Purple sulphur bacteria, in contrast, carry out **anoxygenic photosynthesis**, meaning that water is not used as an electron source and oxygen gas is not produced. Instead, these bacteria use hydrogen sulphide (H_2S) as an electron source and produce elemental sulphur as a by-product. In addition, purple sulphur bacteria have only one photosystem, and they use chlorophyll-like molecules called bacteriochlorophylls as reaction centre pigments[1,2,3].

Purple sulphur bacteria provide just one example of how photosynthesis can vary among different organisms (and how it isn't always identical to the process that takes place in plants). There are many fascinating variations on photosynthesis that occur in different types of bacteria and algae. The image below shows an aerial photograph of a "soda lake" (alkaline lake), one of the natural habitats of purple sulphur bacteria.

Aerial photograph of a soda lake (Owens Lake, California).
Image credit: "Owens Lake, California," by NASA (public domain).

Overview of the light-dependent reactions

Before we get into the details of the light-dependent reactions, let's step back and get an overview of this remarkable energy-transforming process.

The **light-dependent reactions** use light energy to make two molecules needed for the next stage of photosynthesis: the energy storage molecule ATP and the reduced electron carrier NADPH. In plants, the light reactions take place in the thylakoid membranes of organelles called chloroplasts.

Photosystems, large complexes of proteins and pigments (light-absorbing molecules) that are optimized to harvest light, play a key role in the light reactions. There are two types of photosystems: photosystem I (PSI) and photosystem II (PSII).

Both photosystems contain many pigments that help collect light energy, as well as a special pair of chlorophyll molecules found at the core (reaction centre) of the photosystem. The special pair of **photosystem I** is called **P700**, while the special pair of **photosystem II** is called **P680**.

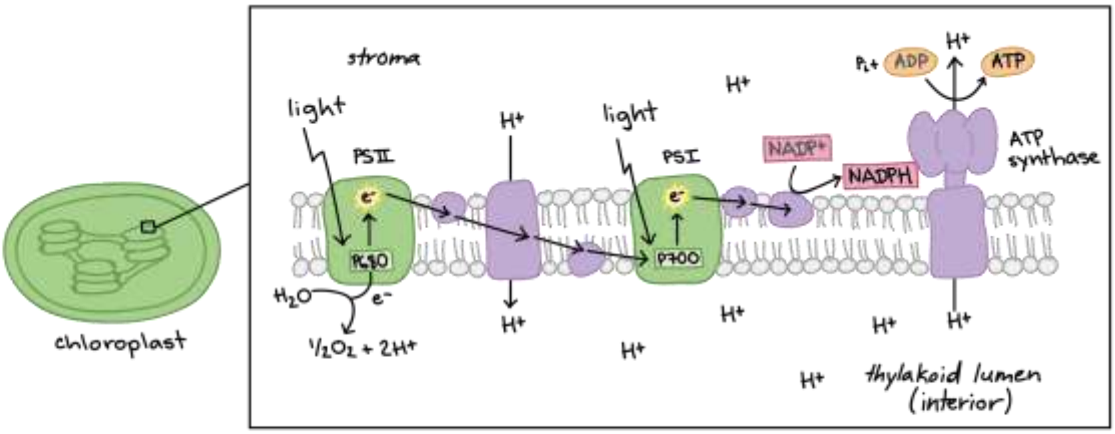


Diagram of non-cyclic photophosphorylation. The photosystems and electron transport chain components are embedded in the thylakoid membrane.

When light is absorbed by one of the pigments in photosystem II, energy is passed inward from pigment to pigment until it reaches the reaction centre. There, energy is transferred to P680, boosting an electron to a high energy level (forming P680*). The high-energy electron is passed to an acceptor molecule and replaced with an electron from water. This splitting of water releases the O_2 we breathe. The basic equation for water splitting can be written as $H_2O \rightarrow 12O_2 + 2H^+$. Water is split on the thylakoid lumen side of the thylakoid membrane, so the protons are released inside the thylakoid, contributing to the formation of a gradient.

The high-energy electron travels down an electron transport chain in, losing energy as it goes. Some of the released energy drives pumping of H^+ ions from the stroma into the thylakoid, adding to the proton gradient. As H^+ ions flow down their gradient and back into the stroma, they pass through ATP synthase, driving ATP production. ATP is produced on the stromal side of the thylakoid membrane, so it is released into the stroma.

The electron arrives at photosystem I and joins the P700 special pair of chlorophylls in the reaction centre. When light energy is absorbed by pigments and passed inward to the reaction centre, the electron in P700 is boosted to a very high energy level and transferred to an acceptor molecule. The special pair's missing electron is replaced by an electron from PSII (arriving via the electron transport chain).

The high-energy electron travels down a short second leg of the electron transport chain. At the end of the chain, the electron is passed to NADP+ (along with a second electron) to make NADPH. NADPH is formed on the stromal side of the thylakoid membrane, so it is released into the stroma.

In a process called **non-cyclic photophosphorylation** (the "standard" form of the light-dependent reactions), electrons are removed from water and passed through PSII and PSI before ending up in NADPH. This process requires light to be absorbed twice, once in each photosystem, and it makes ATP . In fact, it's called photophosphorylation because it involves using light energy (*photo*) to make ATP from ADP (*phosphorylation*). Here are the basic steps:

- **Light absorption in PSII.** When light is absorbed by one of the many pigments in photosystem II, energy is passed inward from pigment to pigment until it reaches the reaction centre. There, energy is transferred to P680, boosting an electron to a high energy level. The high-energy electron is passed to an acceptor molecule and replaced with an electron from water. This splitting of water releases the O_2 we breathe.
- **ATP synthesis.** The high-energy electron travels down an electron transport chain, losing energy as it goes. Some of the released energy drives pumping of H^+ ions from the stroma into the thylakoid interior, building a gradient. (H^+ ions from the splitting of

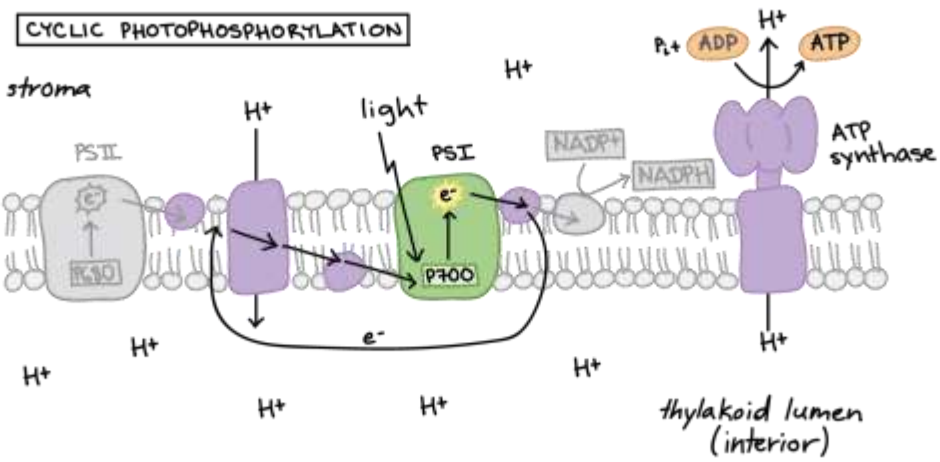
water also add to the gradient.) As H^+ ions flow down their gradient and into the stroma, they pass through ATP synthase, driving ATP production in a process known as **chemiosmosis**.

- **Light absorption in PSI.** The electron arrives at photosystem I and joins the P700 special pair of chlorophylls in the reaction centre. When light energy is absorbed by pigments and passed inward to the reaction centre, the electron in P700 is boosted to a very high energy level and transferred to an acceptor molecule. The special pair's missing electron is replaced by a new electron from PSII (arriving via the electron transport chain).
- **NADPH formation.** The high-energy electron travels down a short second leg of the electron transport chain. At the end of the chain, the electron is passed to $NADP^+$ (along with a second electron from the same pathway) to make NADPH.

The net effect of these steps is to convert light energy into chemical energy in the form of ATP and NADPH. The ATP and NADPH from the light-dependent reactions are used to make sugars in the next stage of photosynthesis, the Calvin cycle. In another form of the light reactions, called **cyclic photophosphorylation**, electrons follow a different, circular path and only ATP (no NADPH) is produced.

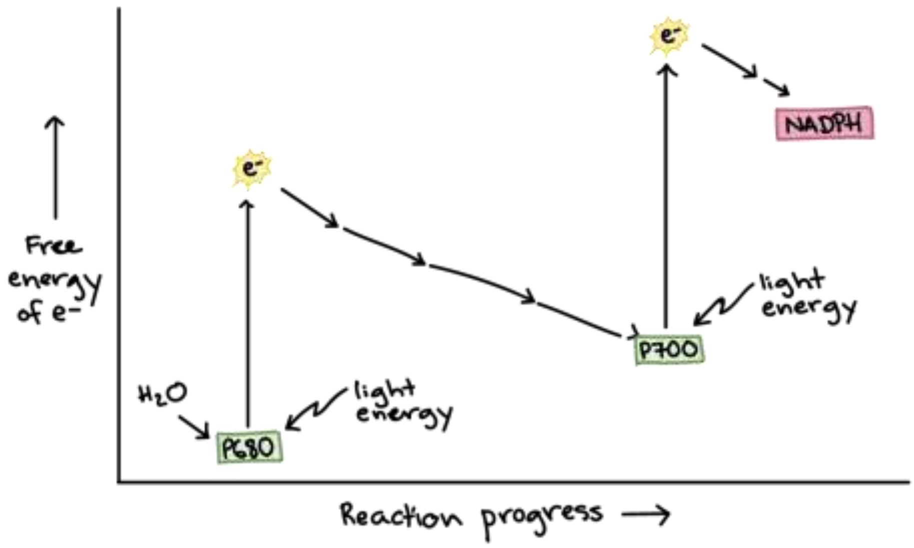
The process described above, in which electrons flow in a line (from water to NADPH), is called non-cyclic photophosphorylation. (*Photophosphorylation* = light-driven addition of a phosphate group to ADP, making ATP).

Plants also carry out another form of the light-dependent reactions called **cyclic photophosphorylation**, in which electrons instead cycle repeatedly through PSI and the first portion of the electron transport chain but do not pass through PSII. You can learn more about cyclic photophosphorylation in later sections of the article.



In cyclic photophosphorylation, an excited electron leaves photosystem I and travels a short distance down the second leg of the electron transport chain. However, instead of being passed to the enzyme that reduces $NADP^+$ to NADPH, the electron is instead carried back to the first leg of the electron transport chain. It travels back down that first leg to photosystem I, where it can repeat the process with absorption of more light energy. Cyclically flowing electrons generate ATP, because passage down the first leg of the electron transport chain causes protons to be pumped into the thylakoid lumen, thus establishing a gradient. However, cyclic electron flow does not make NADPH, nor does it involve the splitting of water or production of oxygen.

It's important to realize that the electron transfers of the light-dependent reactions are driven by, and indeed made possible by, the absorption of energy from light. In other words, the transfers of electrons from PSII to PSI, and from PSI to NADPH, are only energetically "downhill" (energy-releasing, and thus spontaneous) because electrons in P680 and P700 are boosted to very high energy levels by absorption of energy from light.



Energy diagram of photosynthesis. On the Y-axis is the free energy of electrons, while on the X-axis is the progression of the electrons through the light reactions. Electrons start at a low energy level in water, move slightly downhill to reach P680, are excited to a very high energy level by light, flow downhill through several additional molecules, reach P700, are excited to an even higher energy level by light, then flow through a couple more molecules before arriving at NADPH (in which they are still at a quite high energy level, allowing NADPH to serve as a good reducing agent).

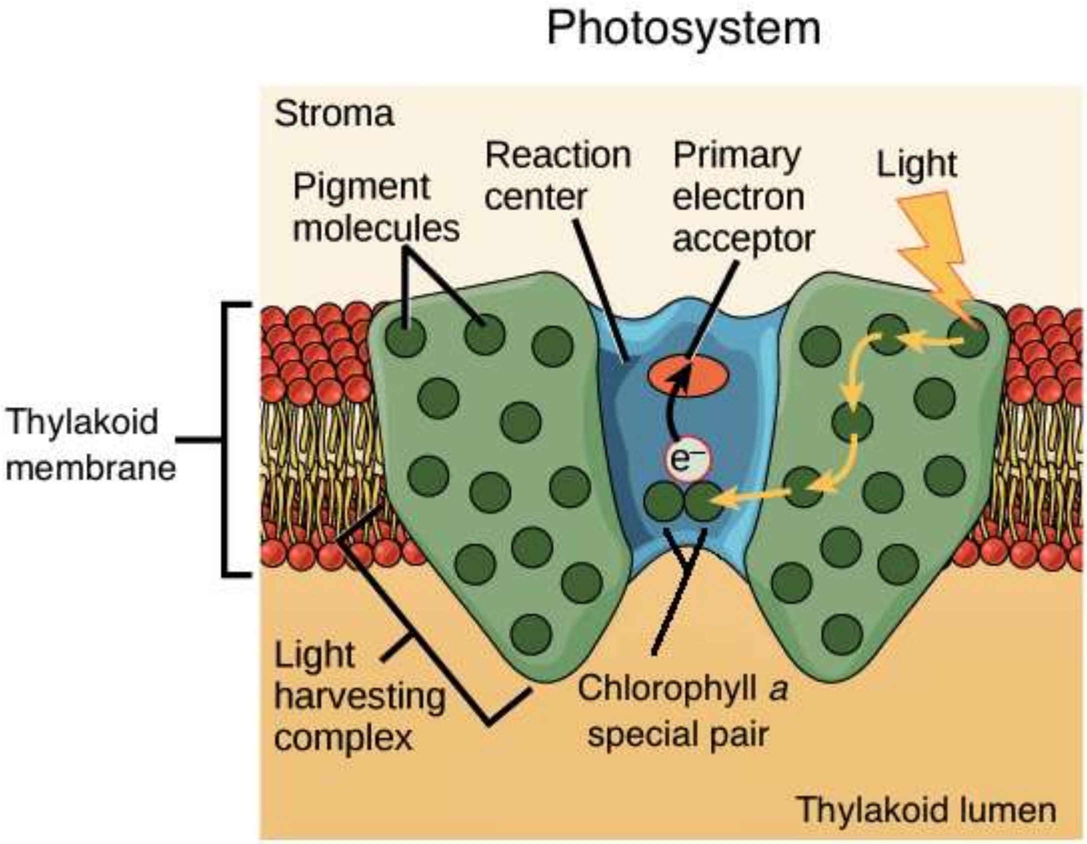
In the rest of this article, we'll look in greater detail at the steps and players involved in the light-dependent reactions.

What is a photosystem?

Photosynthetic pigments, such as chlorophyll *a*, chlorophyll *b*, and carotenoids, are light-harvesting molecules found in the thylakoid membranes of chloroplasts. As mentioned above, pigments are organized along with proteins into complexes called **photosystems**. Each photosystem has **light-harvesting complexes** that contain proteins, 300-400 chlorophylls, and other pigments. When a pigment absorbs a photon, it is raised to an excited state, meaning that one of its electrons is boosted to a higher-energy orbital.

Most of the pigments in a photosystem act as an energy funnel, passing energy inward to a main reaction centre. When one of these pigments is excited by light, it transfers energy to a neighbouring pigment through direct electromagnetic interactions in a process called **resonance energy transfer**. The neighbour pigment, in turn, can transfer energy to one of its own neighbours, with the process repeating multiple times. In these transfers, the receiving molecule cannot require more energy for excitation than the donor, but may require less energy (i.e., may absorb light of a longer wavelength).

Collectively, the pigment molecules collect energy and transfer it towards a central part of the photosystem called the **reaction centre**.



Photosystems are structures within the thylakoid membrane that harvest light and convert it to chemical energy. Each photosystem is composed of several light-harvesting complexes that surround a reaction centre. Pigments within the light-harvesting complexes absorb light and pass energy to a special pair of chlorophyll *a* molecules in the reaction centre. The absorbed energy cause an electron from the chlorophyll *a* to be passed to a primary electron acceptor.

The reaction centre of a photosystem contains a unique pair of chlorophyll *a* molecules, often called **special pair** (actual scientific name—that's how special it is!). Once energy reaches the special pair, it will no longer be passed on to other pigments through resonance energy transfer. Instead, the special pair can actually lose an electron when excited, passing it to another molecule in the complex called the **primary electron acceptor**. With this transfer, the electron will begin its journey through an electron transport chain.

Photosystem I vs. photosystem II

There are two types of photosystems in the light-dependent reactions, **photosystem II (PSII)** and **photosystem I (PSI)**. PSII comes first in the path of electron flow, but it is named as second because it was discovered after PSI. (Thank you, historical order of discovery, for yet another confusing name!)

Here are some of the key differences between the photosystems:

- **Special pairs.** The chlorophyll *a* special pairs of the two photosystems absorb different wavelengths of light. The PSII special pair absorbs best at 680 nm, while the PSI special absorbs best at 700 nm. Because of this, the special pairs are called **P680** and **P700**, respectively.

- **Primary acceptor**. The special pair of each photosystem passes electrons to a different primary acceptor. The primary electron acceptor of PSII is pheophytin, an organic molecule that resembles chlorophyll, while the primary electron acceptor of PSI is a chlorophyll called $A_0$8[7,8].
- **Source of electrons**. Once an electron is lost, each photosystem is replenished by electrons from a different source. The PSII reaction centre gets electrons from water, while the PSI reaction centre is replenished by electrons that flow down an electron transport chain from PSII.

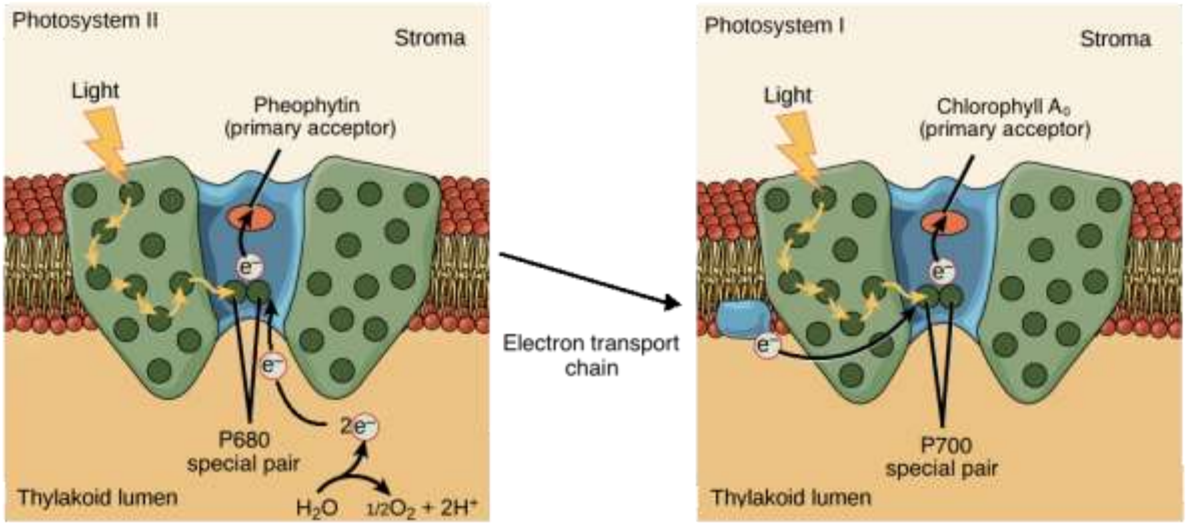


Image modified from "The Light-Dependent Reactions of Photosynthesis: Figure 7," by OpenStax College, Biology (CC BY 4.0.

During the light-dependent reactions, an electron that's excited in PSII is passed down an electron transport chain to PSI (losing energy along the way). In PSII, the electron is excited again and passed down the second leg of the electron transport chain to a final electron acceptor. Let's trace the path of electrons in more detail, starting when they're excited by light energy in PSII.

Photosystem II

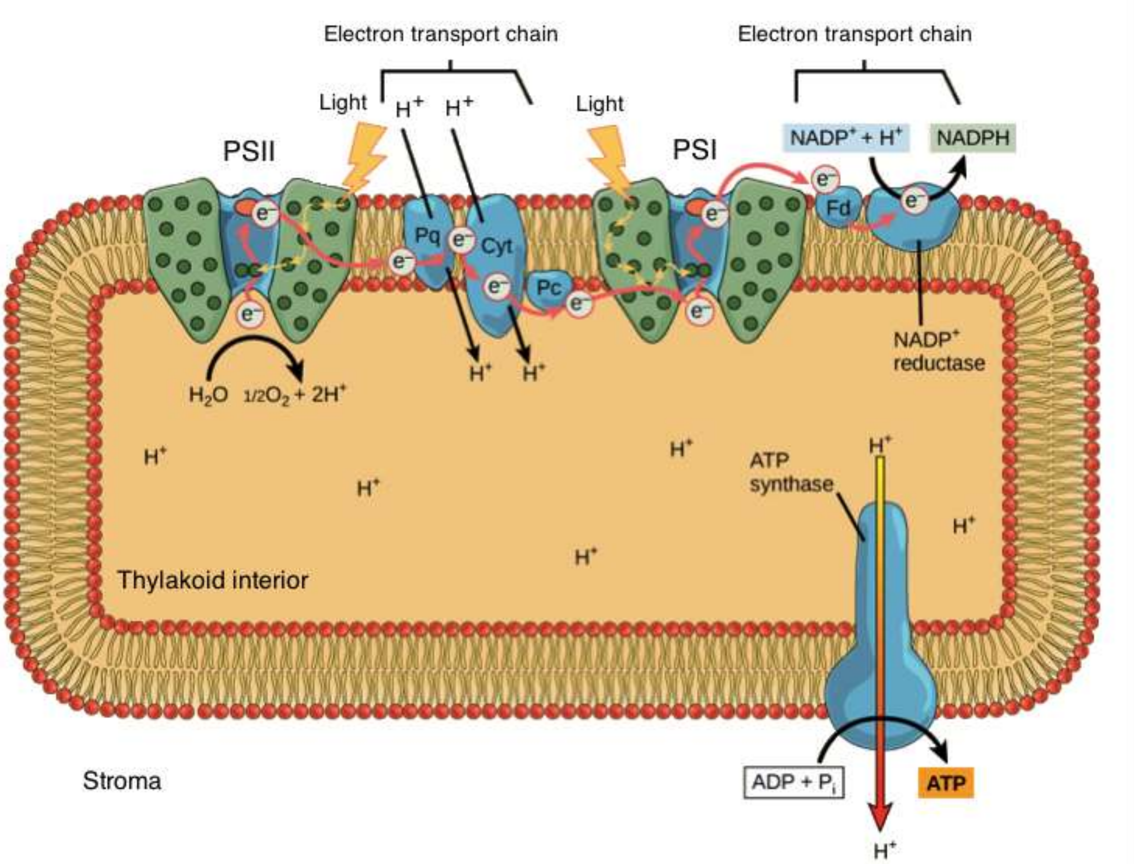
When the P680 special pair of photosystem II absorbs energy, it enters an excited (high-energy) state. Excited P680 is a good electron donor and can transfer its excited electron to the primary electron acceptor, pheophytin. The electron will be passed on through the first leg of the photosynthetic **electron transport chain** in a series of redox, or electron transfer, reactions. After the special pair gives up its electron, it has a positive charge and needs a new electron. This electron is provided through the splitting of water molecules, a process carried out by a portion of PSII called the manganese center. The positively charged P680 can pull electrons off of water (which doesn't give them up easily) because it's extremely "electron-hungry."
When the manganese centre splits water molecules, it binds two at once, extracting four electrons, releasing four H^+ ions, and producing a molecule of O_2.

About 10 percent of the oxygen is used by mitochondria in the leaf to support oxidative phosphorylation. The remainder escapes to the atmosphere where it is used by aerobic organisms (such as us!) to support respiration.

Electron transport chains and photosystem I

When an electron leaves PSII, it is transferred first to a small organic molecule (plastoquinone, Pq), then to a cytochrome complex (Cyt), and finally to a copper-containing protein called plastocyanin (Pc). As the electron moves through this electron transport chain, it goes from a higher to a lower energy level, releasing energy. Some of the energy is used to pump protons (H^+) from the stroma (outside of the thylakoid) into the thylakoid interior.

This transfer of H^+ along with the release of H^+ from the splitting of water, forms a proton gradient that will be used to make ATP (as we'll see shortly).



The light-dependent reactions involve two photosytems (II and I) and an electron transport chain that are all embedded in the thylakoid membrane. Light that is harvested from PSII causes an excited electron of the chlorophyll *a* special pair to be passed down an electron transport chain (Pq, Cyt, and Pc) to PSII. The electron lost from the chlorophyll *a* special pair is replenished by splitting water.

The passing of the electron in the first part of the electron transport chain causes protons to be pumped from the stroma to the thylakoid lumen. A concentration gradient formed (with a higher concentration of protons in the thylakoid lumen than in the stroma). Protons diffuse out of the thylakoid lumen through the enzyme, ATP synthase, producing ATP in the process.
Once the electron reaches PSI, it joins its chlorophyll *a* special pair and re-excited by the absorption of light. It proceeds down a second part of the electron transport chain (Fd and $NADP^+$ reductase) and reduces $NADP^+$ to form NADPH. The electron lost from the chlorophyll *a* special pair is replenished by electrons flowing from PSII.

Once an electron has gone down the first leg of the electron transport chain, it arrives at PSI, where it joins the chlorophyll *a* special pair called P700. Because electrons have lost energy prior to their arrival at PSI, they must be re-energized through absorption of another photon.

Excited P700 is a very good electron donor, and it sends its electron down a short electron transport chain. In this series of reactions, the electron is first passed to a protein called ferredoxin (Fd), then transferred to an enzyme called **$NADP^+$ reductase**. NADP+ reductase transfers electrons to the electron carrier NADP+, plus, end superscript to make NADPH. NADPH will travel to the Calvin cycle, where its electrons are used to build sugars from carbon dioxide.

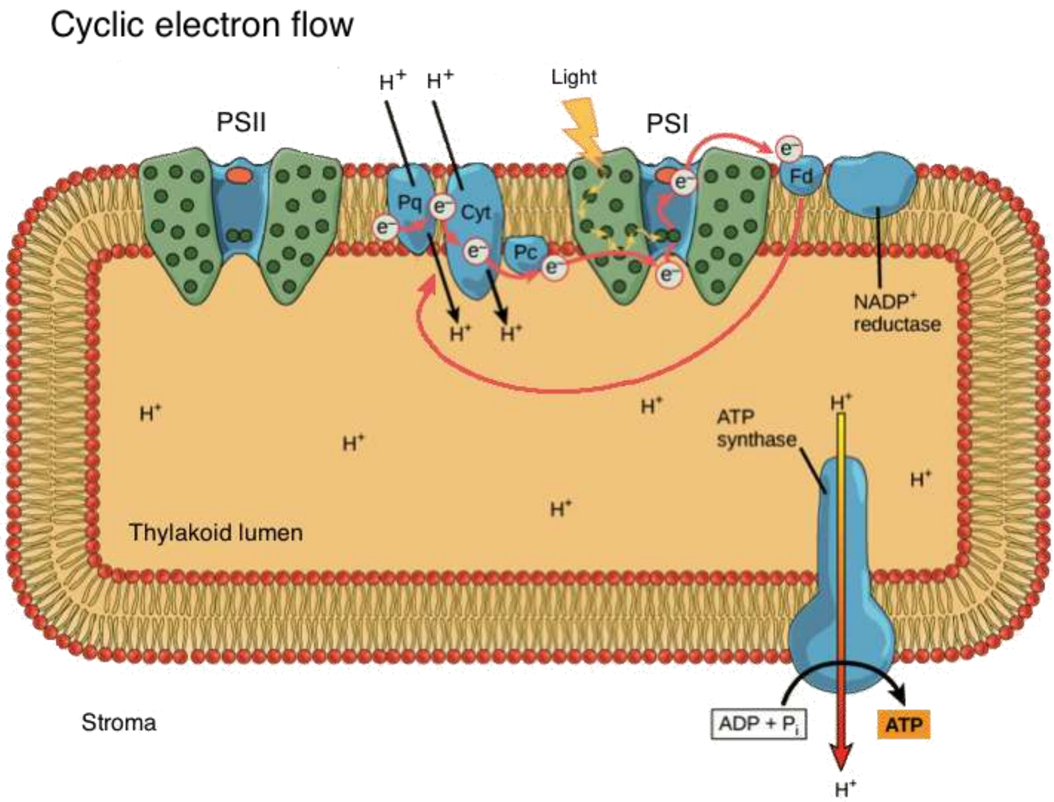
The other ingredient needed by the Calvin cycle is ATP, and this too is provided by the light reactions. As we saw above, H^+, ions build inside the thylakoid interior and make a concentration gradient. Protons "want" to diffuse back down the gradient and into the stroma, and their only route of passage is through the enzyme **ATP synthase**. ATP synthase harnesses the flow of protons to make ATP from ADP and phosphate (Pi). This process of making ATP using energy stored in a chemical gradient is called **chemiosmosis**.

Some electrons flow cyclically

The pathway above is sometimes called **linear photophosphorylation**. That's because electrons travel in a line from water through PSII and PSI to NADPH. (*Photophosphorylation* = light-driven synthesis of ATP.)

In some cases, electrons break this pattern and instead loop back to the first part of the electron transport chain, repeatedly cycling through PSI instead of ending up in NADPH. This is called **cyclic photophosphorylation**.

After leaving PSI, cyclically flowing electrons travel back to the cytochrome complex (Cyt) or plastoquinone (Pq) in the first leg of the electron transport. The electrons then flow down the chain to PSI as usual, driving proton pumping and the production of ATP. The cyclic pathway does not make NADPH, since electrons are routed away from $NADP^+$ reductase.



In cyclic electron flow, electrons are repeatedly cycled through PSI. After an electron in PSI is excited and passed to ferredoxin, it is passed back to the cytochrome complex in the first part of the electron transport chain. Cyclically flowing electrons result in the production of ATP (because protons are pumped into the thylakoid lumen), but do not result in the production of NAPDH (because electrons are not passed to $NADP^+$ reductase.

Why does the cyclic pathway exist? At least in some cases, chloroplasts seem to switch from linear to cyclic electron flow when the ratio of NADPH to $NADP^+$ is too high (when too little NADP+ is available to accept electrons). In addition, cyclic electron flow may be common in photosynthetic cell types with especially high ATP needs (such as the sugar-synthesizing bundle-sheath cells of plants that carry out C4 photosynthesis). Finally, cyclic electron flow may play a photo protective role, preventing excess light from damaging photosystem proteins and promoting repair of light-induced damage.