Ancillary Chemistry-II

Photosynthesis

Dr. Suman Kushwaha

Assistant professor

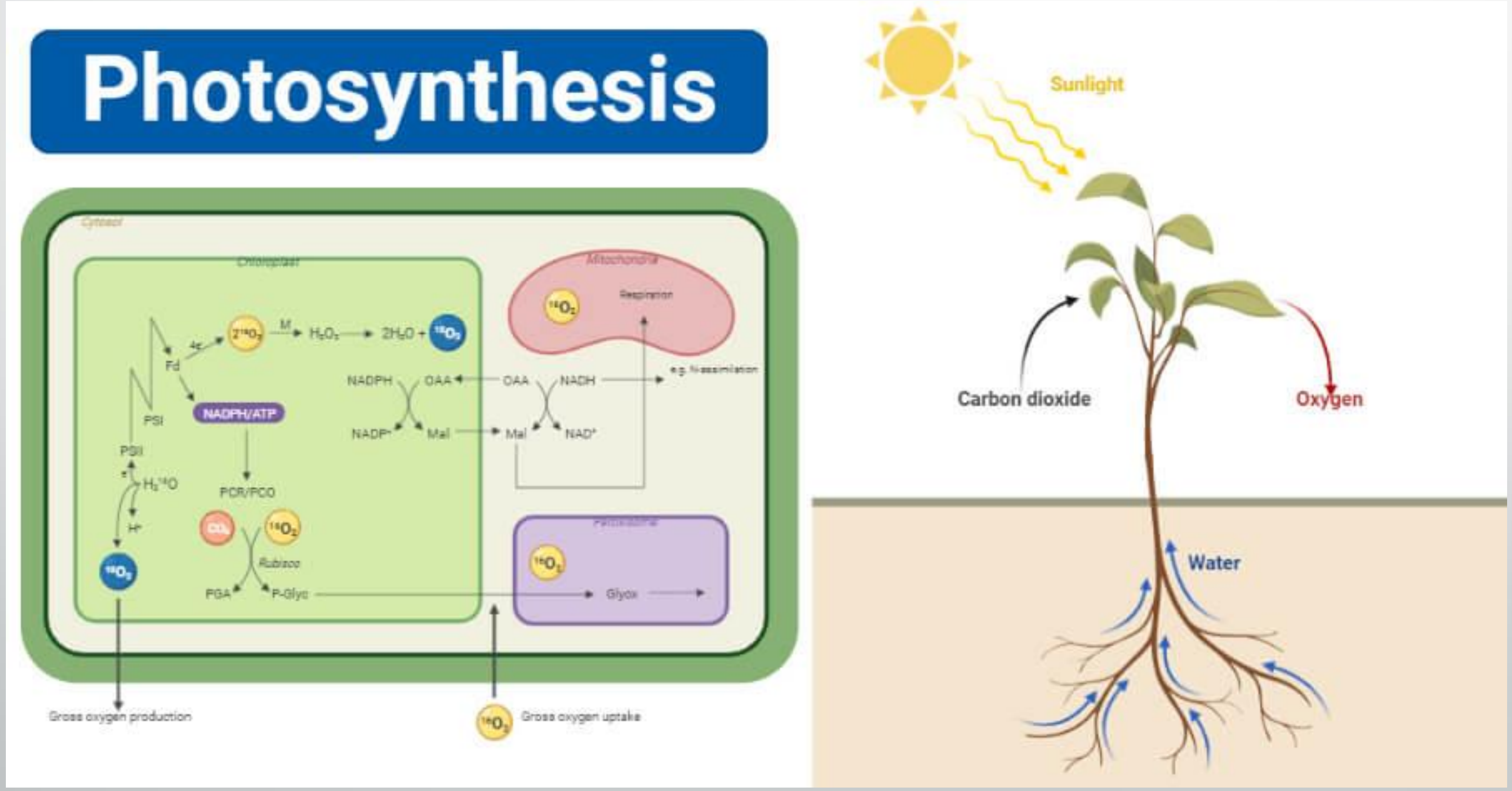
Department of Chemistry

Institute of science

B.H.U Varanasi.

Photosynthesis Definition

Photosynthesis is defined as the process, utilized by green plants and photosynthetic bacteria, where electromagnetic radiation is converted into chemical energy and uses light energy to convert carbon dioxide and water into carbohydrates and oxygen.



Photosynthesis

The study of photosynthesis began in 1771 with observations made by the English clergyman and scientist Joseph Priestley. Priestley had burned a candle in a closed container until the air within the container could no longer support combustion. He then placed a sprig of mint plant in the container and discovered that after several days the mint had produced some substance (later recognized as oxygen) that enabled the confined air to again support combustion.

In 1779 the Dutch physician Jan Ingenhousz expanded upon Priestley's work, showing that the plant had to be exposed to light if the combustible substance (i.e., oxygen) was to be restored. He also demonstrated that this process required the presence of the green tissues of the plant.

In 1782 it was demonstrated that the combustion-supporting gas (oxygen) was formed at the expense of another gas, or “fixed air,” which had been identified the year before as carbon dioxide.

Gas-exchange experiments in 1804 showed that the gain in weight of a plant grown in a carefully weighed pot resulted from the uptake of carbon, which came entirely from absorbed carbon dioxide, and water taken up by plant roots; the balance is oxygen, released back to the atmosphere.

Almost half a century passed before the concept of chemical energy had developed sufficiently to permit the discovery (in 1845) that light energy from the sun is stored as chemical energy in products formed during photosynthesis.

- The carbohydrates formed from photosynthesis provide not only the necessary energy form the energy transfer within ecosystems, but also the carbon molecules to make a wide array of biomolecules.

- Photosynthesis is a light-driven oxidation-reduction reaction where the energy from the light is used to oxidize water, releasing oxygen gas and hydrogen ions, followed by the transfer of electrons to carbon dioxide, reducing it to organic molecules.

- Photosynthetic organisms are called autotrophs because they can synthesize chemical fuels such as glucose from carbon dioxide and water by utilizing sunlight as an energy source.

- Other organisms that obtain energy from other organisms also ultimately depend on autotrophs for energy.

- One of the essential requirements for photosynthesis is the green pigment ‘chlorophyll’ which is present in the chloroplasts of green plants and some bacteria.

- The pigment is essential for ‘capturing’ sunlight which then drives the overall process of photosynthesis.

Photosynthesis equations

The process of photosynthesis differs in green plants and sulfur bacteria.

In plants, water is utilized along with carbon dioxide to release glucose and oxygen molecules.

In the case of sulfur bacteria, hydrogen sulfide is utilized along with carbon dioxide to release carbohydrates, sulfur, and water molecules.

Oxygenic Photosynthesis

The overall reaction of photosynthesis in plants is as follows:

Carbon dioxide + Water + solar energy → Glucose + Oxygen

$$6CO_2 + 6H_2O + \text{solar energy} \rightarrow C_6H_{12}O_6 + 6O_2$$

OR

Carbon dioxide + Water + solar energy → Glucose + Oxygen + Water

$$6CO_2 + 12H_2O + \text{solar energy} \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Anoxygenic Photosynthesis

The overall reaction of photosynthesis in sulfur bacteria is as follows:

$$CO_2 + 2H_2S + \text{light energy} \rightarrow (CH_2O) + H_2O + 2S$$

Photosynthetic pigments

- Photosynthetic pigments are the molecules involved in absorbing electromagnetic radiation, transferring the energy of the absorbed photons to the reaction center, resulting in photochemical reactions in the organisms capable of photosynthesis.

- The molecules of photosynthetic pigments are quite ubiquitous and are always composed of chlorophylls and carotenoids.

- In addition to chlorophyll, photosynthetic systems also contain another pigment, pheophytin (bacteriopheophytin in bacteria), which plays a crucial role in the transfer of electrons in photosynthetic systems.

- Moreover, other pigments can be found in particular photosynthetic systems, such as xanthophylls in plants.

Chlorophyll

Chlorophyll is the pigment molecule, which is the principal photoreceptor in the chloroplasts of most green plants.

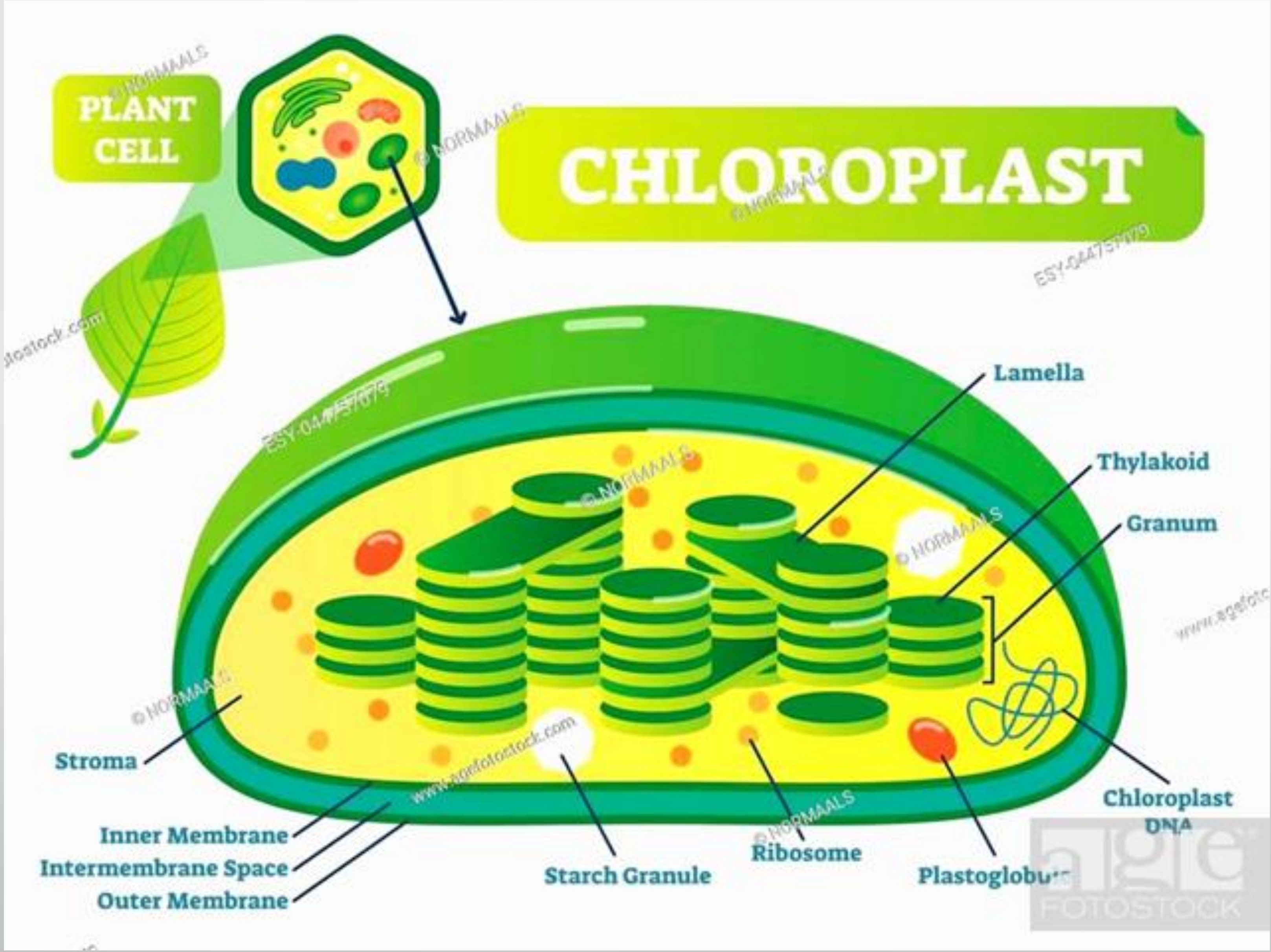
Chlorophylls consist of a porphyrin ring, which is bounded to an ion Mg^{2+}, attached to a phytol chain.

Chlorophylls are very effective photoreceptors because they contain networks of alternating single and double bonds.

In chlorophyll, the electrons are not localized to a particular atomic nucleus and consequently can more readily absorb light energy.

In addition, chlorophylls also have solid absorption bands in the visible region of the spectrum.

Chlorophylls are found either in the cytoplasmic membranes of photosynthetic bacteria, or thylakoid membranes inside plant chloroplasts.


PLANT CELL
CHLOROPLAST
Lamella
Thylakoid
Granum
Stroma
Chloroplast DNA
Inner Membrane
Intermembrane Space
Outer Membrane
Starch Granule
Ribosome

Bacteriorhodopsin

- Bacteriorhodopsin is another class of photosynthetic pigment that exists only in halobacteria.
- It is composed of a protein attached to a retinal prosthetic group.
- This pigment is responsible for the absorption of light photons, leading to a conformational change in the protein, which results in the expulsion of the protons from the cell.

Phycobilins

- Cyanobacteria and red algae employ phycobilins such as phycoerythrobilin and phycocyanobilin as their light-harvesting pigments.
- These open-chain tetrapyrroles have the extended polyene system found in chlorophylls, but not their cyclic structure or central Mg^{2+}.
- Phycobilins are covalently linked to specific binding proteins, forming phycobiliproteins, which associate in highly ordered complexes called phycobilisomes that constitute the primary light-harvesting structures in these microorganisms.

Carotenoids

- In addition to chlorophylls, thylakoid membranes contain secondary light-absorbing pigments, or accessory pigments, called carotenoids.
- Carotenoids may be yellow, red, or purple. The most important are β-carotene, which is a red-orange isoprenoid, and the yellow carotenoid lutein.
- The carotenoid pigments absorb light at wavelengths not absorbed by the chlorophylls and thus are supplementary light receptors.

Overall reaction of photosynthesis

In chemical terms, photosynthesis is a light-energized oxidation–reduction process. (Oxidation refers to the removal of electrons from a molecule; reduction refers to the gain of electrons by a molecule.) In plant photosynthesis, the energy of light is used to drive the oxidation of water (H_2O), producing oxygen gas (O_2), hydrogen ions (H^+), and electrons. Most of the removed electrons and hydrogen ions ultimately are transferred to carbon dioxide (CO_2), which is reduced to organic products. The overall reaction in which carbohydrates—represented by the general formula (CH_2O)—are formed during plant photosynthesis can be indicated by the following equation:

$$6\,CO_2 + 12\,H_2O + hv \longrightarrow C_6H_{12}O_6 + 6\,O_2 + 6\,H_2O$$

This equation is merely a summary statement, for the process of photosynthesis actually involves numerous reactions catalyzed by enzymes (organic catalysts). These reactions occur in two stages: the “light” stage, consisting of photochemical (i.e., light-capturing) reactions; and the “dark” stage, comprising chemical reactions controlled by enzymes. During the first stage, the energy of light is absorbed and used to drive a series of electron transfers, resulting in the synthesis of ATP and the electron-donor-reduced nicotine adenine dinucleotide phosphate (NADPH).

During the dark stage, the ATP and NADPH formed in the light-capturing reactions are used to reduce carbon dioxide to organic carbon compounds. This assimilation of inorganic carbon into organic compounds is called **carbon fixation**.

Difference Between Light and Dark Reaction

Major Difference – Light vs Dark Reaction

Light reaction and dark reaction are the two types of sequential processes that occur during the photosynthesis of plants. Light reaction occurs in the thylakoid membrane of chloroplast whereas the dark reaction occurs in the stroma of the chloroplast. Light energy from sunlight is trapped by chlorophylls during the light reaction of the photosynthesis. Dark reaction is catalyzed by various enzymes. The main difference between light and dark reaction is that light reaction is the first stage of photosynthesis, which traps light energy in order to produce ATP and NADPH whereas dark reaction is the second stage of photosynthesis, which produces glucose by using the energy form ATP and NADPH produced from the light reaction.

LIGHT REACTION VERSUS DARK REACTION

LIGHT REACTION	DARK REACTION
Light reaction occurs in the thylakoid membrane of the chloroplast	Dark reaction occurs in the stroma of the chloroplast
Depends on sunlight	Does not depend on sunlight
Chlorophyll is the pigments involved in this	No pigments are involved
Photolysis occurs in PS II	Photolysis does not occur
Oxygen is liberated	Carbon dioxide is fixed
ATP and NADPH are produced	Glucose is produced by using the energy from ATP and NADPH

What is Light Reaction

Light reaction is the first stage of photosynthesis, which produces ATP and NADPH by trapping the energy of sunlight by pigments called chlorophyll. Light reaction occurs in the thylakoid membrane of chloroplasts. Since light reaction depends on sunlight, it only occurs in the presence of sunlight. Chlorophyll A and B are the major types of chlorophylls involved in the light reaction. Chlorophyll A is the principal pigment trapping light energy, and chlorophyll B is the accessory pigment, which traps light and passes to chlorophyll A. The energy trapped by chlorophyll A is passed to the photosystem II (PS II) and photosystem I (PSI) in the form of high energy electrons. Exited PS II takes electrons by splitting water molecules into molecular oxygen, generating high energy electrons, which are transferred through a series of electron carriers into PS I. Splitting of water at PS II is called photolysis. PS I also generates high energy electrons by the energy of sunlight. These electrons are used in the formation of NADPH by the enzyme, NADP reductase. ATP synthase utilizes H ions, which are generated by photolysis in order to produce ATP. Light reaction is shown in figure 1. +

What is Dark Reaction

Dark reaction is the second stage of photosynthesis, which produces glucose from the energy of ATP and NADPH produced in the light reaction. It occurs in the stroma of the chloroplast. The dark reaction occurs in two reaction mechanisms: C3 cycle and C4 cycle. C3 cycle is called Calvin cycle whereas C4 cycle is called HatchStack cycle.

Calvin cycle occurs in three steps. During the first step, carbon dioxide is fixed into ribulose 1,5bisphosphate, forming an unstable six carbon compound, which is then hydrolyzed into three carbon compound, 3 phosphoglycerate. The enzyme involved in the process is rubisco. Due to the catabolic imperfection of rubisco, photorespiration occurs in the presence of low carbon dioxide concentrations. During the second step, some of the 3 phosphoglycerates are reduced in order to produce hexose phosphates. The remaining 3phosphoglycerates are used in the recycling of ribulose 1,5phosphate.

During C_4 cycle, double fixation of carbon dioxide is observed, increasing the efficiency of photosynthesis. Before entering into Calvin cycle, carbon dioxide is fixed into phosphoenol pyruvate, forming a four carbon compound, oxaloacetate. Oxaloacetate is converted into malate and transferred into bundle sheath cells in order to enter into Calvin cycle by removing carbon dioxide. Calvin cycle is shown in figure 2

The Pathway of Photosynthesis

C_3 Pathway (Calvin Cycle)

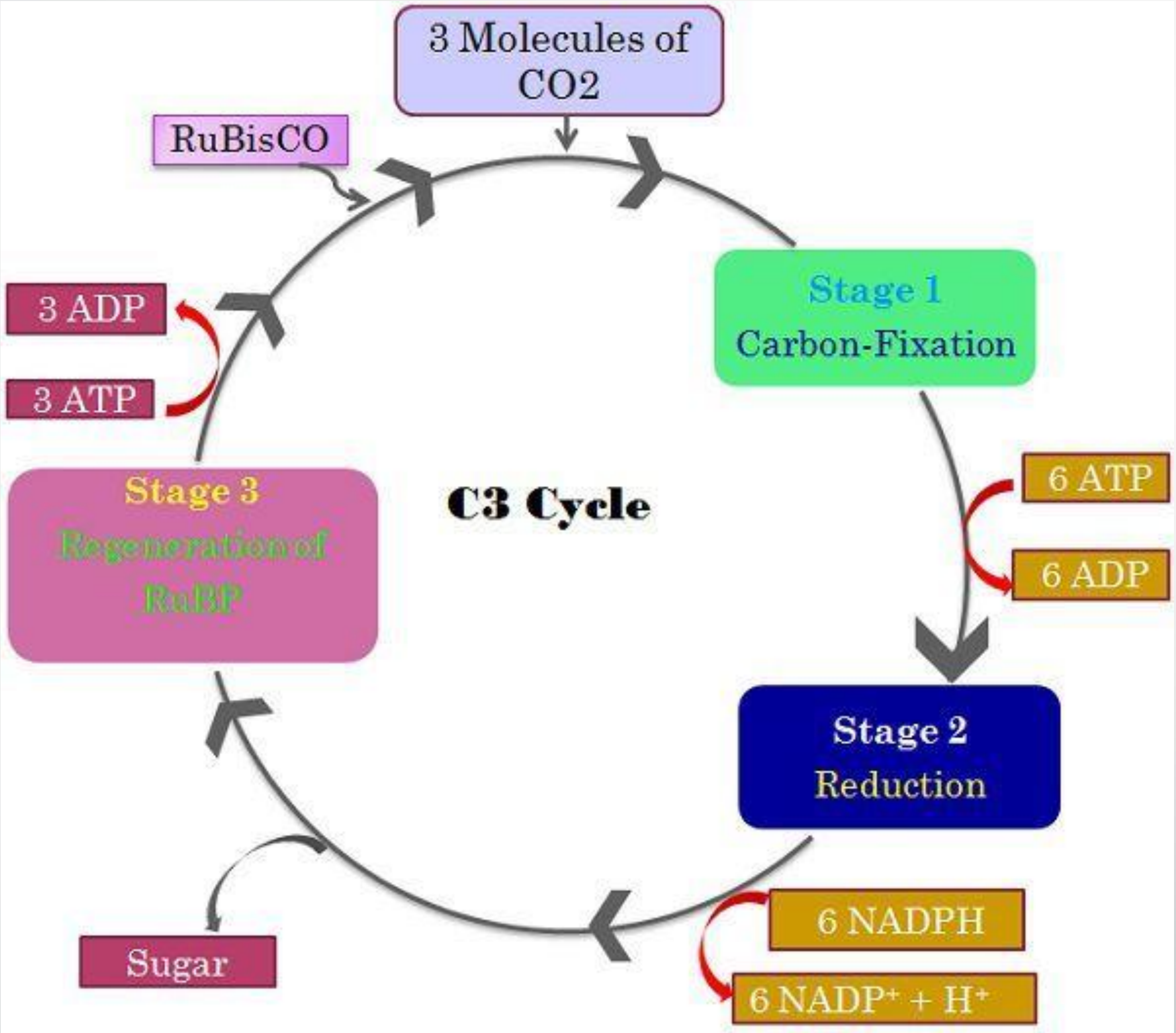
The majority of plants produce 3-carbon acid called 3-phosphoglyceric acid (PGA) as a first product during carbon dioxide fixation. Such a pathway is known as the C_3 pathway which is also called the Calvin cycle.

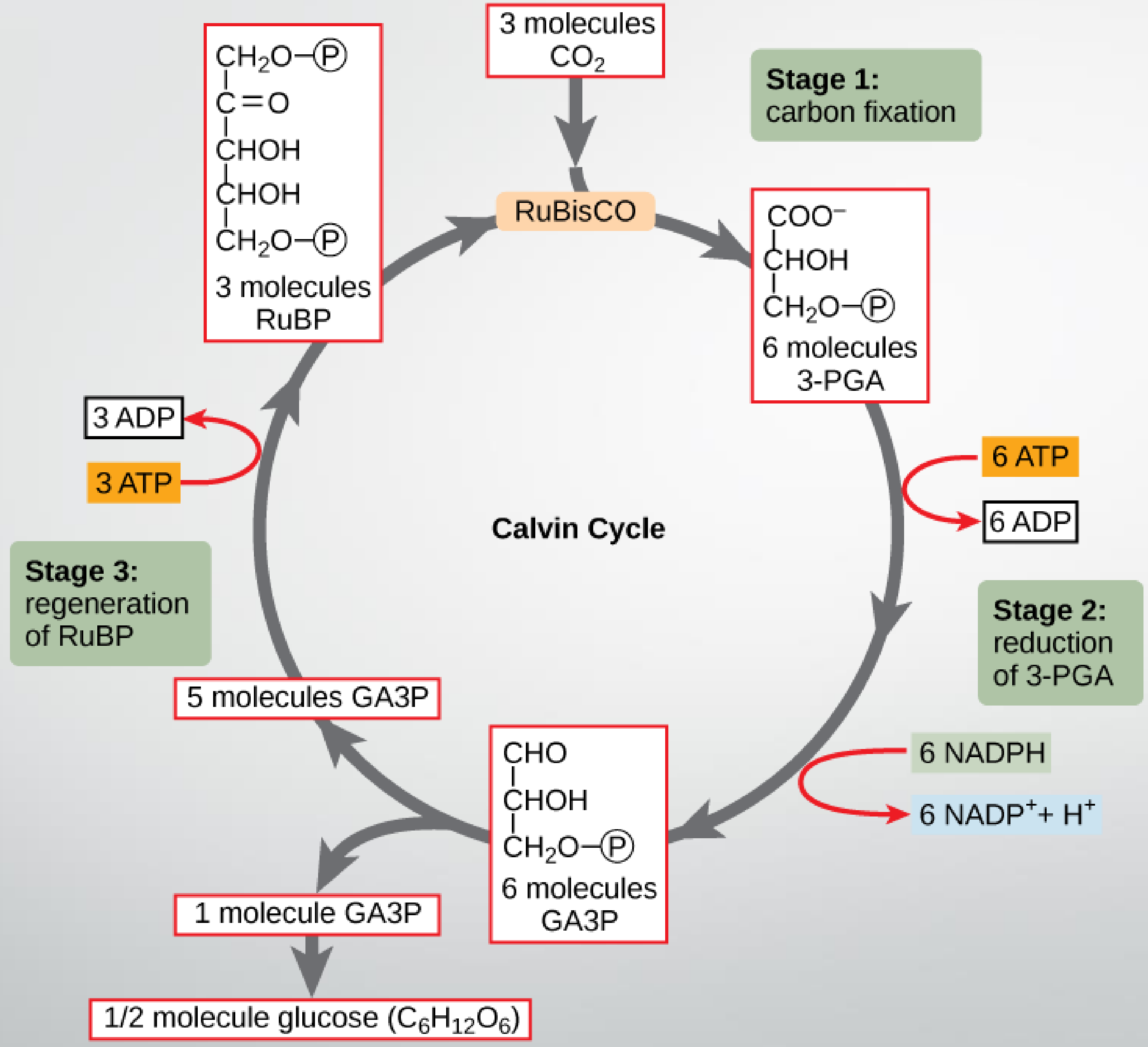
Calvin Cycle occurs in three steps:

1. **carboxylation**
2. **reduction**
3. **Regeneration**

In the first step, the two molecules of 3-phosphoglyceric acid (PGA) are produced with the help of the enzyme called RuBP carboxylase. Later in the second and third steps, the ATP and NADPH phosphorylate the 3-PGA and ultimately produces glucose. Then the cycle restarts again by regeneration of RuBP.

Beans, Rice, Wheat, and Potatoes are an example of plants that follow the C_3 pathway


3 Molecules of CO2
RuBisCO
Stage 1
Carbon-Fixation
6 ATP
6 ADP
Stage 2
Reduction
6 NADPH
6 NADP+ + H+
Sugar
Stage 3
Regeneration of RuBP
3 ATP
3 ADP
C3 Cycle



3 molecules CO_2
Stage 1: carbon fixation
RuBisCO
CH_2O-P | $C=O$ | CHOH | CHOH | CH_2O-P
3 molecules RuBP
COO⁻ | CHOH | CH_2O-P
6 molecules 3-PGA
6 ATP
6 ADP
Stage 2: reduction of 3-PGA
6 NADPH
6 $NADP^+$ + H^+
Calvin Cycle
3 ADP
3 ATP
Stage 3: regeneration of RuBP
5 molecules GA3P
CHO | CHOH | CH_2O-P
6 molecules GA3P
1 molecule GA3P
1/2 molecule glucose ($C_6H_{12}O_6$)

C4 Pathway (Hatch and Slack Pathway)

Every photosynthetic plant follows Calvin cycle, but in some plants, there is a primary stage to the Calvin Cycle known as C4 pathway. Plants in tropical desert regions commonly follow the C4 pathway. Here, a 4-carbon compound called oxaloacetic acid (OAA) is the first product by carbon fixation. Such plants are special and have certain adaptations as well.

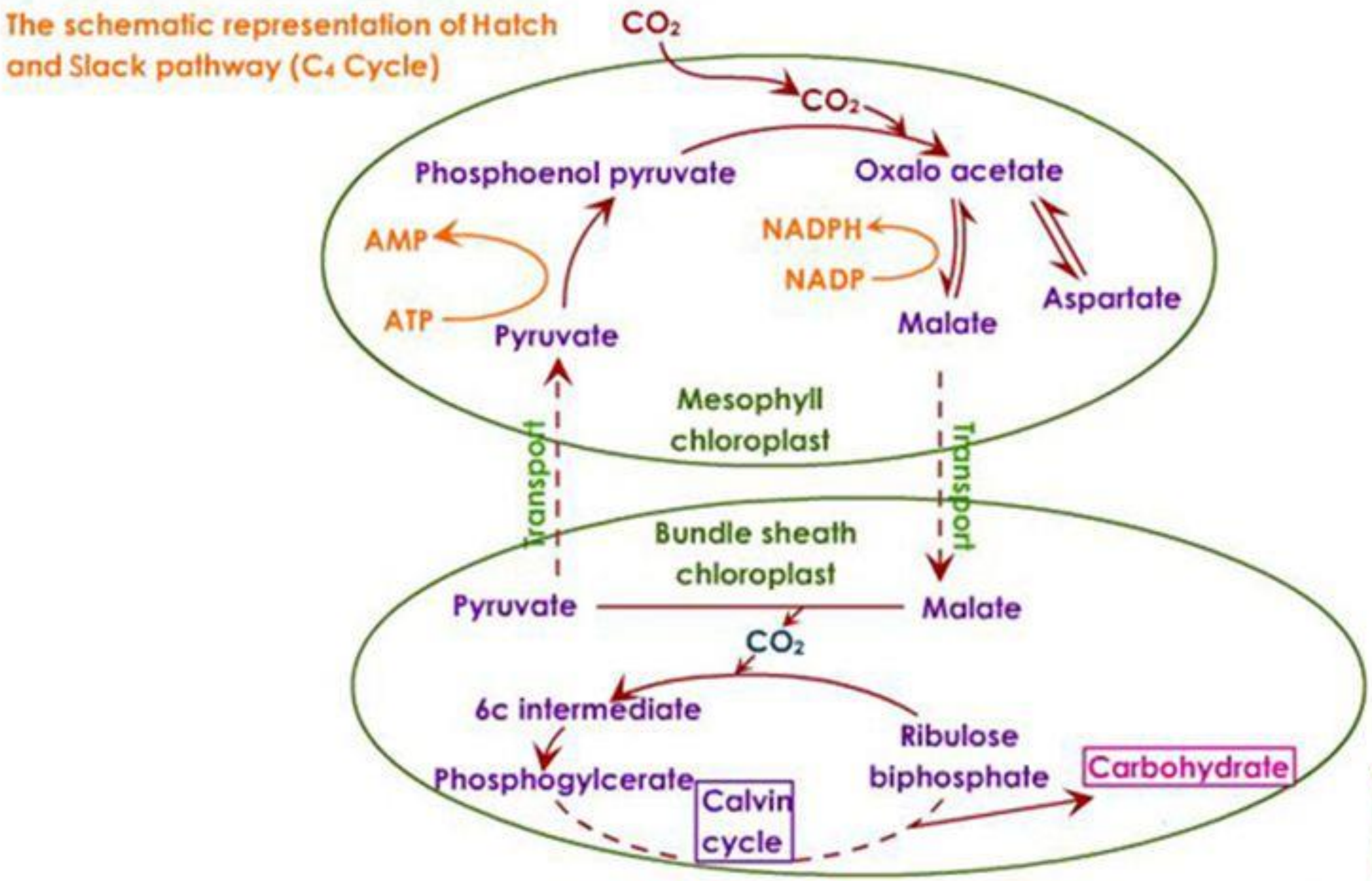
The C4 pathway initiates with a molecule called phosphoenolpyruvate (PEP) which is a 3-carbon molecule. This is the primary CO2 acceptor and the carboxylation takes place with the help of an enzyme called PEP carboxylase. They yield a 4-C molecule called oxaloacetic acid (OAA).

Eventually, it is converted into another 4-carbon compound known as malic acid. Later, they are transferred from mesophyll cells to bundle sheath cells. Here, OAA is broken down to yield carbon dioxide and a 3-C molecule.

The CO_2 thus formed, is utilized in the Calvin cycle, whereas 3-C molecule is transferred back to mesophyll cells for regeneration of PEP.

Corn, sugarcane and some shrubs are examples of plants that follow the C4 pathway. Calvin pathway is a common pathway in both C3 plants and C4 plants, but it takes place only in the mesophyll cells of the C3 Plants but not in the C4 Plants.

C4 cycle


The schematic representation of Hatch and Slack pathway (C_4 Cycle)
CO_2
CO_2
Phosphoenol pyruvate
Oxalo acetate
AMP
ATP
Pyruvate
NADPH
NADP
Malate
Aspartate
Mesophyll chloroplast
Transport
Transport
Bundle sheath chloroplast
Pyruvate
Malate
CO_2
6c intermediate
Ribulose biphosphate
Phosphogylcerate
Calvin cycle
Carbohydrate

Difference Between Light and Dark Reaction

Light Reaction: Light reaction occurs in the thylakoid membrane of the chloroplast.
Dark Reaction: Dark reaction occurs in the stroma of the chloroplast.

Light Reaction: Light reaction depends on the sunlight.
Dark Reaction: Dark reaction is independent of sunlight.

the decomposition or separation of molecules by the action of light.

Light Reaction: Chlorophylls are the pigments involved in the light reaction.
Dark Reaction: No pigments are involved in the dark reaction.

Light Reaction: Photolysis occurs in PS II during the light reaction.
Dark Reaction: No photolysis occurs during the dark reaction. Oxygen/Carbon dioxide

Light Reaction: Oxygen is liberated during the light reaction.
Dark Reaction: Carbon dioxide is fixed during the dark reaction.

Light Reaction: ATP and NADPH are produced during the light reaction.
Dark Reaction: Glucose is produced by using the energy from ATP and NADPH, produced in the light reaction.

Main Difference – Photosystem 1 vs 2

Photosystem I (PS I) and photosystem II (PS II) are two multi-subunit membrane-protein complexes involved in oxygenic photosynthesis.
Chlorophyll is the pigment involved in capturing light energy.
PS 1 contains chlorophyll B, chlorophyll A-670, Chlorophyll A-680, chlorophyll A-695, chlorophyll A-700 and carotenoids.
Chlorophyll A-700 is the active reaction center of PS 1.

PS 2 contains chlorophyll B, chlorophyll A-660, chlorophyll A-670, chlorophyll A-680, chlorophyll A-695, chlorophyll A-700, phycobilins and xanthophylls.
Chlorophyll A-680 is the active reaction center of photosystem 2.
The **main difference** between photosystem 1 and 2 is that **PS I absorbs longer wavelengths of light (>680 nm)** whereas **PS II absorbs shorter wavelengths of light (<680 nm)**.

PS I	PSII
Photosystem 1 is located on the outer surface of the thylakoid membrane	Photosystem 2 is located on the inner surface of the thylakoid membrane
The photocenter is P700	The photocenter is P680
Pigments absorb longer wavelengths of light (>680 nm)	Pigments absorb shorter wavelengths of light (<680 nm)
Involved in both cyclic and non-cyclic photophosphorylation	Only involved in cyclic photophosphorylation
No photolysis of water occurs	Photolysis of water occurs

Involved in both cyclic and non-cyclic photophosphorylation	Only involved in cyclic photophosphorylation
No photolysis of water occurs	Photolysis of water occurs
Main function is NADPH synthesis	Main function is ATP synthesis and hydrolysis of water
Contains chlorophyll B, chlorophyll A-670, Chlorophyll A-680, chlorophyll A-695, chlorophyll A-700 and carotenoids	Contains chlorophyll B, chlorophyll A-660, chlorophyll A-670, chlorophyll A-680, chlorophyll A-695, chlorophyll A-700, phycobilins and xanthophylls
Core is made up of psaA and psaB subunits	Core is made up of D1 and D2 subunits

What is Photosystem 1

PS I is the collection of pigments of chlorophyll, absorbing mostly the wavelength of light at 700 nm. The final stage of the light reaction is catalyzed by PS I. The reaction center of PS I consists of chlorophyll A-700. The core of the PS I is made up of psa A and psa B subunits.

Core subunits of the PS I are larger than the core subunits of PS II.

PS I is made up of chlorophyll A-670, Chlorophyll A-680, chlorophyll A-695, chlorophyll A-700, chlorophyll B and carotenoids. Photons from light are absorbed by accessory pigments and passed into the reaction center.

Reaction center itself is capable of absorbing photons. The energy of absorbed photons is released from the reaction center as high energy electrons. These electrons are transferred through series of electron carriers and finally taken up by $NADP^+$ reductase.

The enzyme, NADP+ reductase produces NADPH from these electrons. A schematic diagram of a photosystem is shown in *figure 1*.

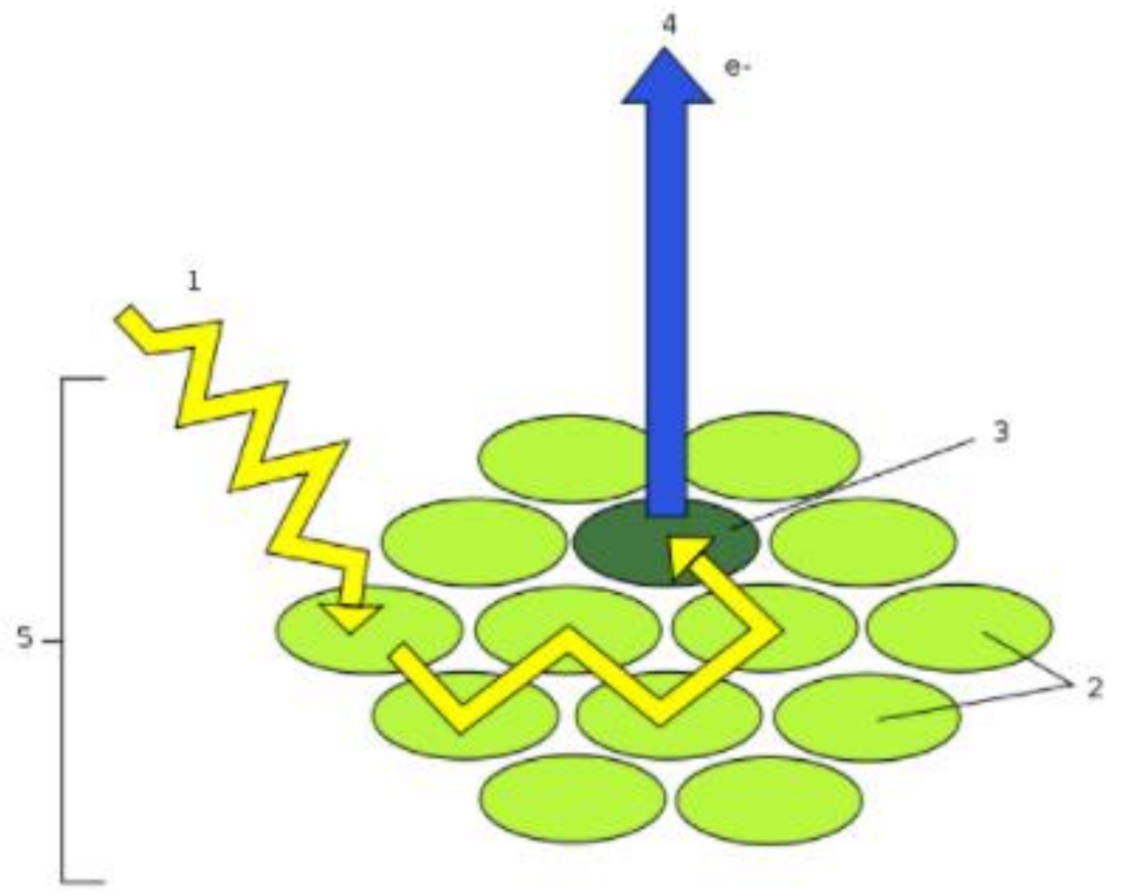


Figure 1: A photosystem

1 – Sunlight, 2 – Pigments, 3 – Reaction center, 4 – high energy electron flow, 5 – photosystem

What is Photosystem 2

PS II is the collection of pigments of chlorophyll, absorbing mostly the wavelength of light at 680 nm. The first stage of the light reaction is catalyzed by PS II. The reaction center of PS II consists of chlorophyll A-680.

PS II is an integral membrane protein, which consists of a core made up of D1 and D2 subunits.

PS II consists of a lot of other proteins and pigments arranged in the photosystem. The pigments are chlorophyll A-660, chlorophyll A-670, chlorophyll A-680, chlorophyll A-695, chlorophyll A-700, chlorophyll B and phycobilins and xanthophylls.

PS II achieves energy from absorbing photons or associated accessory pigments in the antenna complex. High energy electrons are generated from the energy of the absorbed photons. These electrons are passed through an electron transport chain.

During the electron transport chain, PS II passes electrons to plastoquinone (PQ), which carries the electrons to cytochrome *bf* complex. In PS II, photolysis of water occurs in order to replace the released electrons from PS II. For each water molecule, that is hydrolyzed, two molecules of PQH2 are formed.

The overall reaction in PS II is shown below.

2PQ (Plastoquinone) + $2H_2O \rightarrow O2 + 2PQH_2$ (Plastoquinol)

Difference Between Photosystem 1 and 2

Location

Photosystem 1: Photosystem 1 is located on the outer surface of the thylakoid membrane.

Photosystem 2: Photosystem 2 is located on the inner surface of the thylakoid membrane.

Photocenter

Photosystem 1: The photocenter of the photosystem 1 is P700.

Photosystem 2: The photocenter of the photosystem 2 is P680.

Absorbing Wavelength

Photosystem 1: Pigments absorb longer wavelengths of light (>680 nm).

Photosystem 2: Pigments absorb shorter wavelengths of light (<680 nm).

Photophosphorylation

Photosystem 1: Photosystem 1 is involved in both cyclic and non-cyclic photophosphorylation.

Photosystem 2: photosystem 2 is only involved in cyclic photophosphorylation.

Photolysis

Photosystem 1: No photolysis of water occurs in photosystem 1.

Photosystem 2: Photolysis of water occurs in photosystem 2.

Main Function

Photosystem 1: The main function of the photosystem 1 is NADPH synthesis.

Photosystem 2: The main function of the photosystem 2 is ATP synthesis and hydrolysis of water.

Electron Replacement

Photosystem 1: Released high energy electrons are replaced by the releasing energy of photolysis.

Photosystem 2: Released high energy electrons are replaced by the electrons released from photosystem II.

Pigments

Photosystem 1: PS 1 contains chlorophyll B, chlorophyll A-670, Chlorophyll A-680, chlorophyll A-695, chlorophyll A-700 and carotenoids.

Photosystem 2: PS 2 contains chlorophyll B, chlorophyll A-660, chlorophyll A-670, chlorophyll A-680, chlorophyll A-695, chlorophyll A-700, phycobilins and xanthophylls.

Compositon of the Core

Photosystem 1: The core of the PS I is made up of psaA and psaB subunits.

Photosystem 2: The core of the PS II is made up of D1 and D2 subunits.

Conclusion

PS I and PS II are the two photosystems which drive the light reaction of photosynthesis. The **first stage of the light reaction occurs in PS II** whereas the final stage of the light reaction occurs in PS I. Each of the two photosystems are made up of a collection of proteins and pigments. Chlorophylls are the major pigments found in photosystems. The reaction center of PS I consists of chlorophyll A-700 and the reaction center of PS II consists of chlorophyll A-680.

Other than chlorophylls, carotenoids are also present in photosystems. The core of the PS I is made up of large subunits of psaA and psaB proteins. The core of the PS II is made up of comparatively small subunits of D1 and D2. Water molecules are hydrolyzed at PS II in order to replace the releasing electrons of each of the two photosystems. Electrons released from PS I are used by NADP+ reductase, producing NADPH. However, the main difference between Photosystem 1 and 2 is the wavelengths of sunlight, which are absorbed by each of the reaction centers of photosystems.

Thank you