UNIT 3(3.1)

Photophosphorylation: Cyclic and Non Cyclic

Photophosphorylation is the process of utilizing light energy from photosynthesis to convert ADP to ATP. It is the process of synthesizing energy-rich ATP molecules by transferring the phosphate group into ADP molecule in the presence of light.

Who discovered Photophosphorylation?

Photophosphorylation was discovered in chloroplasts by D. Arnon and coworkers, and in bacterial 'chromatophores' (inter cytoplasmic membranes) by A. **Frenkel**.

Why is it called Photophosphorylation?

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).

Where does Photophosphorylation occur?

This **occurs** in the chloroplasts of cells, specifically, in the thylakoid membranes. In **photophosphorylation**, or the light-dependent reactions, light is absorbed by chlorophyll and other pigment molecules. The light energy is used to create a high-energy electron donor and a lower-energy electron acceptor. Electrons then move spontaneously from donor to acceptor through an electron transport chain. All organisms produce ATP, which is the universal energy currency of life. In photosynthesis this commonly involves photolysis, or photo-dissociation of water and a continuous unidirectional flow of electrons from water to photoststem-II. Only two sources of energy are available to living organisms: Sunlight and reduction-oxidation (redox) reactions.

Photophosphorylation is of two types: **Non-Cyclic Photophosphorylation** and **Cyclic Photophosphorylation**.

Non-cyclic photophosphorylation:

Non-cyclic photophosphorylation is a two-stage process involving two different chlorophyll photosystems. Being a light reaction, non-cyclic photophosphorylation occurs in the thylakoid membrane. First, a water molecule is broken down into $2H^+ + 1/2\ O_2 + 2e^-$ by a process called photolysis (or *light-splitting*). The two electrons from the water molecule are kept in photosystem II, while the $2H^+$ and $1/2O_2$ are left out for further use. Then a photon is absorbed by chlorophyll pigments surrounding the reaction core center of the photosystem. The light excites the electrons of each pigment, causing a chain reaction that eventually transfers energy to the core of photosystem II, exciting the two electrons that are transferred to the primary electron acceptor, pheophytin. The deficit of electrons is replenished by taking electrons from another molecule of water. The electrons transfer from pheophytin to plastoquinone which takes the $2e^-$ from Pheophytin, and two H^+ Ions from the stroma and forms PQH_2, which later is broken into PQ, the $2e^-$ is released to Cytochrome b_6f complex and the two H^+ ions are released into thylakoid lumen. The electrons then pass through the Cyt b_6 and Cyt f. Then they are passed to plastocynin providing the energy for hydrogen ions (H^+) to be pumped into the thylakoid space. This creates a gradient, making H^+ ions flow back into the stroma of the chloroplast, providing the energy for the regeneration of ATP. The photosystem II complex replaced its lost electrons from an external source; however, the two other electrons are not returned to photosystem II as they would in the analogous cyclic pathway. Instead, the still-excited electrons are transferred to a photosystem I complex, which boosts their energy level to a higher level using a second solar photon. The highly excited electrons are transferred to the acceptor molecule, but this time is passed on to an enzyme called Ferredoxin-$NADP^+$ reductase which uses them to catalyze the reaction (as shown):

$$NADP^+ + 2H^+ + 2e^- \rightarrow NADPH + H^+$$

This consumes the H^+ ions produced by the splitting of water, leading to a net production of molecular O_2, ATP, and $NADPH+H^+$ with the consumption of solar photons and water. The concentration of NADPH in the chloroplast may help regulate which pathway electrons take through the light reactions. When the chloroplast runs low on ATP for the Calvin Cycle, NADPH will accumulate and the plant may shift from noncyclic to cyclic electron flow. This pathway is also called as the 'Z-scheme of photosynthesis' because the redox diagram from P_{680} to P_{700} looks like a big alphabet 'Z'. In this scheme of electron transport, the electron ejected from PSII did not return to its place of origin, instead it was passed on to PSI. Similarly, the electron emitted from PSI did not cycle back but was used to reduce $NADP^+$ into NADPH + H^+. Therefore, this electron transport has been called as Non-Cyclic electron transport and the phosphorylation as Non- Cyclic Photophosphorylation. Thus in this system, the PSI is reduced by electrons coming from PSII and the PSII is reduced by electrons coming from water. This is associated with photo-oxidation of water releasing molecular O^2.

Significance of Non-Cyclic Photophosphorylation

Non-Cyclic electron transport/ Photophosphorylation comprises of the sequence of electron transport where $NADP^+$ is reduced by PSI, the PSI is reduced by PSII and finally PSII is reduced by electrons coming from photo-oxidation of water. Thus the cycle is broken during this electro transport and therefore, it is called non-cyclic. The photo-oxidation of water and evolution of molecular oxygen is associated with this type of electron transport. It released a major portion of protons which finally generate proton motive force to produce ATP. The non- cyclic electron transport is most important in photosynthesis as it supplies assimilatory power in the form of NADPH and ATP for CO_2 assimilation and purifies the atmospheric air.

Cyclic photophosphorylation:

This form of photophosphorylation occurs on the stroma lamella or fret channels. In cyclic photophosphorylation, the high energy electron released from P_{700} of PS1 flow down in a cyclic pathway. In cyclic electron flow, the electron begins in a pigment complex called photosystem I, passes from the primary acceptor to ferredoxin and then to plastoquinone, then to cytochrome b_6f (a similar complex to that found in mitochondria), and then to plastocynin before returning to photosystem-I. This transport chain produces a proton-motive force, pumping H^+ ions across the membrane; this produces a concentration gradient that can be used to power ATP synthase during chemiomosis. This pathway is known as cyclic photophosphorylation, and it produces neither O_2 nor NADPH. Unlike non-cyclic photophosphorylation, $NADP^+$ does not accept the electrons; they are instead sent back to cytochrome b_6f complex.

In bacterial photosynthesis, a single photosystem is used, and therefore is involved in cyclic photophosphorylation. It is favored in anaerobic conditions and conditions of high irradiance and CO_2 compensation points. Cyclic photophosphorylation occurs in both aerobic and anaerobic conditions. In this electron transport system, the electron which was ejected from P_{700} molecule is cycled back, thus the process is known as cyclic electron transport and the phosphorylation as cyclic photophosphorylation.

■ **What is the purpose of Cyclic Photophosphorylation?**

Cyclic photophosphorylation can be used to produce a steady supply of ATP in the presence of sunlight. However, ATP is a highly reactive molecule and hence cannot be readily stored within the cell. **Non-cyclic photophosphorylation** produces NADPH in addition to ATP (this requires the presence of water)

■ **What is produced in cyclic Photophosphorylation**?

Under certain conditions, the photo-excited electrons take an alternative path called **cyclic** electron flow, which uses photosystem I (P_{700}) but not photosystem II (P_{680}. This process **produces** no NADPH and no O_2, but it does make ATP. This is called **cyclic photophosphorylation**

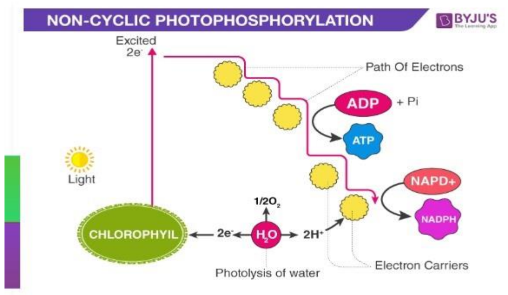
■ **What is the importance/significance of cyclic Photophosphorylation?**

In this electron transport system, the electron which was emitted from P_{700} molecule (PSI) is cycled back. It provides ATP for dark reaction which is non-sufficiently produced in non –cyclic process. The cyclic transport is not common and occurs under special conditions when NADPH starts accumulating in the chloroplast.

■ **What are the products of Photophosphorylation?**

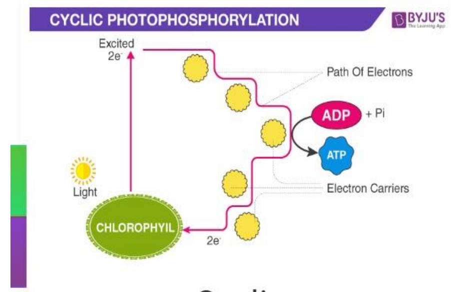
The products of linear photophosphorylation, **ATP** and **NADPH**, are used in the light-independent reactions of photosynthesis (also termed the carbon fixation cycle or the **Calvin cycle**). This cycle uses **ATP** and **NADPH** to convert **CO_2** into simple sugar.

Non-Cyclic Photophosphorylation

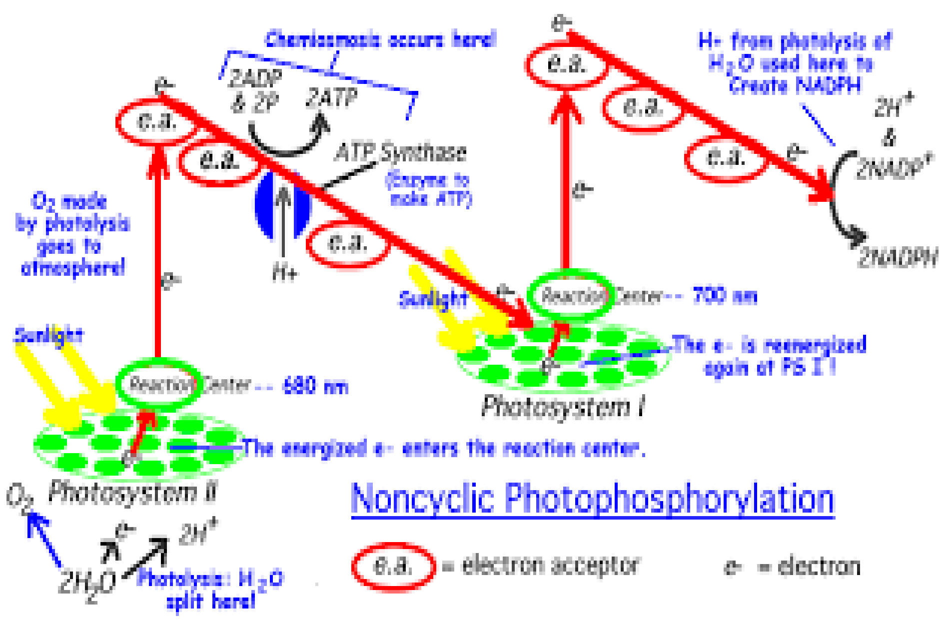


Non-cyclic Photophosphorylation

Cyclic Photophosphorylation



Cyclic Photophosphorylation



Distinguish between non-cyclic and cyclic photophosphorylation

Features	Non-cyclic photophosphorylation	Cyclic photophosphorylation.
Conditions under which process occurs.	When plants require ATP and NADPH	When plants require only ATP.
Pathway of electrons.	Non-cyclic	Cyclic
For electron donor (source of electrons)	Water	Photosystem I
Last electron acceptor (destination of electrons)	NADP+	Photosystem I
Establishing proton gradient for the synthesis of ATP	High hydrogen ion concentration in the thylakoid space is due to photolysis of water and active transport of hydrogen ions from the stroma, across the thylakoid membrane, into the thylakoid space.	High hydrogen ion concentration in the thylakoid space is due to active transport of hydrogen ions from the stroma, across the thylakoid membrane, into the thylakoid space.
Products	ATP,NADPH and oxygen	Only ATP.

Difference between cyclic and noncyclic electron transport and photophosphorylation

Cyclic photophosphorylation	Noncyclic photophosphorylation
1. It is related with PS I	1. It is associated with both PS I and PS II.
2. The electron expelled from chlorophyll molecule is cycled back	2. The electrons are not cycled back but compensated by the electrons from photolysis of water.
3. Photolysis of water and oxygen do not occur.	3. Photolysis of water and evolution of evolution of oxygen occurs.
4. Photophosphorylation occurs at two places.	4. Photophosphorylation takes place only at one place.
5. NADP is not reduced.	5. $NADP^+$ is reduced to $NADPH_2$.

Mechanisms of Phosphorylation

In the process of Phosphorylation, the production of ATP from ADP and inorganic phosphate requires energy which ultimately comes from light. There are evidences that light driven electron transport and photophosphorylation are coupled where energy released in electron transport is trapped in the synthesis of ATP. However, the mechanism by which the ATP is produced in photosynthesis is not well known. There are three possible mechanisms which explain photophosphorylation:

1. Conformational Coupling. 2. Chemical Coupling 3. Chemiosmotic Coupling

1. Conformational Coupling Hypothesis: According to this, the thylakoid membrane under goes some structural changes including high energy states which favour ATPase catalyzed production of ATP. Further evidences and detailed mechanism is missing.

2. Chemical Coupling Hypothesis: This hypothesis was proposed by Slater (1954). According to this, the electron transport and ATP production are coupled and an unknown coupling factor (probably a protein) acts as energy transfer agent. Though this hypothesis was supported by many evidences, it has not much following as compared to Chemiosmotic coupling hypothesis.

3. Chemiosmosis Coupling Hypothesis: The most accepted and well established model for photophosphorylation was proposed by Peter Mitchell (1961, 1968 and 1976), known as Mitchell's Chemiosmotic Hypothesis. This hypothesis is based on the following assumptions:

A multicomponent enzyme complex – the ATPase complex (also known as coupling factor) is plugged through a thylakoid membrane at various places. The complex is localized both within and upon the surface of membrane. It consists of an extrinsic protein CF_1 which binds to a hydrophobic compound CF_0 which serves as a Proton channel. The ATPase complex utilizes the proton motive force (i.e. an electric potential gradient and a pH difference) to catalyze ATP synthesis from ADP and inorganic phosphate. Though the actual mechanism by which CF makes use of energy released from the downhill movement of H+ to convert ADP and Phosphate to ATP, is not clear, an outline of the hypothesis is as:

i) The photo induced transport of electrons, in the light reaction, is accompanied by release of protons in the internal space of thylakoid sac. These protons are released in the lumen from—(a)

Water oxidizing component of PSII, (b) Plastoquinone pool when PQH_2 is oxidized back to PQ and (c) Cyclic electron transport around PSII (through $PQH_2 \rightarrow PQ$).

ii) There are sufficient evidences that $8H^+$ are released by non-cyclic transport (i.e. 4 from H_2O oxidation and 4 from PQ function) and $4H^+$ by cyclic electron transport (through $PQH_2 \rightarrow PQ$). Thus a total of $12H^+$ are released into the inner space when two molecules of H_2O are oxidized, one molecule of O_2 is evolved and 2 molecules of $NADP^+$ are reduced.

iii) Released of H^+ into inner space of thylakoid creates a great difference in pH (about 3pH units)between the outside and inside of thylakoid membrane. It has been estimated that the pH of outside medium becomes around 8 whereas that of thylakoid lumen around 5 i.e., H^+ concentration inside the lumen becomes 1000 times as great as in the stroma. Under such conditions of electron transport cannot continue until the proton from lumen is translocated out.

iv) Thylakoid membrane itself is not permeable to protons. The protons, therefore, flow towards the outside of thylakoid membrane through ATPase complex. The return flow of proton electrochemical gradient creates a proton motive force. The CF_o of ATPase complex provides a channel for H^+ translocation across the membrane. The flow of protons, down the electrochemical gradient when reaching the coupling factor CF_1, results in the formation of ATP from ADP and inorganic phosphate.

v) It is now well established that single molecule of ATP is formed for every $3H^+$ passing through ATPase complex. Thus, about 4ATP molecules will be formed for $12H^+$ released during non-cyclic and cyclic electron transport. These ATP molecules are just enough to fix one molecule of CO_2 into a sugar phosphate.

REFERENCE/ SYLLABUS BOOKS (for material and diagrams)

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2. A Textbook of Plant Physiology by SK Verma (S. Chand Publications)

3. Plant Physiology and Metabolism by Dr. H. N. Srivastava (Pradeep Publications)

4. Plant Physiology and Metabolism by Dr. Kamaljit and co-workers (S. VINESH &Co.)