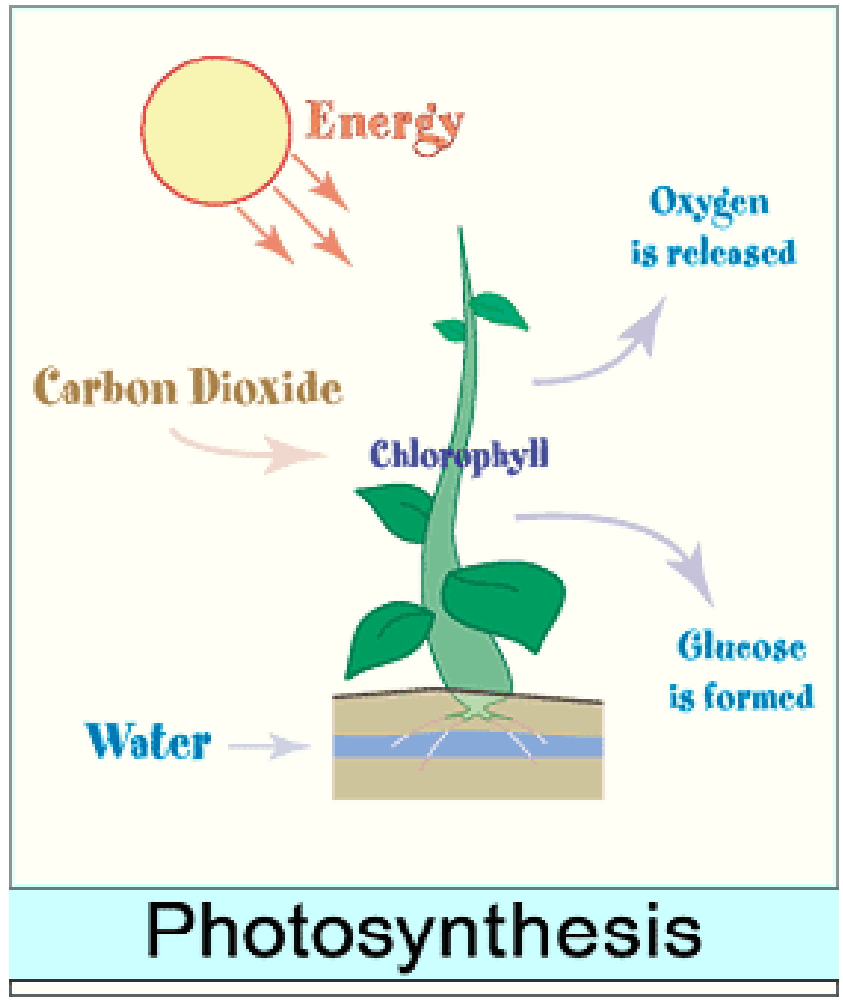
Lecture 20

Bioenergetics part 2

Photosynthesis

- Photosynthesis is a process in which green plants use energy from the sun to transform water, carbon dioxide, and minerals into oxygen and organic compounds.
- Photosynthesis happens when water is absorbed by the roots of green plants and is carried to the leaves by the xylem, and carbon dioxide is obtained from air that enters the leaves through the stomata and diffuses to the cells containing chlorophyll. The green pigment chlorophyll is uniquely capable of converting the active energy of light into a form that can be stored (in food) and used when needed.
- Photosynthesis provides us with most of the oxygen we need in order to breathe. We, in turn, exhale the carbon dioxide needed by plants. Plants are source of food for humans and animals.



Energetics of Photosynthesis

- Sunlight is absorbed into the leaf by a green pigment called **chlorophyll**
- The light energy is then converted into a chemical energy in the form of starch or sugar:

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

- This equation translates as six molecules of **water** (6H2O) plus six molecules of **carbon dioxide** (6CO2) produce one molecule of **sugar** (C6H12O6) plus six molecules of **oxygen** (O2).

Photosynthesis and cell respiration

photosynthesis

$$CO_2 + H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + O_2$$

Needs energy from sun

and plant pigment system

Energy conversion and storage

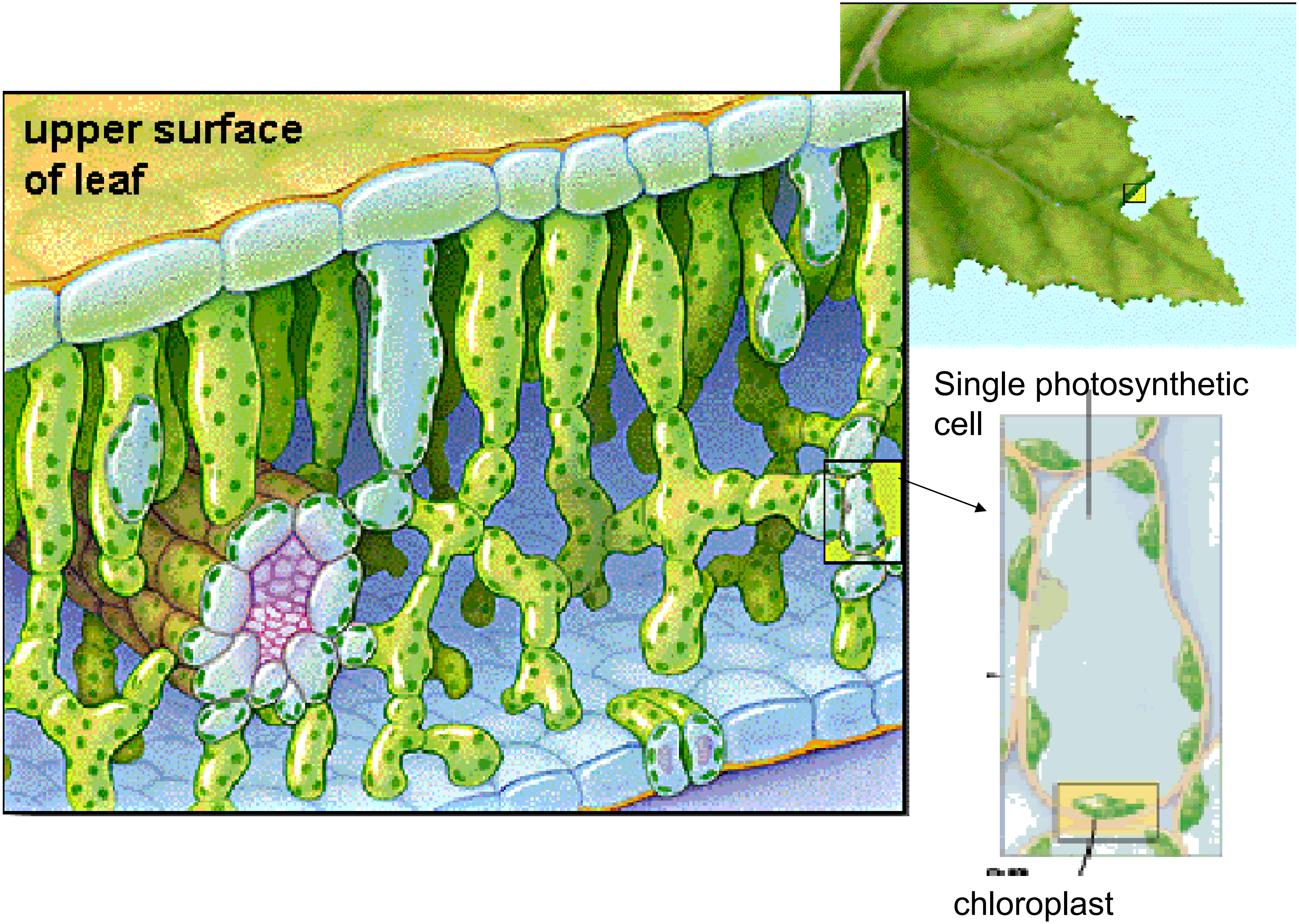
cell respiration

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

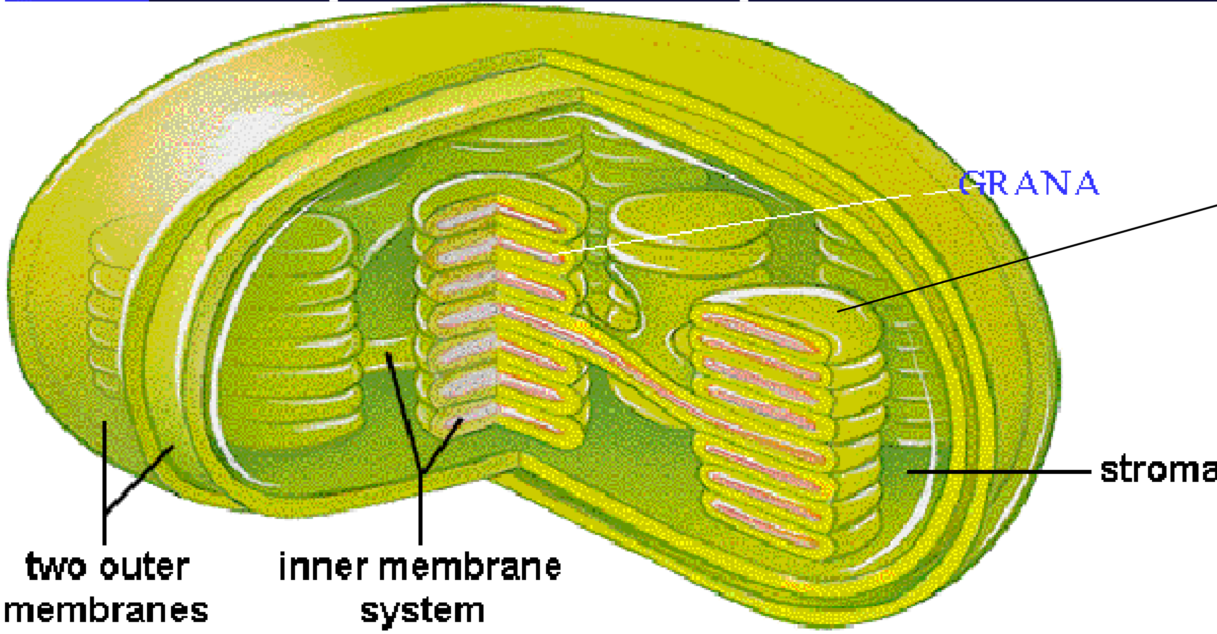
Energy conversion and release

Photosynthesis

- Energy storage process in autotropic plant cells
- Photosynthesis takes place primarily in plant leaves,
- in organelle called **chloroplast,** which is
- double membrane bound structure


upper surface of leaf
Single photosynthetic cell
chloroplast

Chloroplast compartments



Thylakoid is the structural unit of photosynthesis.

Both photosynthetic prokaryotes and eukaryotes have these flattened sacs/vesicles containing photosynthetic chemicals.

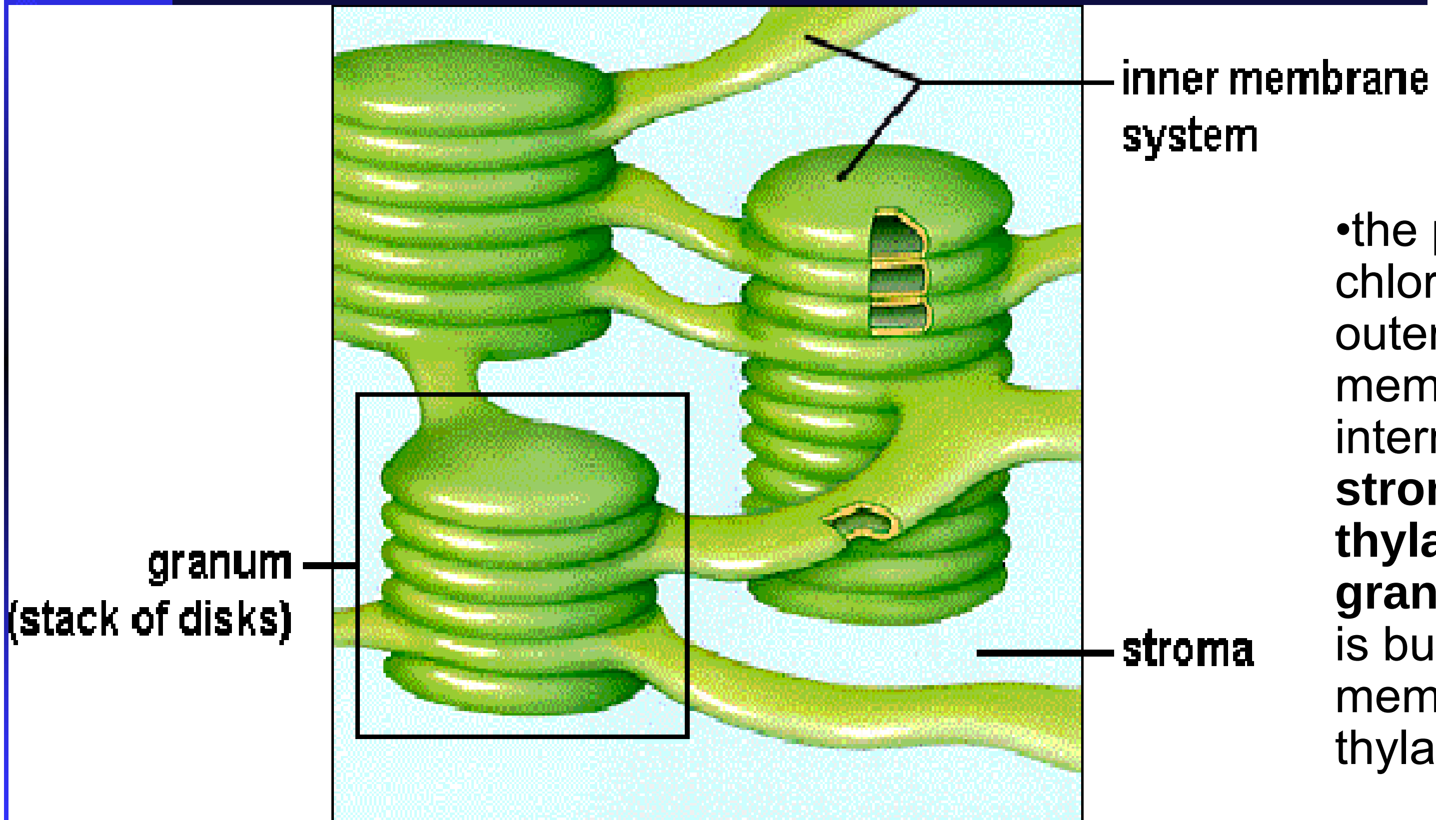
Inner membrane – series of stacked membrane = granum (grana - plural)

Each granum is made of number of individual membrane units called thylakoid

Granum is a stack of thylakoids

Clear non-membrane portion of chloroplast - stroma

DETAILS OF CHLOROPLAST STRUCTURE
INNER MEMBRANES

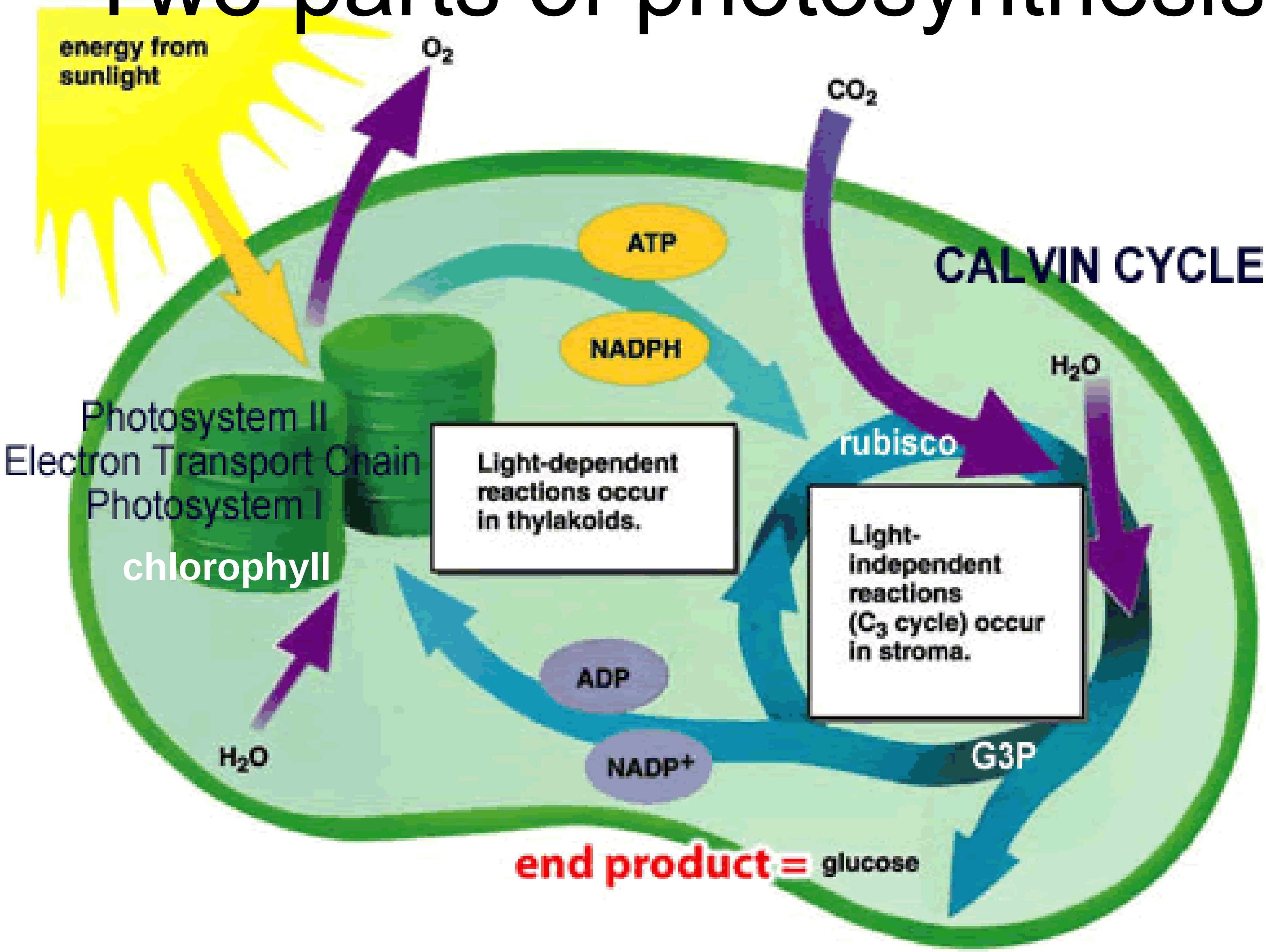


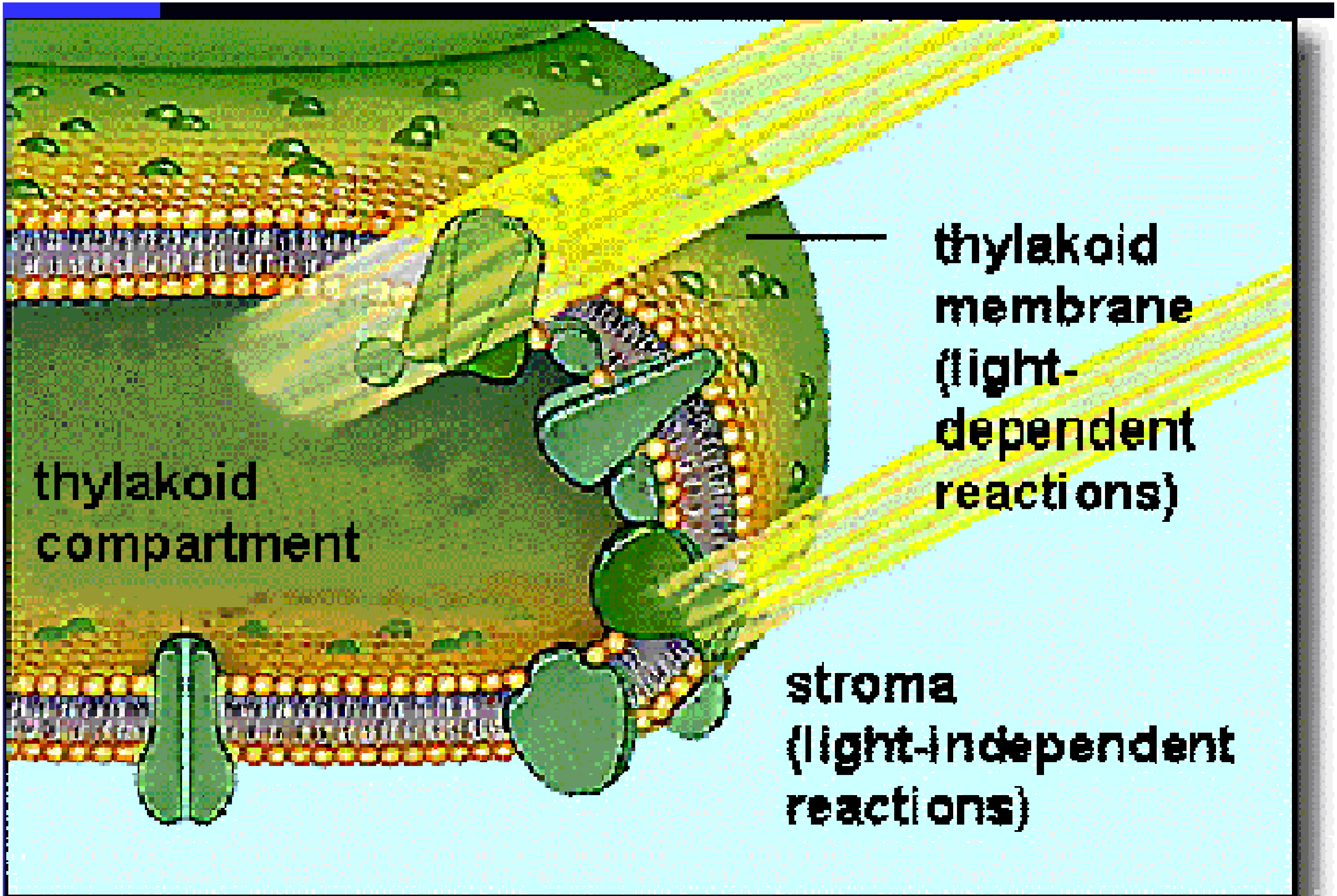
•the parts of a chloroplast include the outer and inner membranes, intermembrane space, **stroma**, and **thylakoids** stacked in **grana**. The chlorophyll is built into the membranes of the thylakoids.

Light dependent part of photosynthesis takes place in grana, requires light energy

Dark – light independent part – takes place in stroma, does not require light energy

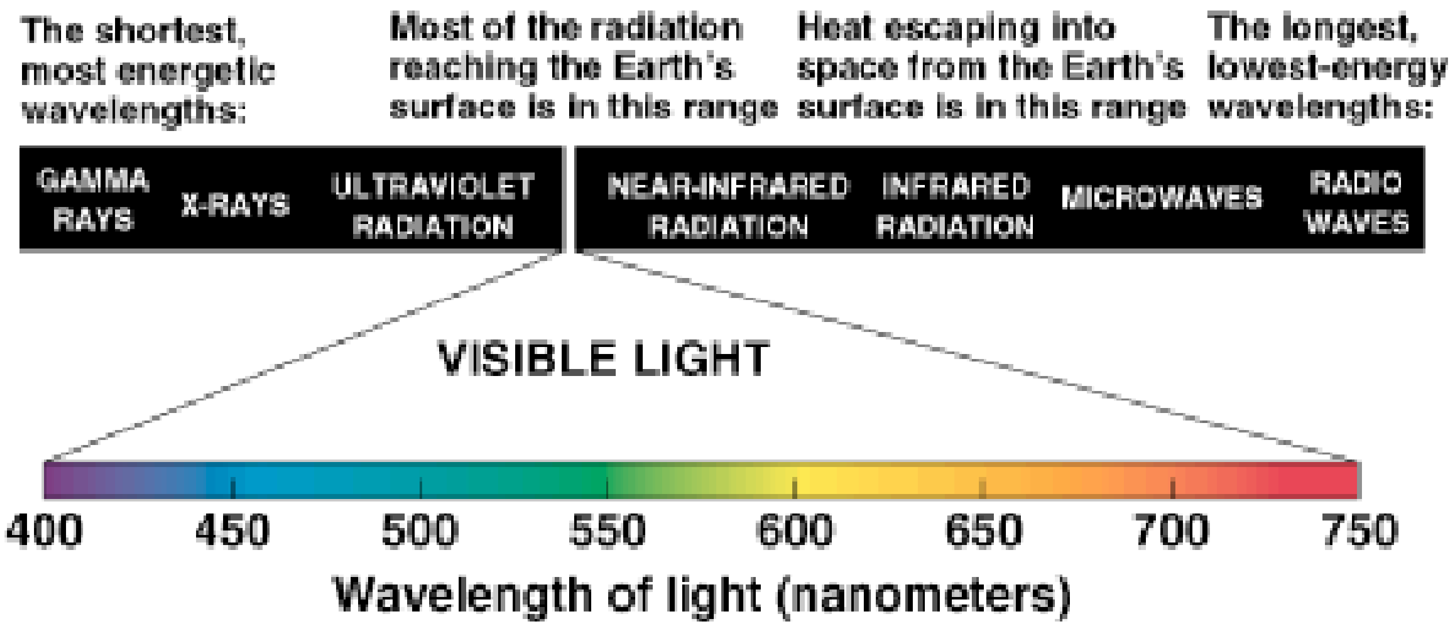
Two parts of photosynthesis




thylakoid membrane (light-dependent reactions)
thylakoid compartment
stroma (light-independent reactions)

Photosynthesis – visible light

- Photosynthesis responsive to certain wave lengths (colors) of light
- Visible spectrum: violet – red



- Light energy is adsorbed by pigments which are concentrated in the inner membrane portion of chloroplast

Photosynthesis requires pigments

- The **light reaction** happens in the thylakoid membrane and converts light energy to chemical energy. This chemical reaction must, therefore, take place in the light.

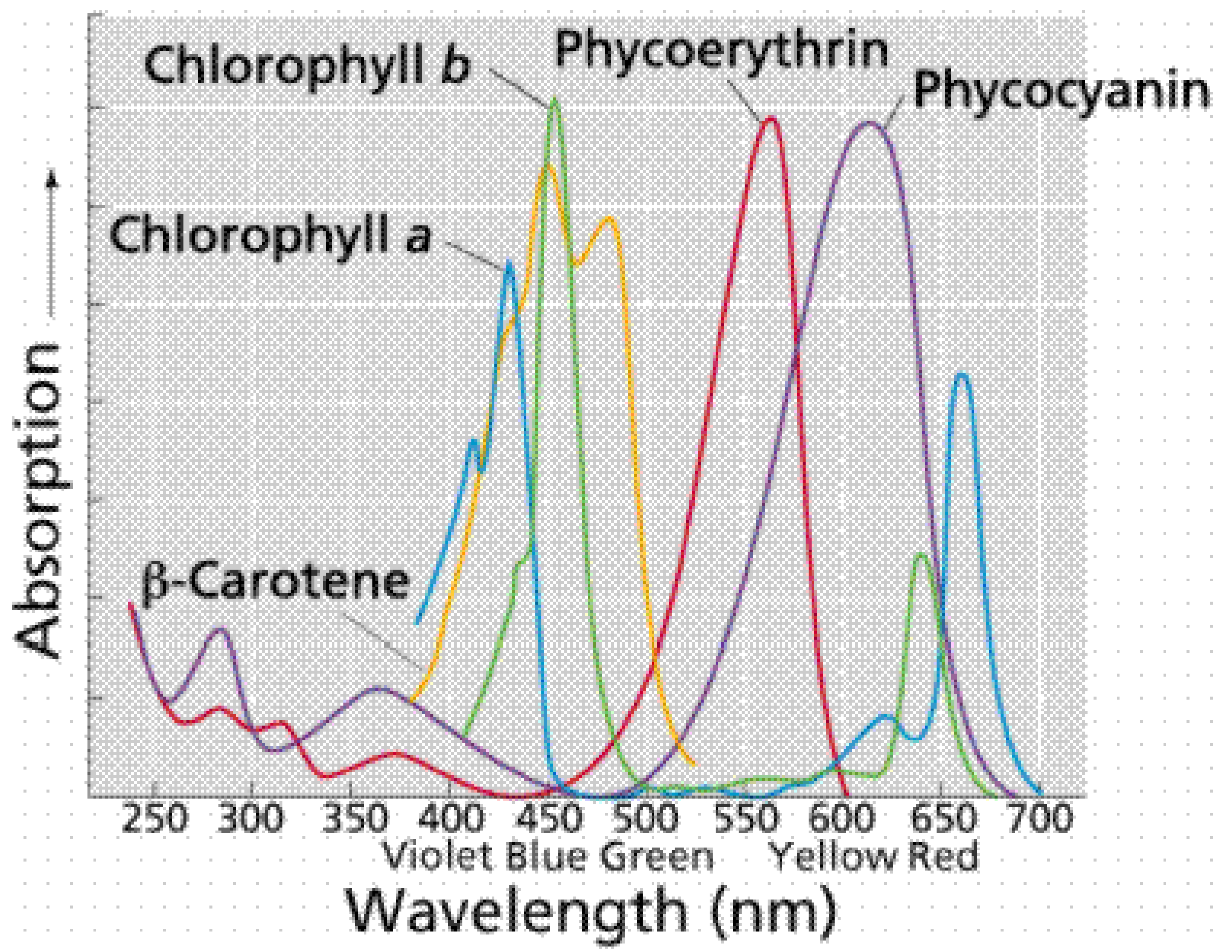
- Light is absorbed by pigments.
- A pigment is any substance that absorbs light. The color of the pigment comes from the wavelengths of light reflected (in other words, those not absorbed).

- **Chlorophyll** and several other pigments such as **beta-carotene** are organized in clusters in the thylakoid membrane and are involved in the light reaction.

- Chlorophyll looks green because it absorbs red and blue light, making these colors unavailable to be seen by our eyes. It is the green light which is NOT absorbed that finally reaches our eyes, making chlorophyll (and plants) appear green.

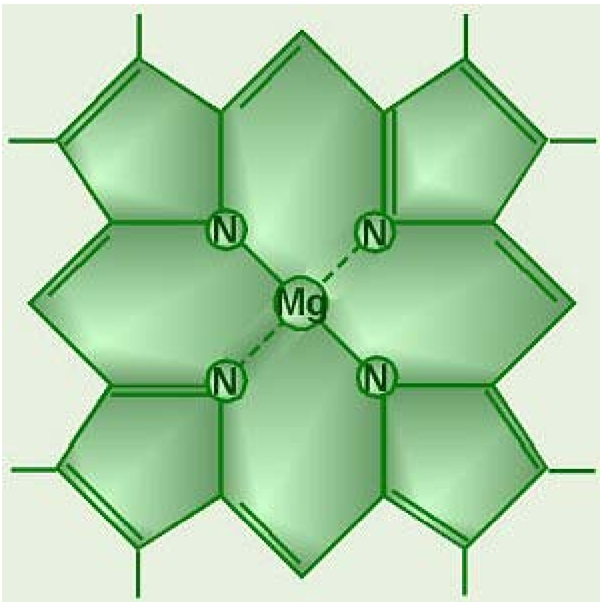
Absorption spectra of photopigments

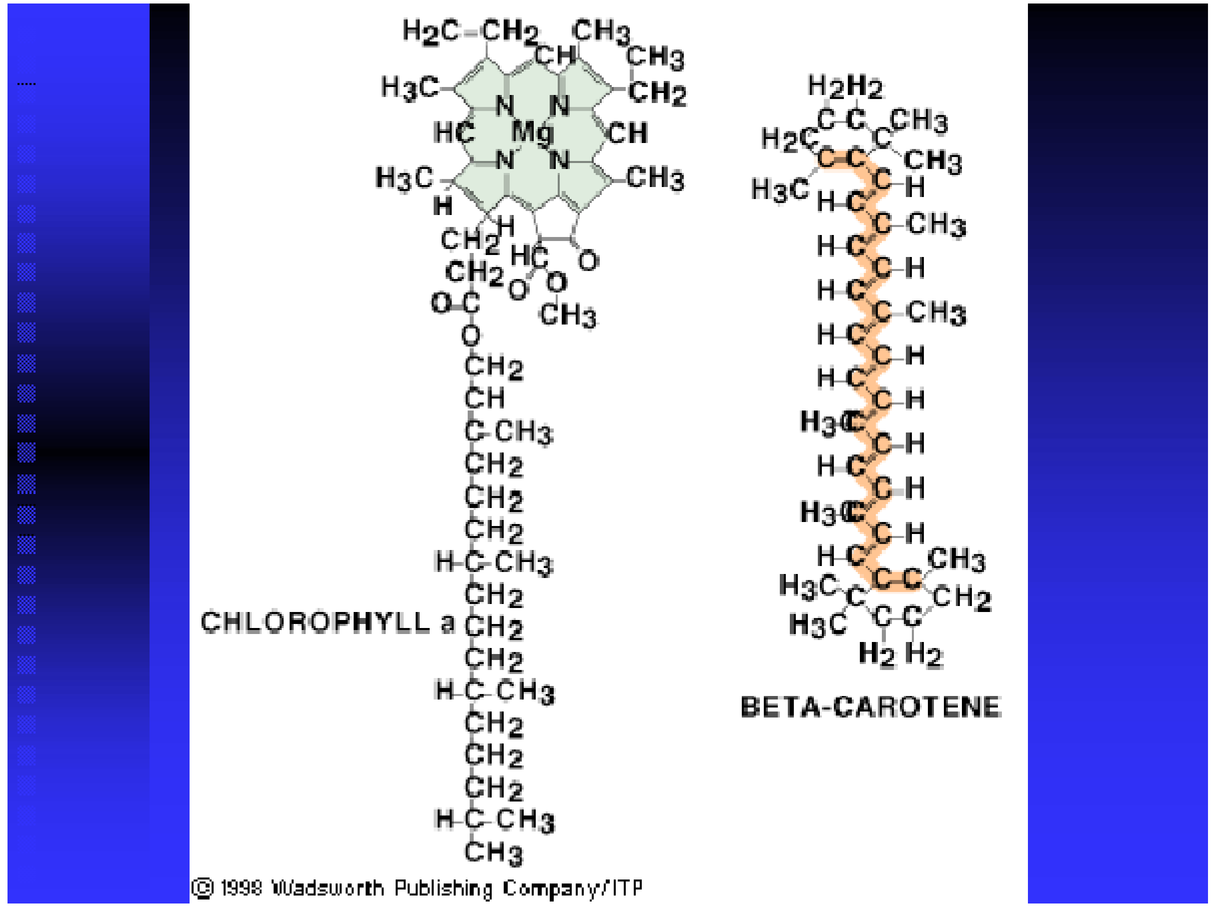
•Each of these differently-colored pigments can absorb a slightly different color of light and pass its energy to the central reaction molecule to do photosynthesis.



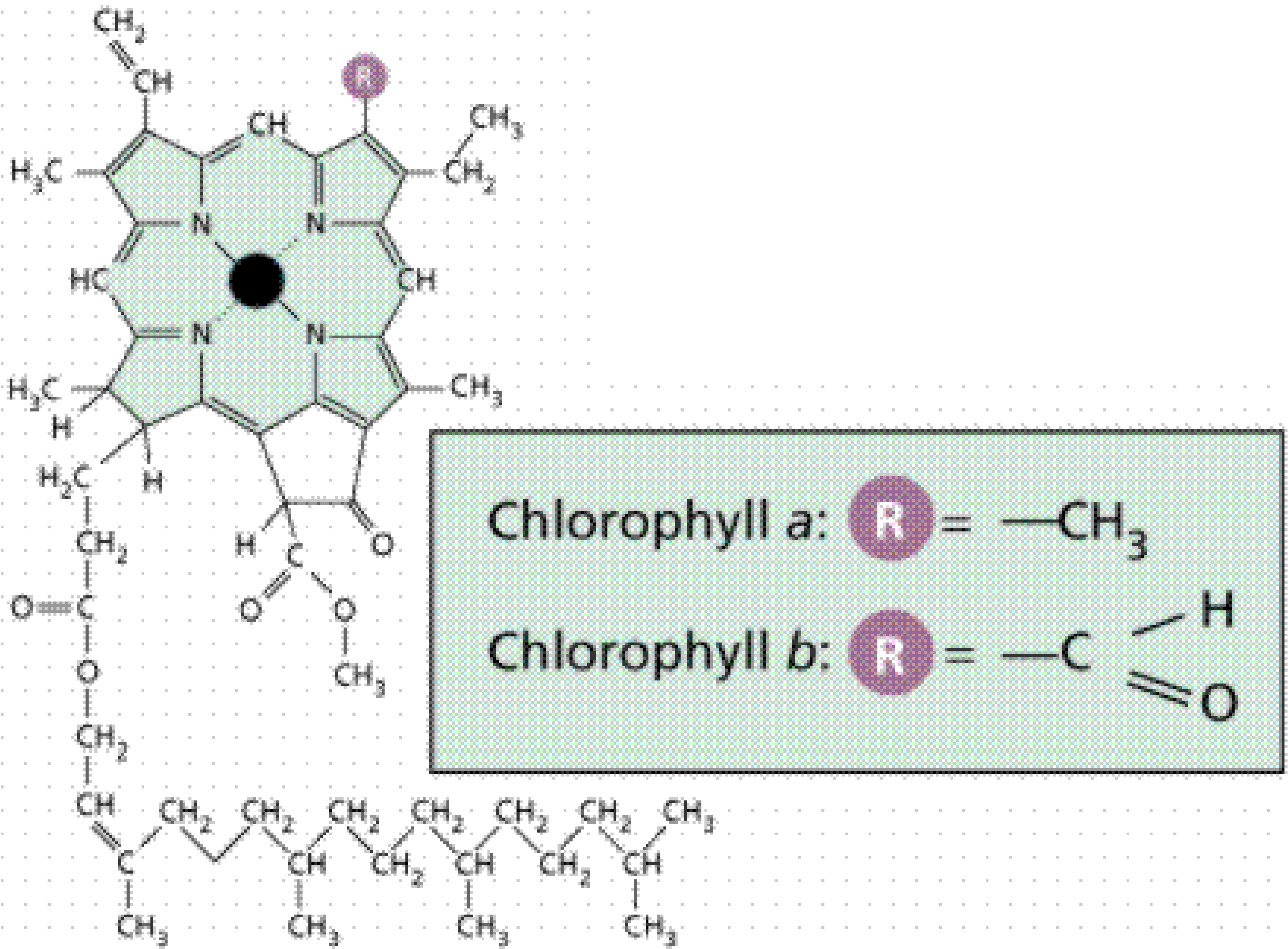
Chlorophyll

- Chlorophyll, the green pigment common to all photosynthetic cells,
- Chlorophyll looks green because it absorbs red and blue light, making these colors unavailable to be seen by our eyes. It is the green light which is NOT absorbed that finally reaches our eyes, making chlorophyll appear green.
- It is the energy from the red and blue light that are absorbed that is, thereby, able to be used to do photosynthesis. The green light we can see is not/cannot be used for photosynthesis
-
- Chlorophyll is not very stable and is constantly synthesized by the cell

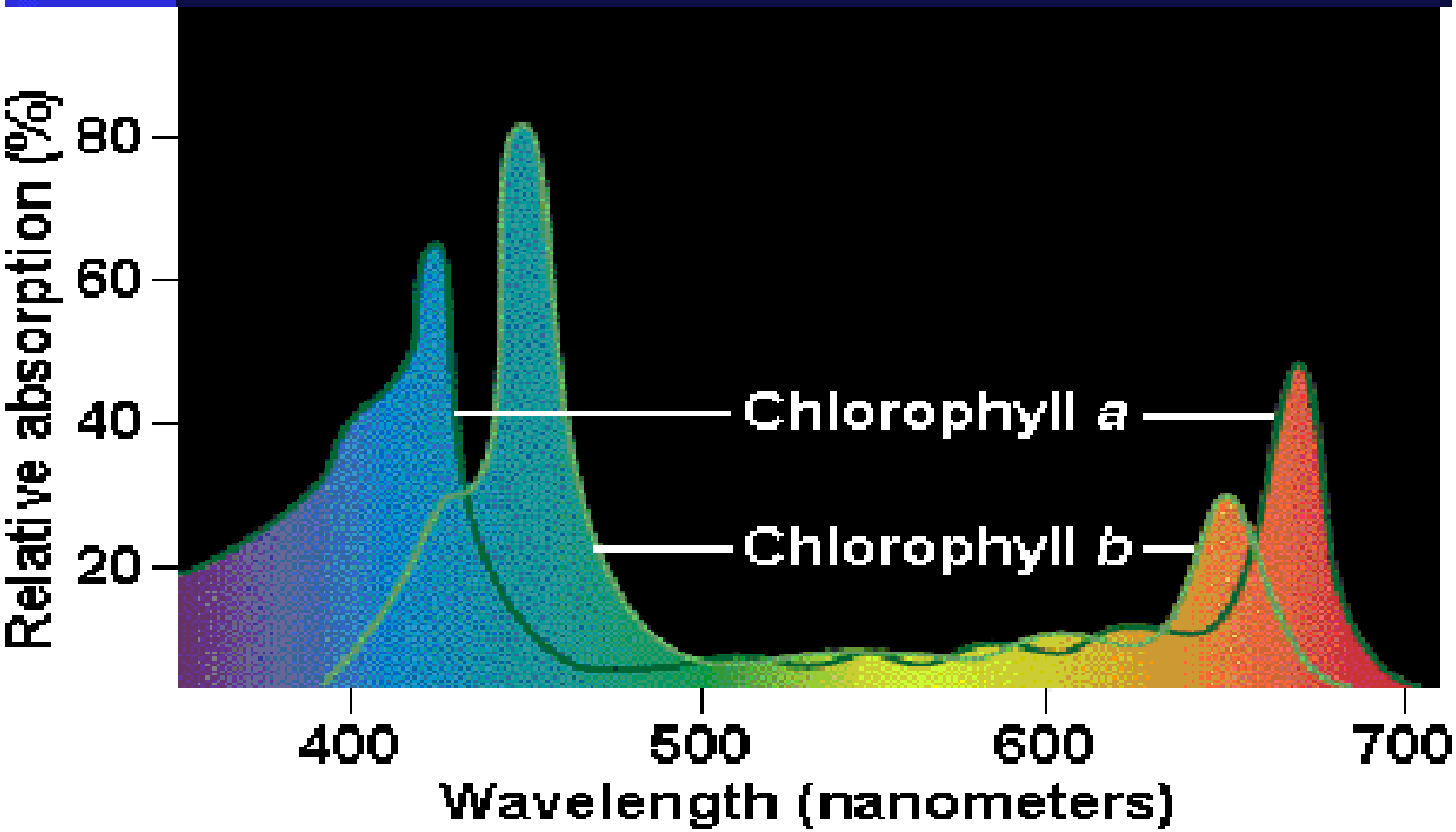




•The central part of the chemical structure of a chlorophyll molecule is a **porphyrin ring**, which consists of several fused rings of carbon and nitrogen with a magnesium ion in the center.

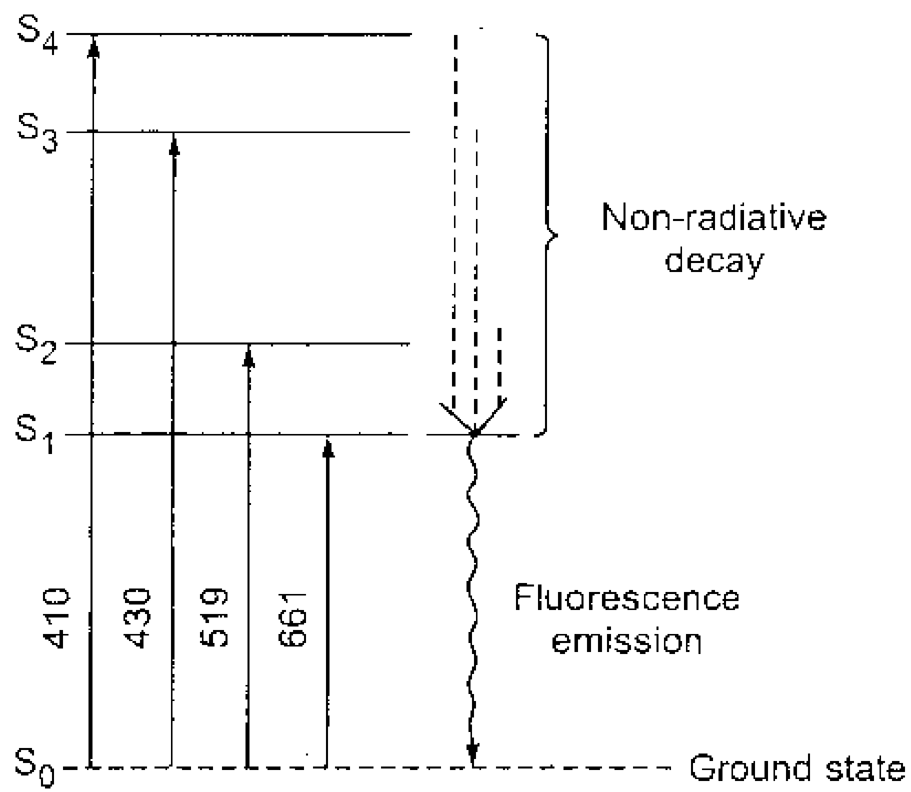

Chlorophyll a: R = —CH3
Chlorophyll b: R = —C(H)=O

CHLOROPHYLL PIGMENTS



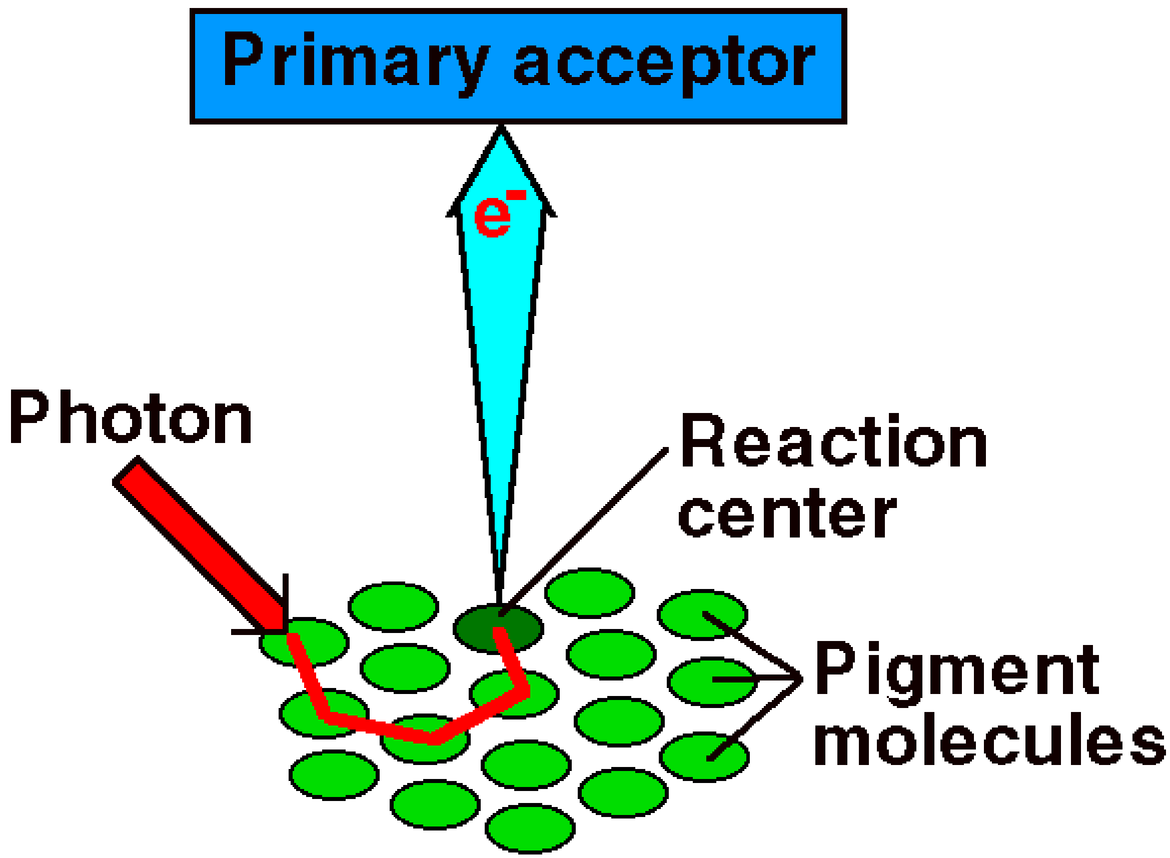
Excitation of photo-pigment by light

- If a pigment absorbs light energy, it becomes excited, then one of three things will occur:
- Energy is dissipated as heat.
- The energy is emitted - fluorescence.
- Energy is transferred without radiation to another molecule
- Energy can cause charge/electron transfer and trigger a chemical reaction, as in photosynthesis.



Chlorophyll only triggers a chemical reaction when it is associated with proteins embedded in a membrane (as in a chloroplast) or the membrane found in photosynthetic prokaryotes such as cyanobacteria and prochlorobacteria – needs antenna system

Reaction center and antenna system



Reaction center – chlorophyll molecule

Other pigments serve to collect light energy and transfer it to the reaction center through the non-radiative energy transfer (RET),

$$D^* + A \longrightarrow D + A^*$$

Similar to FRET

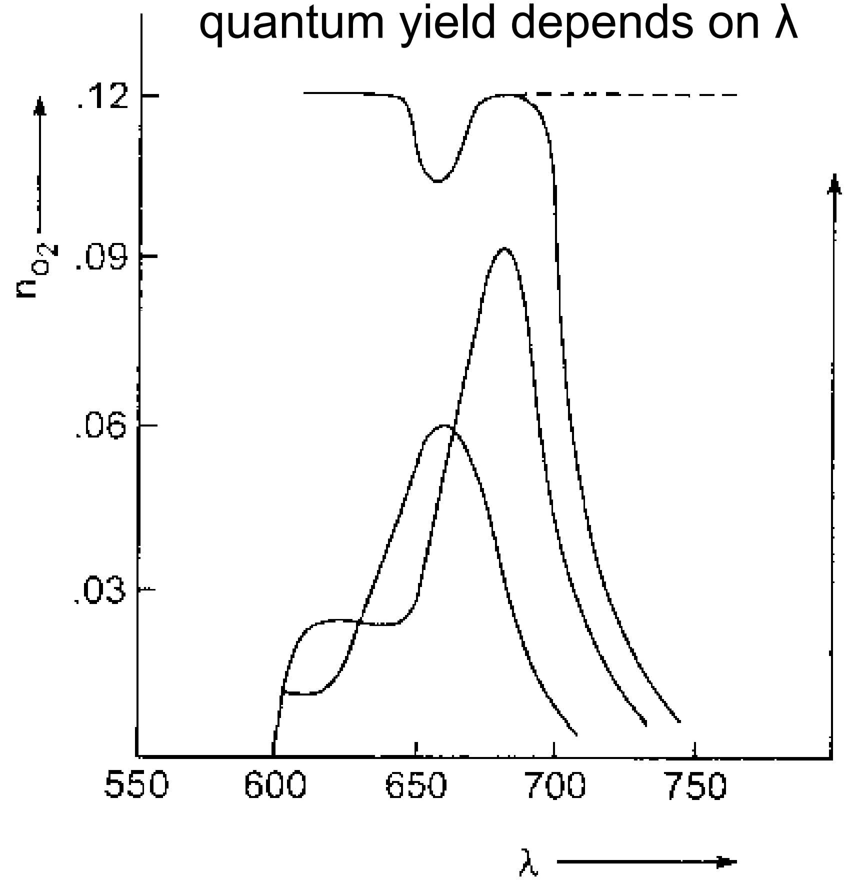
Collected light energy is transferred into chemical energy by the reaction center and leads to electron transfer

Emerson effect

- The efficiency of photosynthesis depends on the wavelength of the incident light and probability of its absorption.
- Photosynthesis produces oxygen, the efficiency (quantum yield) is measured by the ratio of the number of oxygen molecules produced to the number of photons absorbed
- quantum yield of photosynthesis:

$$\phi(\lambda) = \frac{n_{O_2}}{I_{abs}}$$

quantum yield depends on λ

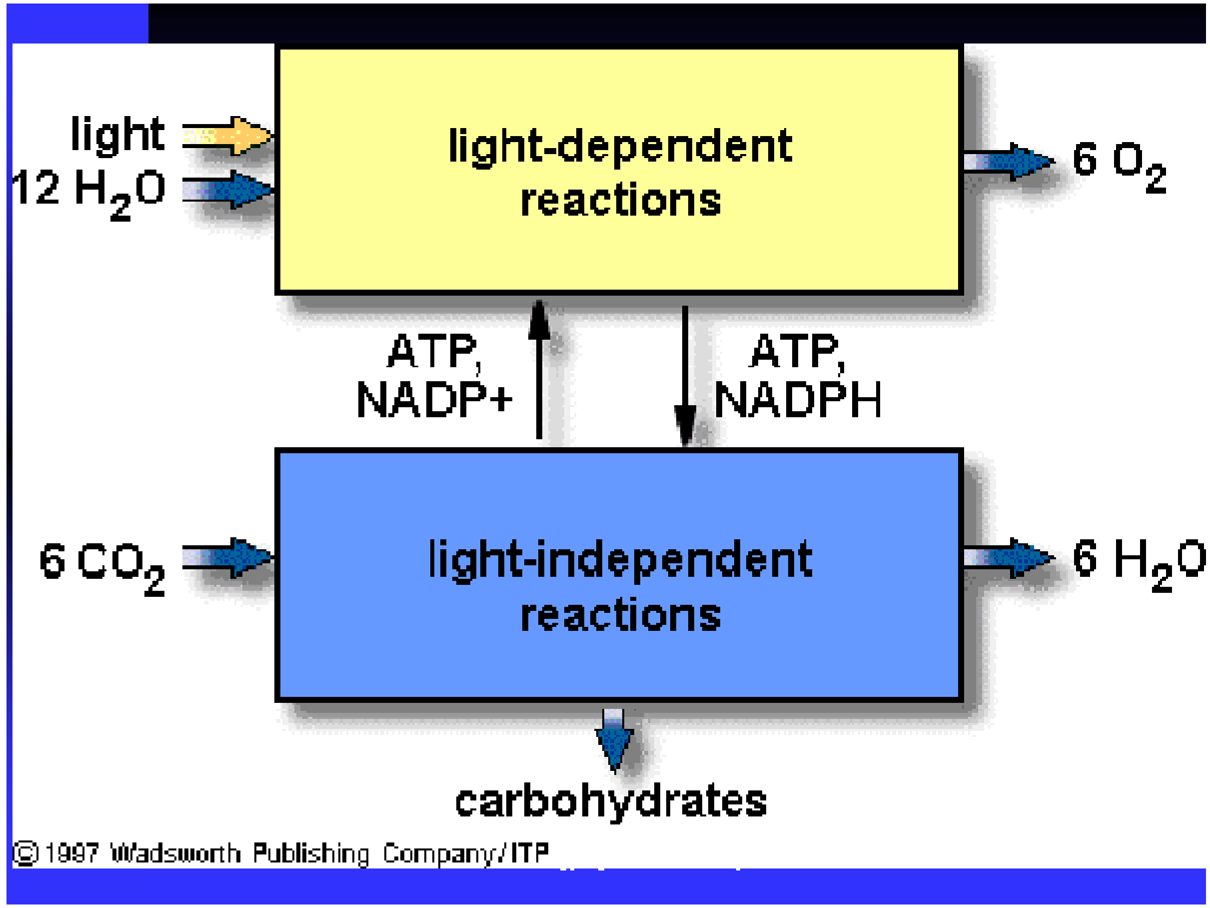


When lights of 650 combined with 700 nm - enhancement in quantum yield – Emerson effect

Light reactions

The energy produced in light reaction is stored by forming a molecule of **ATP (adenosine triphosphate)**,

NADPH is also produced



Dark reactions

The dark reaction takes place in the stroma within the chloroplast, and converts CO2 to sugar. This reaction doesn't directly need light in order to occur, but it does need the products of the light reaction (ATP and another chemical called NADPH). The dark reaction involves a cycle called the **Calvin cycle** in which CO2 and energy from ATP are used to form sugar.

Light reactions

- Light dependent: require light energy to make products:

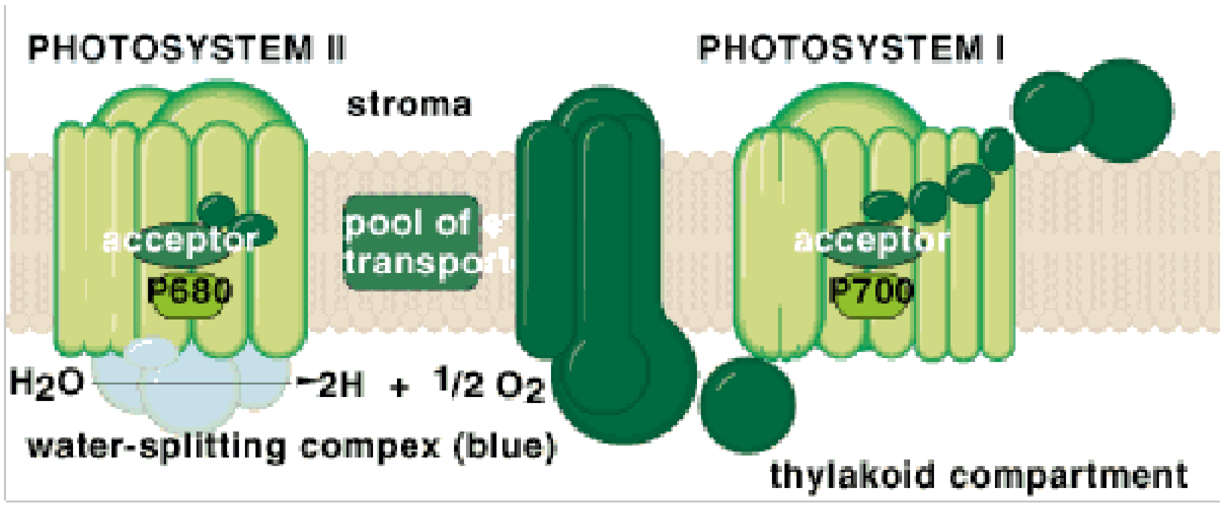
- Light strikes pigment chlorophyll a in such a way as to excite electrons to a higher energy state.

- In a series of reactions the energy is converted (along an electron transport process) into ATP and NADPH.

- Products:
- ATP (serves as energy transporter)
- NADPH (serves as electron/hydrogen carrier)
- Oxygen molecule O_2 (water is split in the process, releasing oxygen as a by-product of the reaction).

- Light reactions involve Photosystems I and II

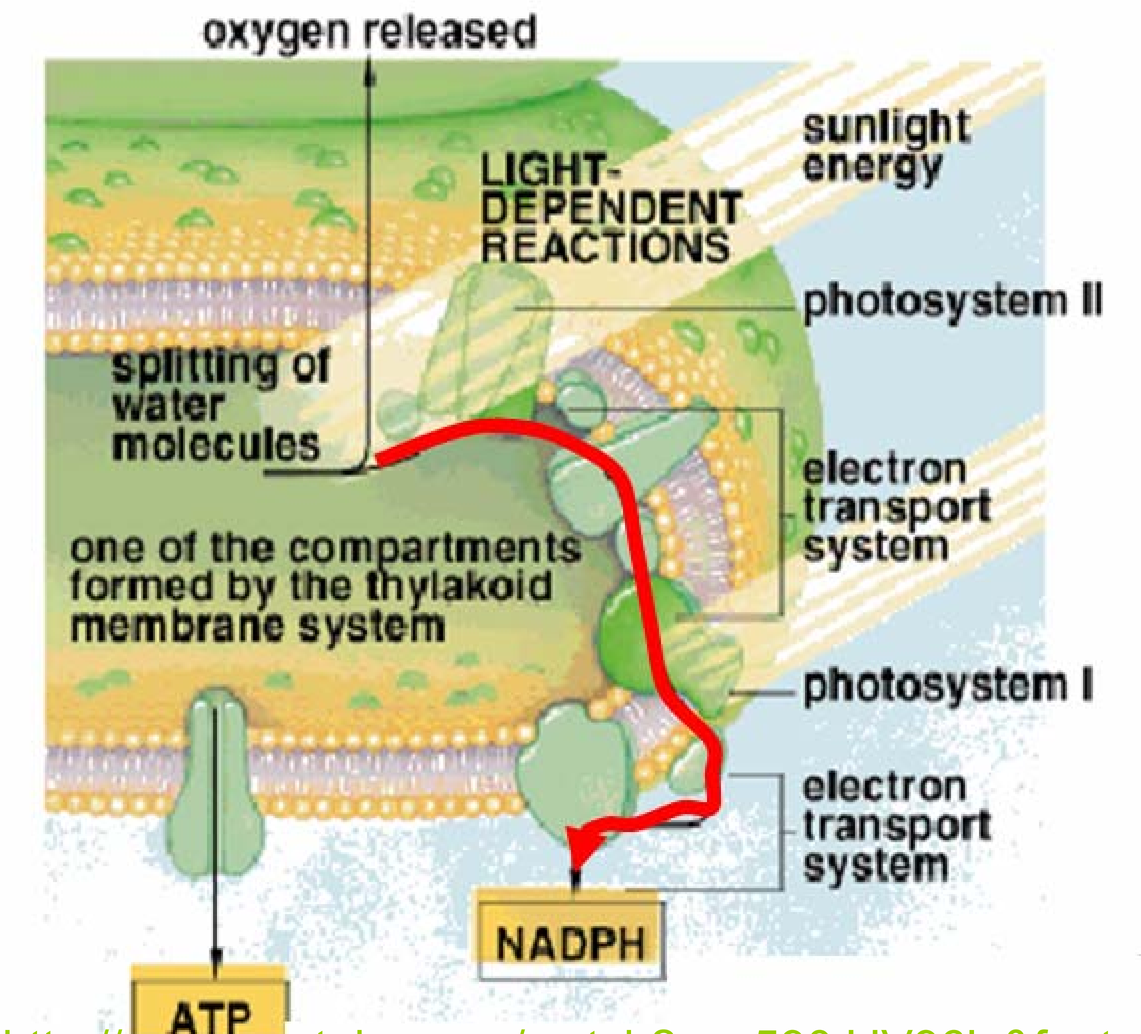
Photosystems I and II



Photosystems I and II are separated by more that 100 A but are coupled through other proteins (cytochromes).

- Photosystems are arrangements of chlorophyll and other pigments and proteins packed into thylakoids.
- Many Prokaryotes have only one photosystem - Photosystem II
- Eukaryotes have Photosystem II plus Photosystem I.
- Photosystem I uses chlorophyll a, in the form referred to as P700.
- Photosystem II uses a form of chlorophyll b known as P680.

Photosynthesis: http://vcell.ndsu.nodak.edu/animations/photosynthesis/movie-flash.htm
Photosystem II: http://vcell.ndsu.nodak.edu/animations/photosystemII/movie-flash.htm



Light energy is absorbed by chlorophyll.

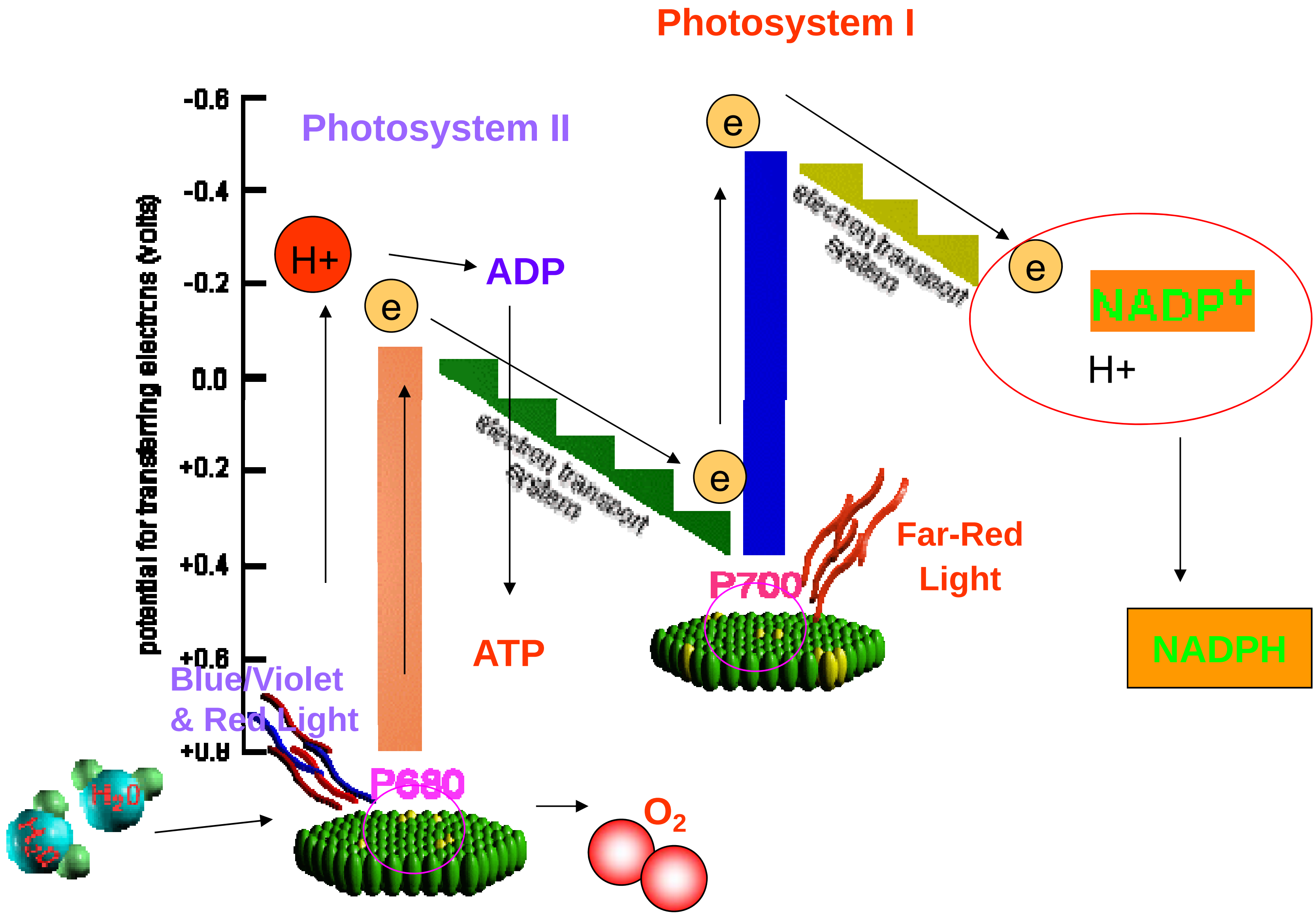
Electrons from excited CHL are raised to higher energy level, and transferred to electron acceptor.

Transfer of e through electron transfer chain.

Electron transfer chain links PS II and PS I

Electrons are supplied by photolysis of water

http://www.youtube.com/watch?v=v590JJV96Ic&feature=related

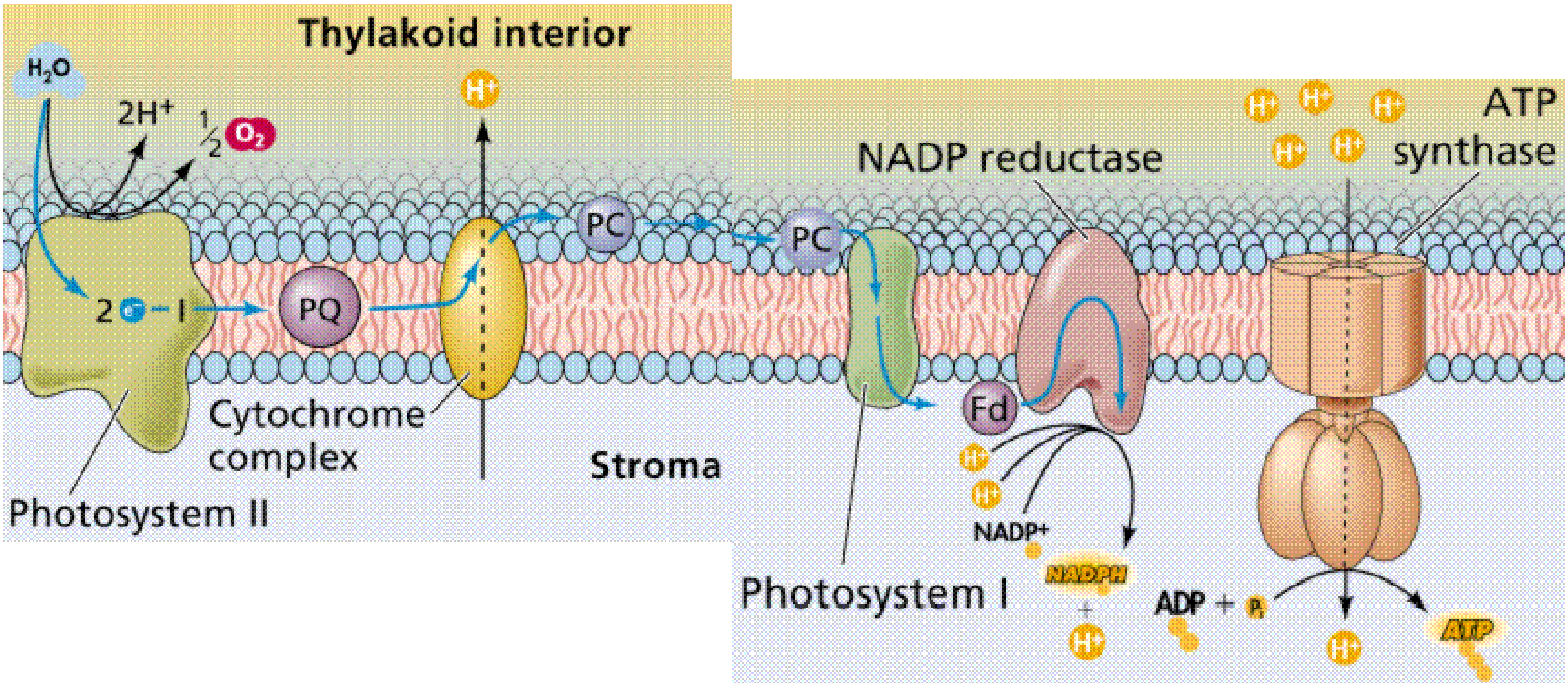


$2H_2O + 4\ Chlor^{+}\ =\ O_2 = 4H^{+} + 4\ Chlor$

Photo-phosphorylation

- Photophosphorylation is the process of converting energy from a light-excited electron into the pyrophosphate bond of an ADP molecule. This occurs when the electrons from water are excited by the light in the presence of P680. The energy transfer is similar to the chemiosmotic electron transport occurring in the mitochondria. Light energy causes the removal of an electron from a molecule of P680 that is part of Photosystem II. The P680 requires an electron, which is taken from a water molecule, breaking the water into H^+ ions and O^{2-} ions. These O^{2-} ions combine to form the diatomic O_2 that is released. The electron is "boosted" to a higher energy state and attached to a primary electron acceptor, which begins a series of red-ox reactions, passing the electron through a series of electron carriers, eventually attaching it to a molecule in Photosystem I. Light acts on a molecule of P700 in Photosystem I, causing an electron to be "boosted" to a still higher potential. The electron is attached to a different primary electron acceptor (that is a different molecule from the one associated with Photosystem II). The electron is passed again through a series of re-dox reactions, eventually being attached to NADP+ and H+ to form NADPH, an energy carrier needed in the Light Independent Reaction. The electron from Photosystem II replaces the excited electron in the P700 molecule. There is thus a continuous flow of electrons from water to NADPH. This energy is used in Carbon Fixation. Cyclic Electron Flow occurs in some eukaryotes and primitive photosynthetic bacteria. No NADPH is produced, only ATP. This occurs when cells may require additional ATP, or when there is no NADP+ to reduce to NADPH. In Photosystem II, the pumping to H ions into the thylakoid and the conversion of ADP + P into ATP is driven by electron gradients linked with the proton gradients established in the thylakoid membrane.

According to chemiosmotic theory



the process of electron transfer is linked to proton transfer, which drives chemiosmotic synthesis of ATP, electron transport is also coupled to NADPH production

Jagendorf experiment

ATP synthesis was performed without light or oxygen, only due to the proton gradient induced artificially in the lab experiment

this proved the proton gradient and presence of ADP is enough to produce ATP molecules

this proved chemiosmotic theory – proton gradient is a driving force for ATP production

another facts:

Halobacteria, which grow in extremely salty water, can grow when oxygen is absent. Purple pigments, known as retinal (a pigment also found in the human eye) act similar to chlorophyll. The complex of retinal and membrane proteins is known as bacteriorhodopsin, which generates electrons which establish a proton gradient that powers an ADP-ATP pump, generating ATP from sunlight without chlorophyll. This supports the theory that chemiosmotic processes are universal in their ability to generate ATP.

Role of PS II

- Light energy (red and blue) is absorbed by chlorophyll in PS II. Activated only when λ< or = 680 nm

- Electrons from excited CHL-a are raised to higher energy level, and transferred to electron acceptor.

- Ionized CHL molecule reacts with water and light to produce oxygen and proton:

$$2H_2O + 4\text{chlorophyll}^{+} \rightarrow O_2 + 4\text{H}^{+} + 4\text{chlorophyll}$$

- Transfer of e occurs through electron transfer chain and goes from PS II to PS I.

- Proton gradient is developed which together with access of energy produces ATP from ADP

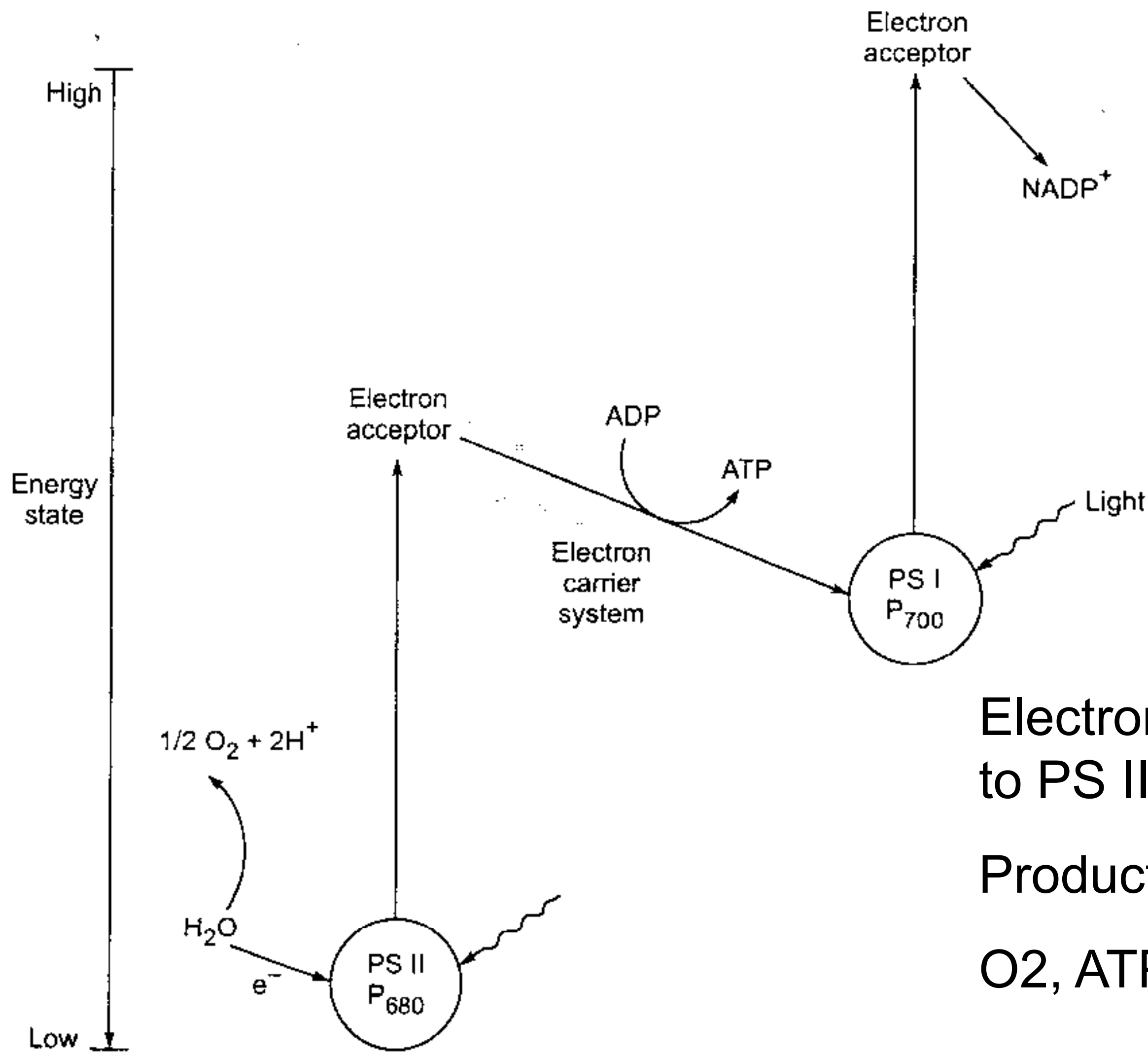
Role of PS I

- Electrons from PS II are transferred to PS I,
- Special form of CHL-a called P-700 is in PS I
- PS I is excited by far–red light, $\lambda > 680$ nm, PS II is not activated by this light
- Electrons excited by light are picked up from P-700 by another electron acceptor (ferredoxin), electron goes through the electron chain transfer and produces NADPH from NADP+ and proton

$$\mathrm{NADP}^{+} + 2e^{-} + \mathrm{H}^{+} \rightarrow \mathrm{NADPH}$$

- Lost electrons are supplied again from PS II
- Balance and current flow of electrons

Non-cyclic photo-phosphorylation

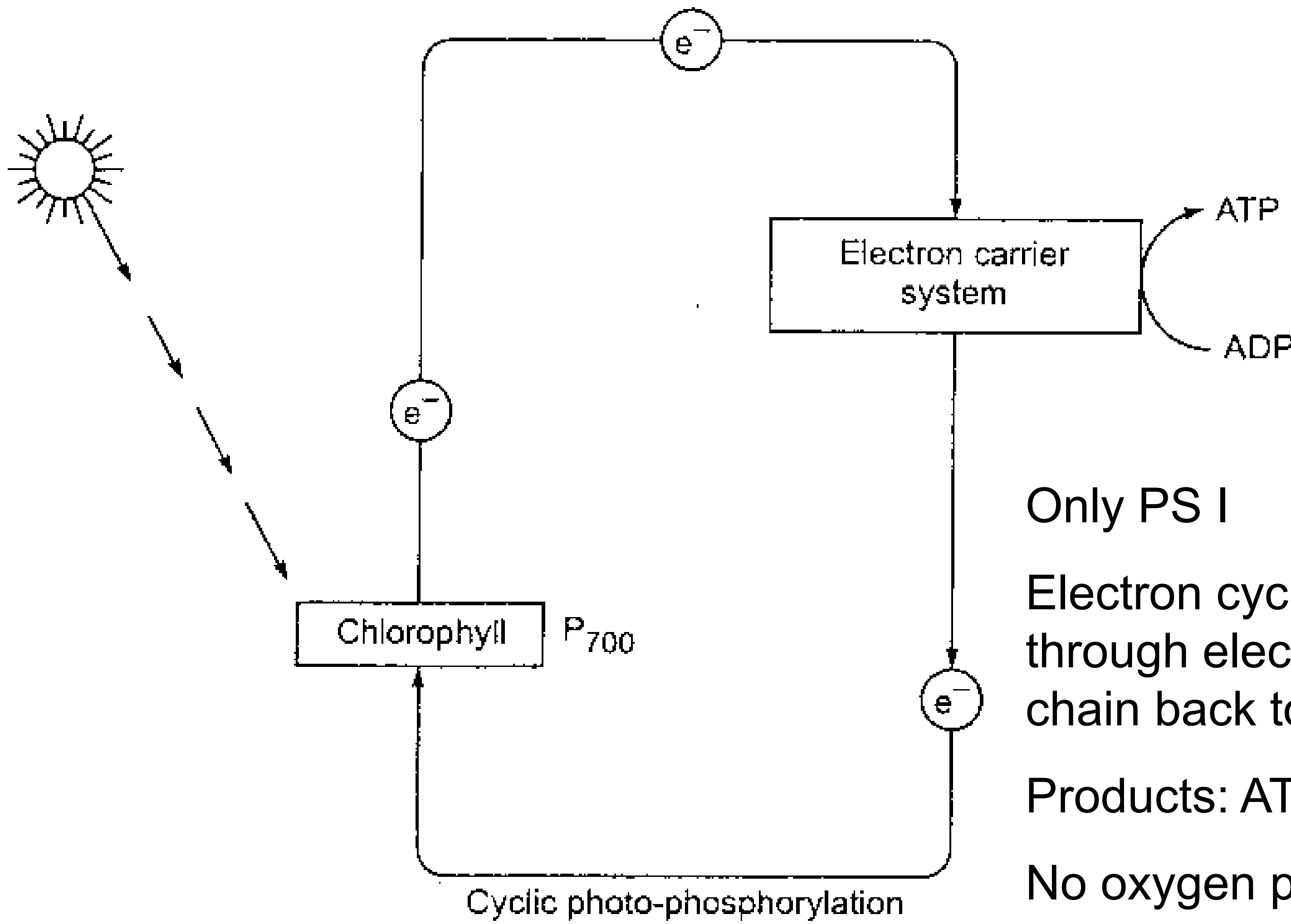


Electrons flow from water to PS II and to PS I

Products:

O2, ATP, NADPH

Cyclic photo-phosphorylation

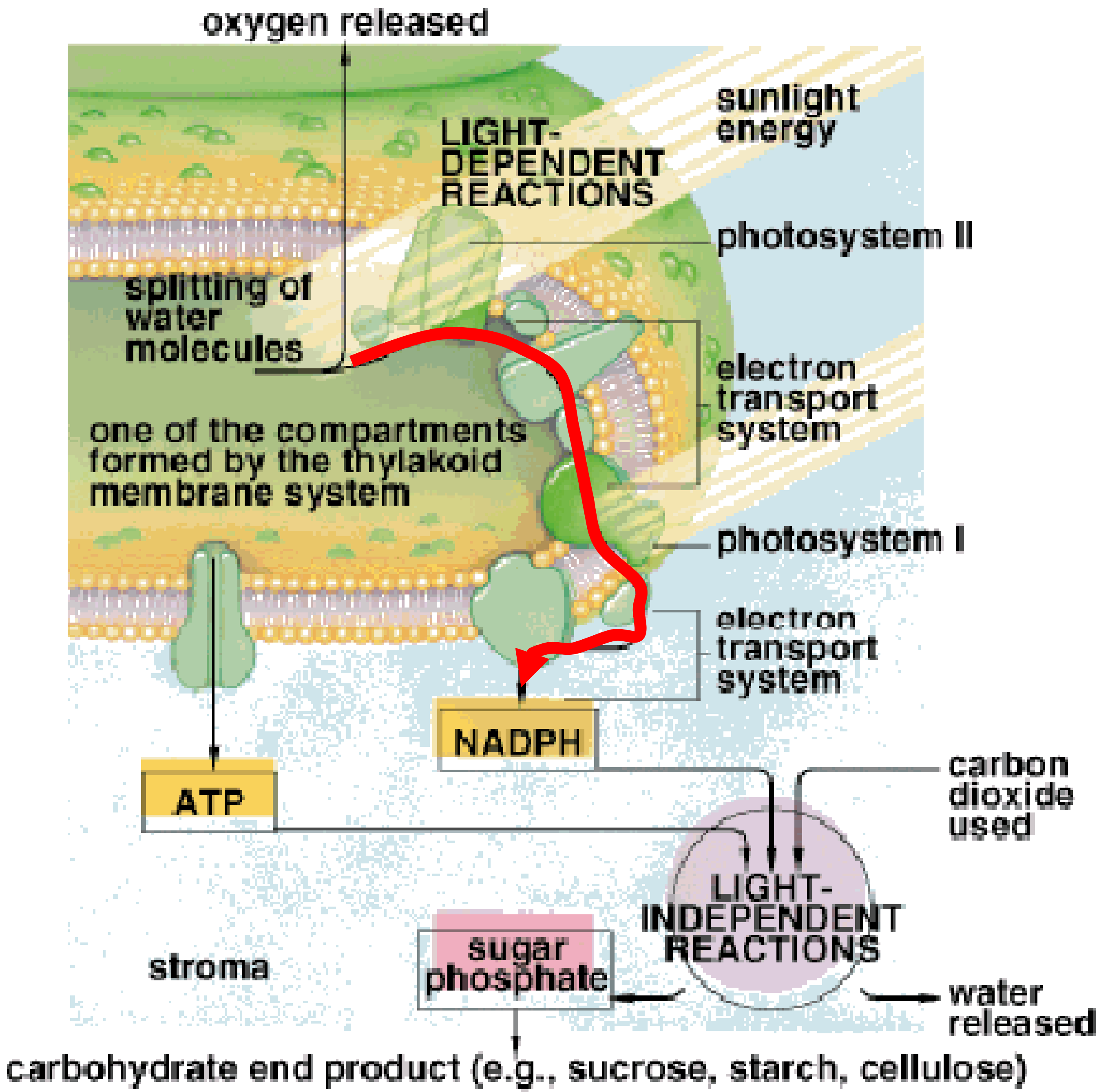


Only PS I

Electron cycles from PS I through electron transfer chain back to PS I

Products: ATP

No oxygen produced



Light phase:

Photosynthetic phosphorylation: produces ATP

and also NADPH

Which are used in dark phase to produce sugar using CO2

Light Independent Process,

- In the Light Independent Process, carbon dioxide from the atmosphere (or water for aquatic/marine organisms) is captured and modified by the addition of Hydrogen to form carbohydrates (general formula of carbohydrates is $[CH_2O]_n$).
- incorporation of carbon dioxide into organic compounds is known as **carbon fixation**.
- The energy for this comes from the first phase of the photosynthetic process.
- Living systems cannot directly utilize light energy, but can, through a complicated series of reactions, convert it into C-C bond energy that can be released by glycolysis and other metabolic processes (cell respiration).

Dark reactions

- Takes place in stroma of chloroplast
- Does not require light energy directly, but products of light phase : ATP and NADPH
- Carbon dioxide – is used here to build glucose molecule
- Uses ATP as a source of energy
- Uses NADPH as a source of hydrogen molecules to build glucose molecule

$$\mathrm{CO_2 + 2NADPH + 3ATP + 2H_2O \rightarrow}$$

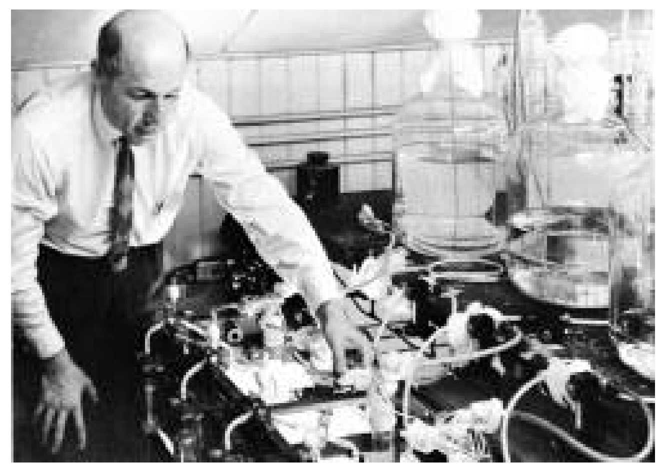
$$\mathrm{\rightarrow CH_2O + 2NADP^+ + 3ADP + 3P}_i \mathrm{+ H^+}$$

Calvin Cycle

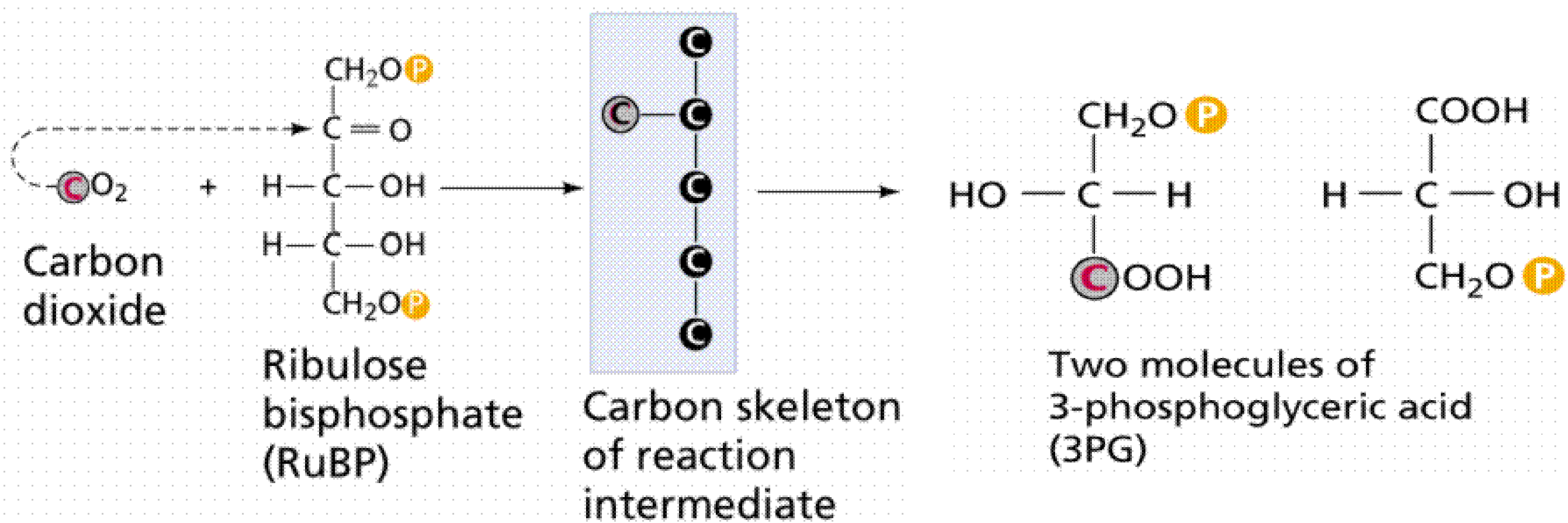
- Carbon-Fixing Reactions are also known as the Dark Reactions occur in a cycle of biochemical enzyme catalyzed reactions called Calvin cycle.
- The Calvin Cycle occurs in the stroma of chloroplasts.
- Carbon dioxide is captured by the chemical ribulose biphosphate (RuBP). RuBP is a 5-C chemical. Six molecules of carbon dioxide enter the Calvin Cycle, eventually producing one molecule of glucose.

•The reactions in this process were worked out by Melvin Calvin. The accomplishment brought him the Nobel prize in chemistry in 1961

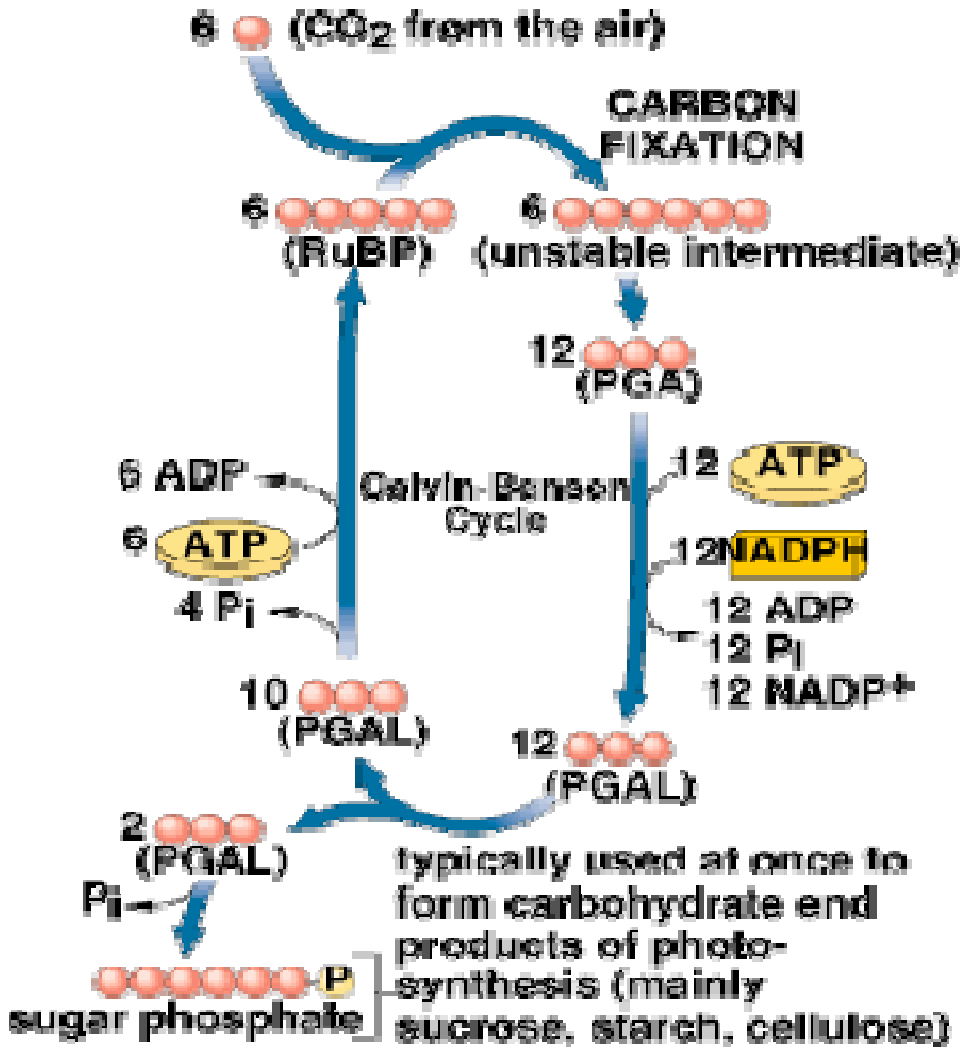
•Ernest Orlando Lawrence Berkeley National Laboratory.



First step in Calvin Cycle



The first stable product of the Calvin Cycle is phosphoglycerate (PGA), a 3-C chemical.



The energy from ATP and NADPH energy carriers generated by the photosystems is used to attach phosphates to (phosphorylate) the PGA.

Eventually there are 12 molecules of glyceraldehyde phosphate (also known as phosphoglyceraldehyde or PGAL, a 3-C), two of which are removed from the cycle to make a glucose.

The remaining PGAL molecules are converted by ATP energy to re-form 6 RuBP molecules, and thus start the cycle again. Each reaction in this process, is catalyzed by a different reaction-specific enzyme.

Energetics of photosynthesis

The sum total of photosynthesis in green plants is a light driven process in which atmospheric CO_2 is reduced to carbohydrates:

$$CO_2 + H_2O \xrightarrow{hv} CH_2O + O_2$$

470 kJ or 112 kcal required

Simple carbohydrate unit

For glucose:

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

2820 kJ required

$$CO_2 + H_2O \xrightarrow{h\nu} CH_2O + O_2$$

Transfer of 4 electrons,

oxidant reductant

Reaction require 4.84 eV of energy per molecule,

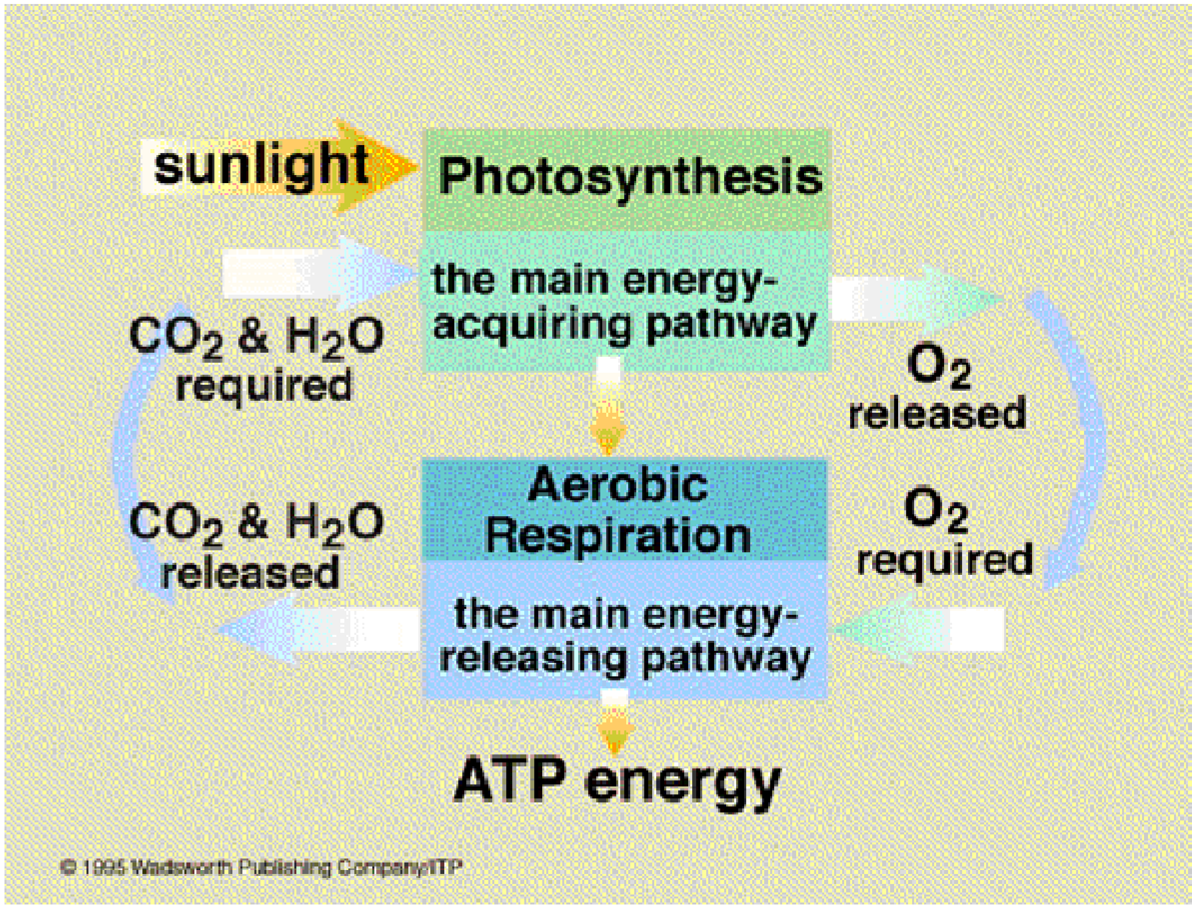
This energy is from sun light (680 nm):

$$h\nu = \frac{hc}{\lambda} = 1.82eV$$

8 photons are used to produce one molecule CH_2O, 8 x 1.82 = 14.6 eV

Efficiency of photosynthesis : $\phi = \frac{4.84}{14.6} \times 100 = 33\%\ \text{(approx.)}$

Relation of photosynthesis to cell respiration



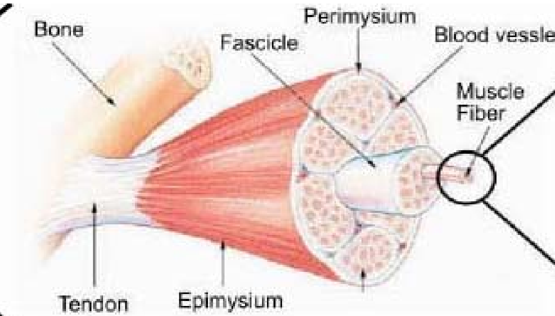
- **Additional information:**
- Plants may be viewed as carbon sinks, removing carbon dioxide from the atmosphere and oceans by fixing it into organic chemicals. Plants also produce some carbon dioxide by their respiration, but this is quickly used by photosynthesis. Plants also convert energy from light into chemical energy of C-C covalent bonds. Animals are carbon dioxide producers that derive their energy from carbohydrates and other chemicals produced by plants by the process of photosynthesis.
- The balance between the plant carbon dioxide removal and animal carbon dioxide generation is equalized also by the formation of carbonates in the oceans. This removes excess carbon dioxide from the air and water (both of which are in equilibrium with regard to carbon dioxide). Fossil fuels, such as petroleum and coal, as well as more recent fuels such as peat and wood generate carbon dioxide when burned. Fossil fuels are formed ultimately by organic processes, and represent also a tremendous carbon sink. Human activity has greatly increased the concentration of carbon dioxide in air. This increase has led to global warming, an increase in temperatures around the world, the Greenhouse Effect. The increase in carbon dioxide and other pollutants in the air has also led to acid rain, where water falls through polluted air and chemically combines with carbon dioxide, nitrous oxides, and sulfur oxides, producing rainfall with pH as low as 4. This results in fish kills and changes in soil pH which can alter the natural vegetation and uses of the land. The Global Warming problem can lead to melting of the ice caps in Greenland and Antarctica, raising sea-level as much as 120 meters. Changes in sea-level and temperature would affect climate changes, altering belts of grain production and rainfall patterns.

Bioenergetics of Muscle contraction

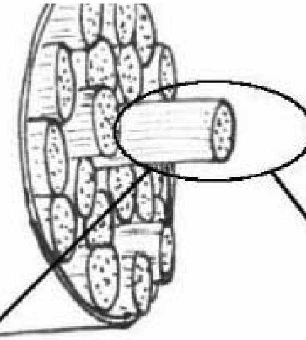
Energy rich molecules (ATP) produced are used to perform useful work:

mechanical work, nerve pulses, biosynthesis

Muscle contraction is ATP driven mechanical work



Fiber – elongated cell, 4 cm long, D=100 microns



~1000 myofibrils
In a cell

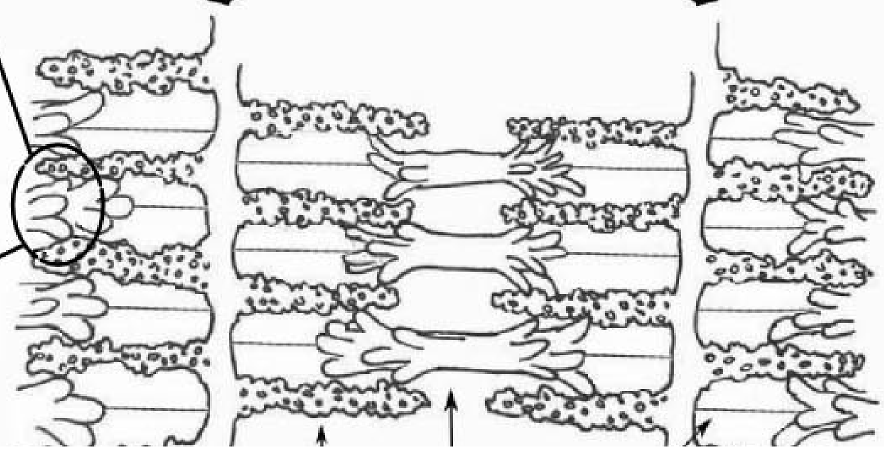
Skeletal muscles

40 % of the weight

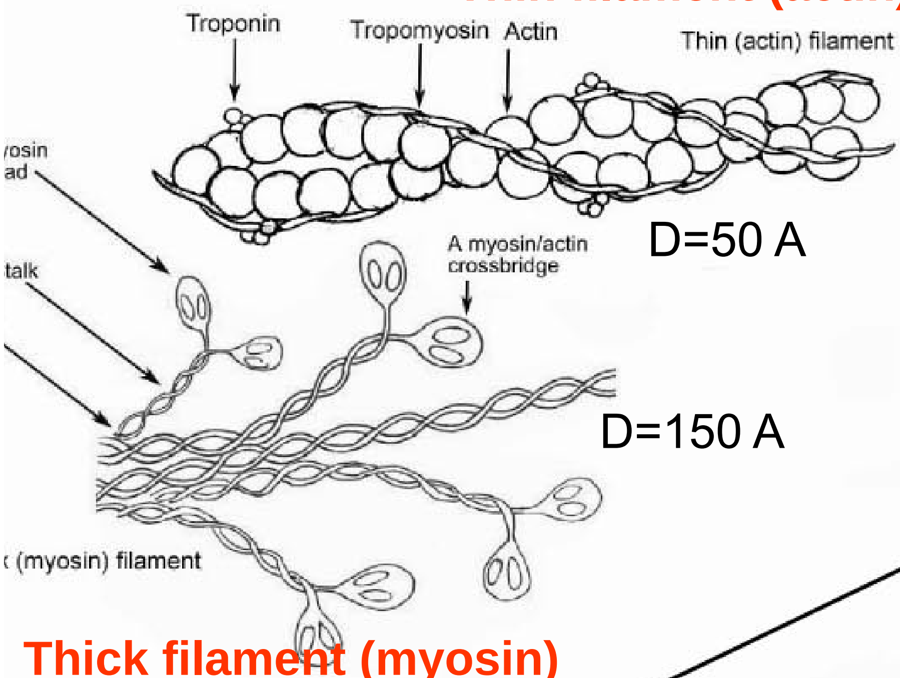
Myofibril

D=1mic

1 Sarcomere



Thin filament (actin)



D=50 A

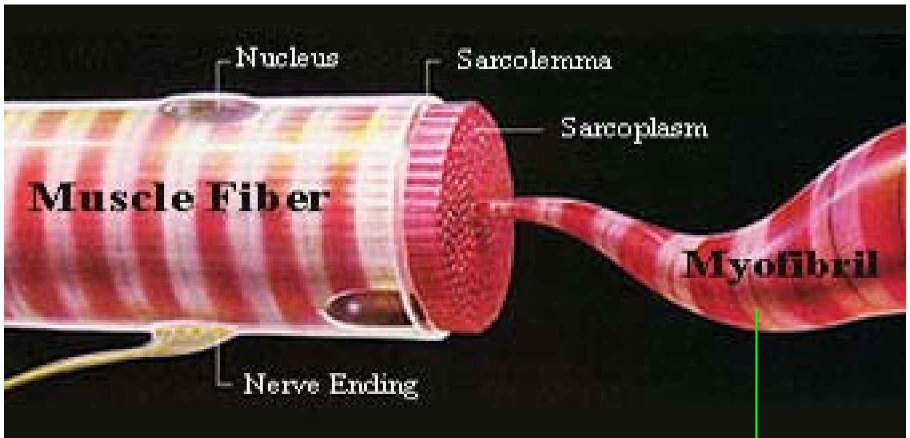
D=150 A

Thick filament (myosin)

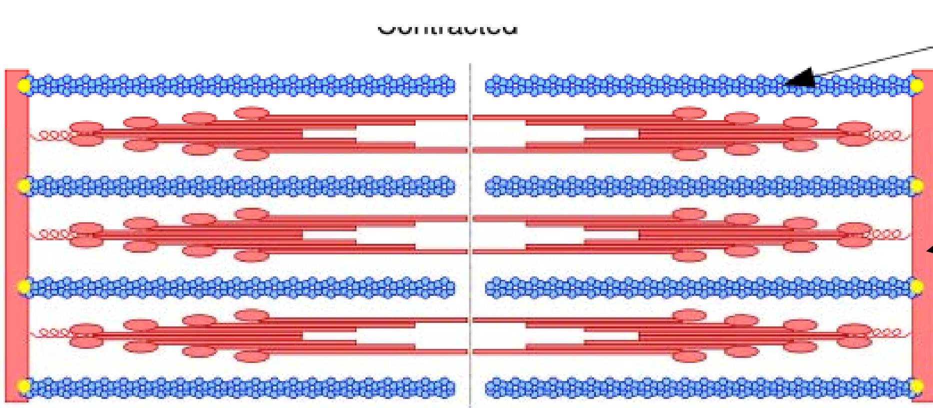
Cell membrane in muscle

- The cell membrane of a muscle cell is called the sarcolemma, covers a muscle cell and this membrane, like that of neurons, maintains a membrane potential.
- Sarcoplasmic reticulum is inside the cell, surrounds the myofibrils the cell contains mitochondia and nucleous
- Impulses travel along muscle cell membranes just as they do along nerve cell membranes.
- However, the 'function' of impulses in muscle cells is to bring about contraction

Sacromere

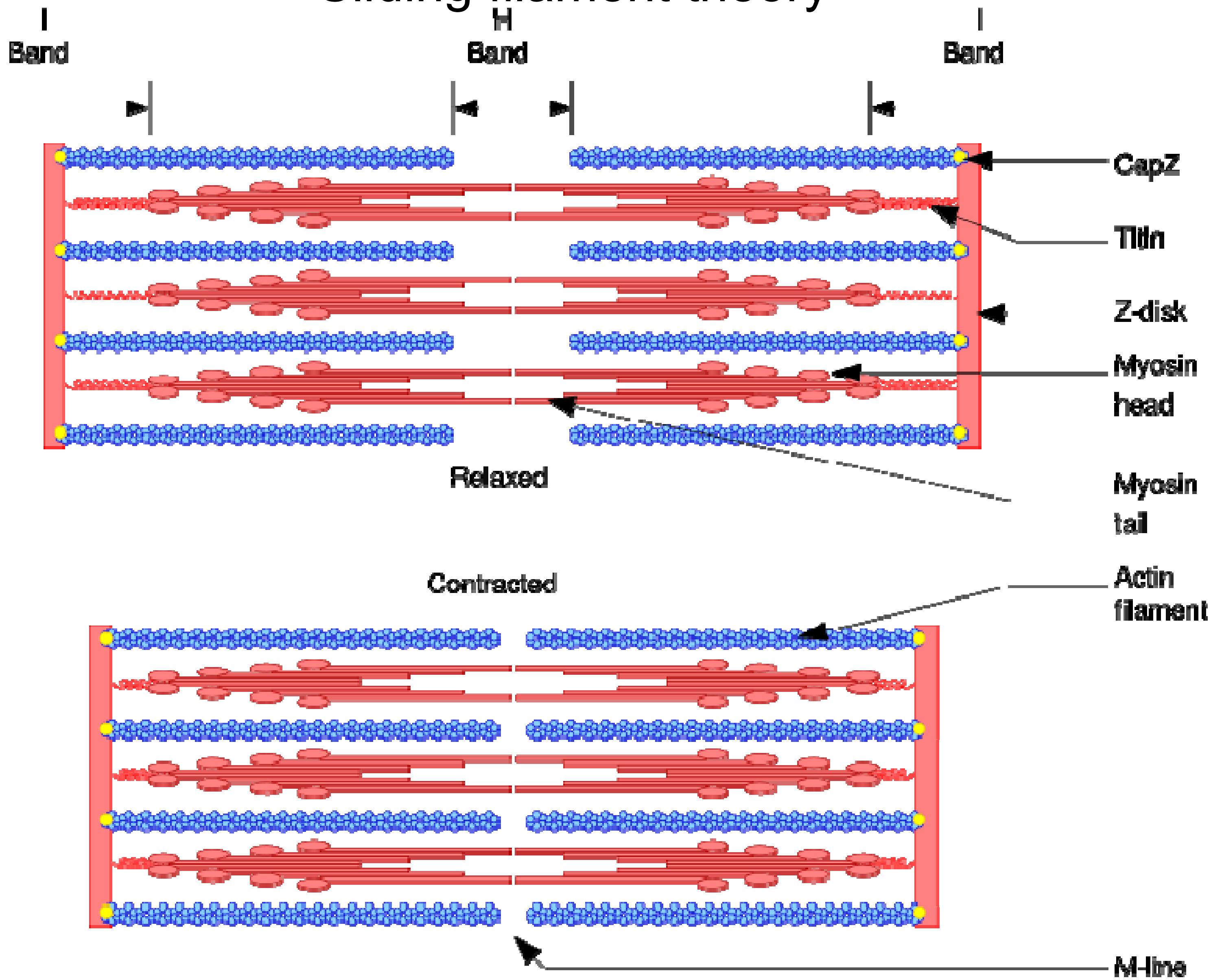


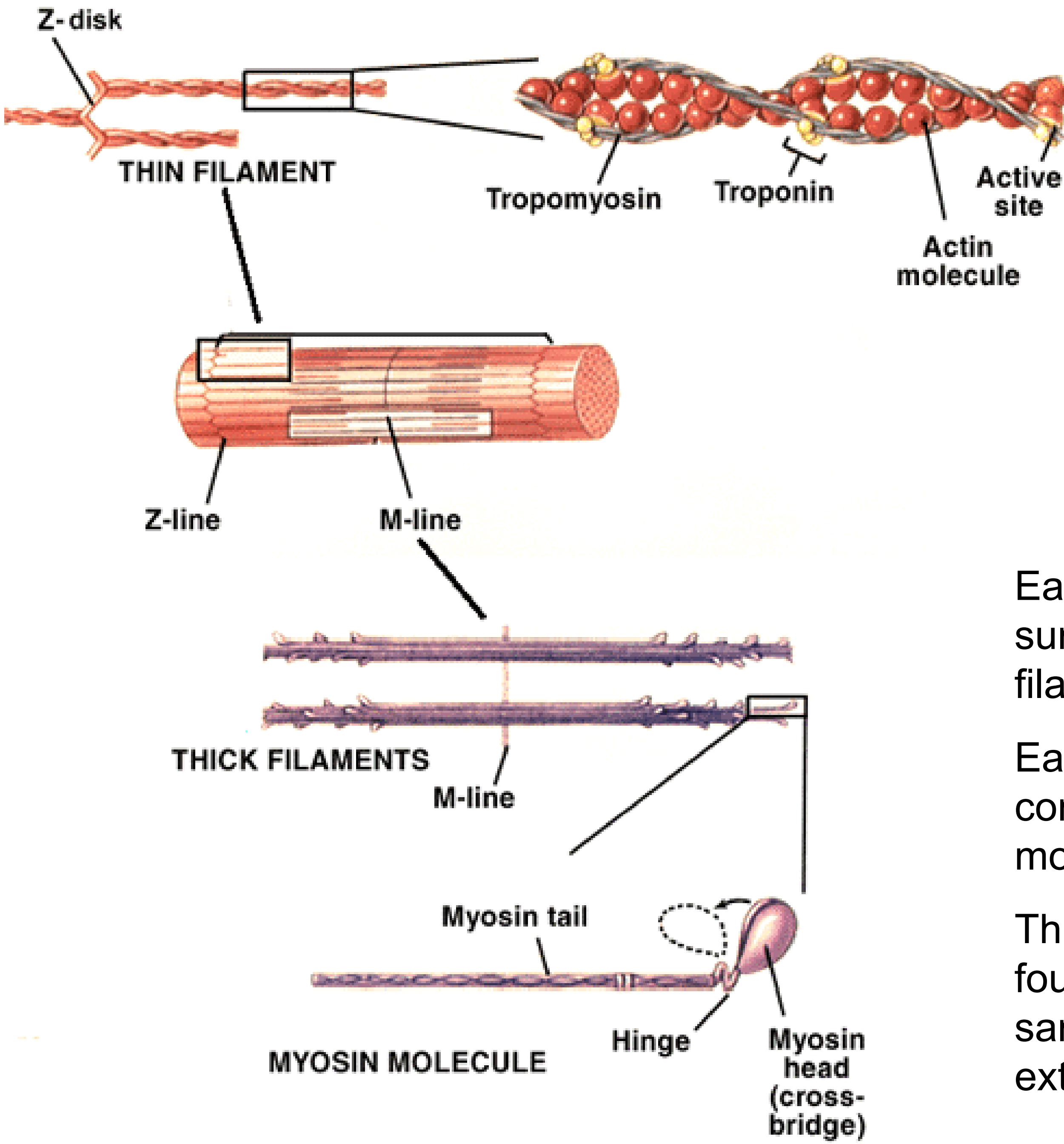
Each myofibril consists of chain of basic functional units – sacromeres, jointed together



Each sacromere is a segment of myofibril between two rigid disks, called Z-disks

Sliding filament theory





Thin filament 7 nm in diameter, contains

Actin (60-70%)

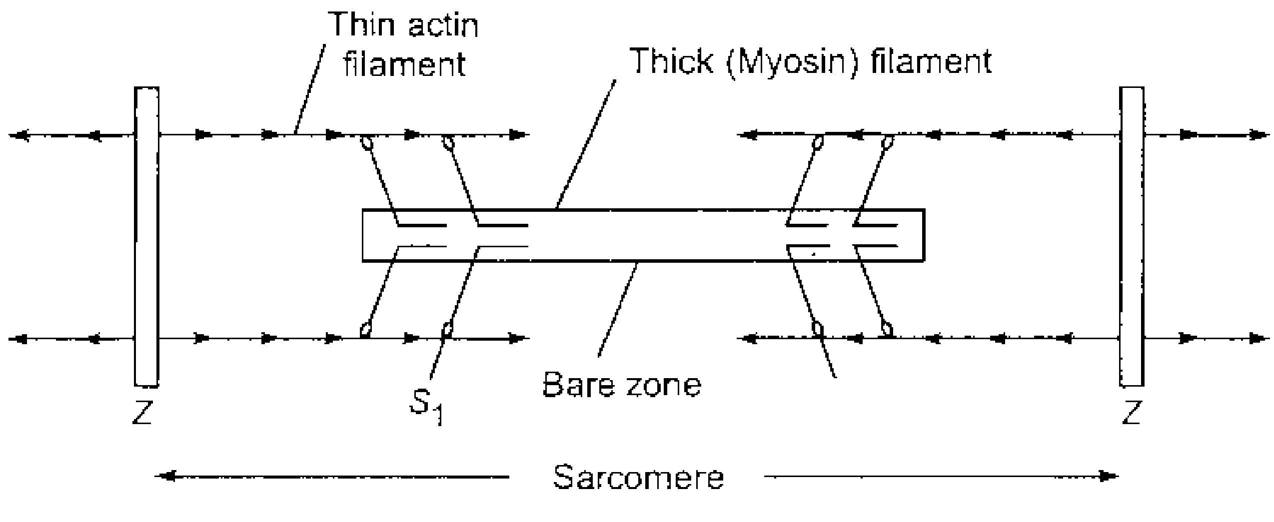
Tropomyosin

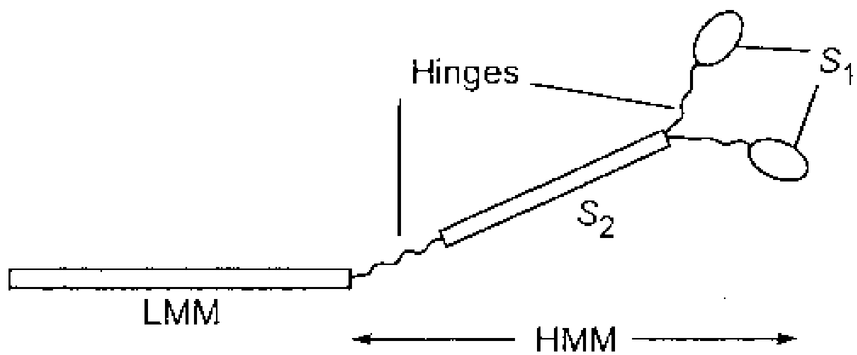
Troponin

Each thick filament is surrounded by 6 thin filaments

Each thick filament contains 300-400 myosin molecules

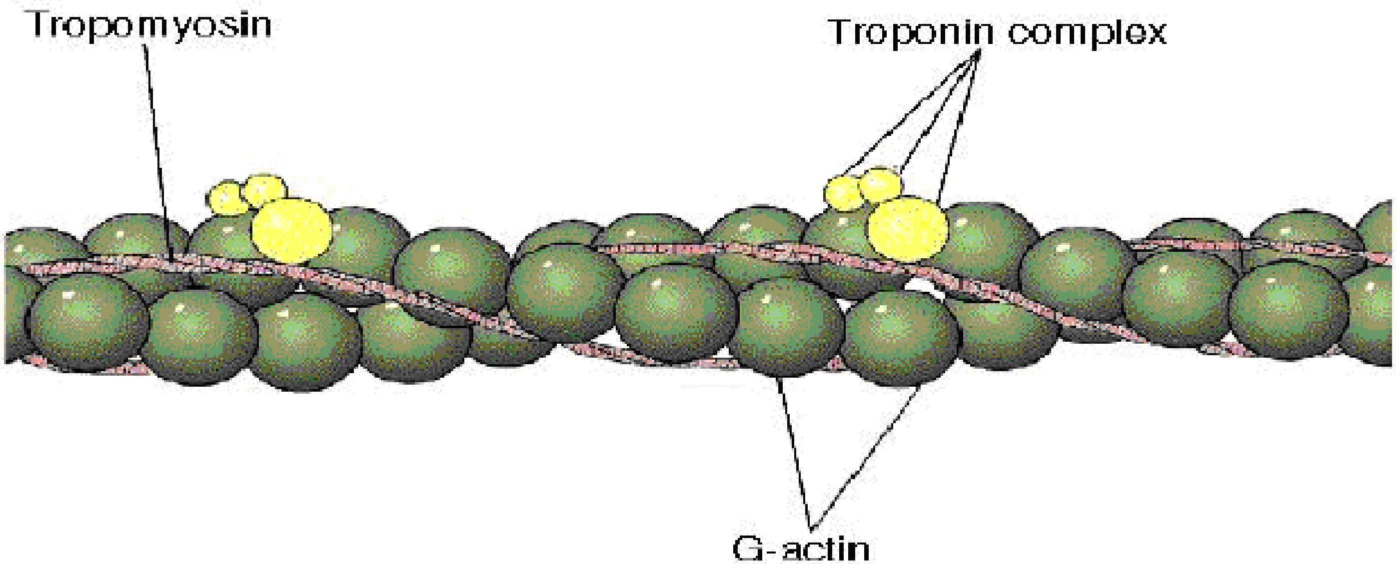
Thick myofilaments are found in the middle of the sarcomere and do not extend to the ends





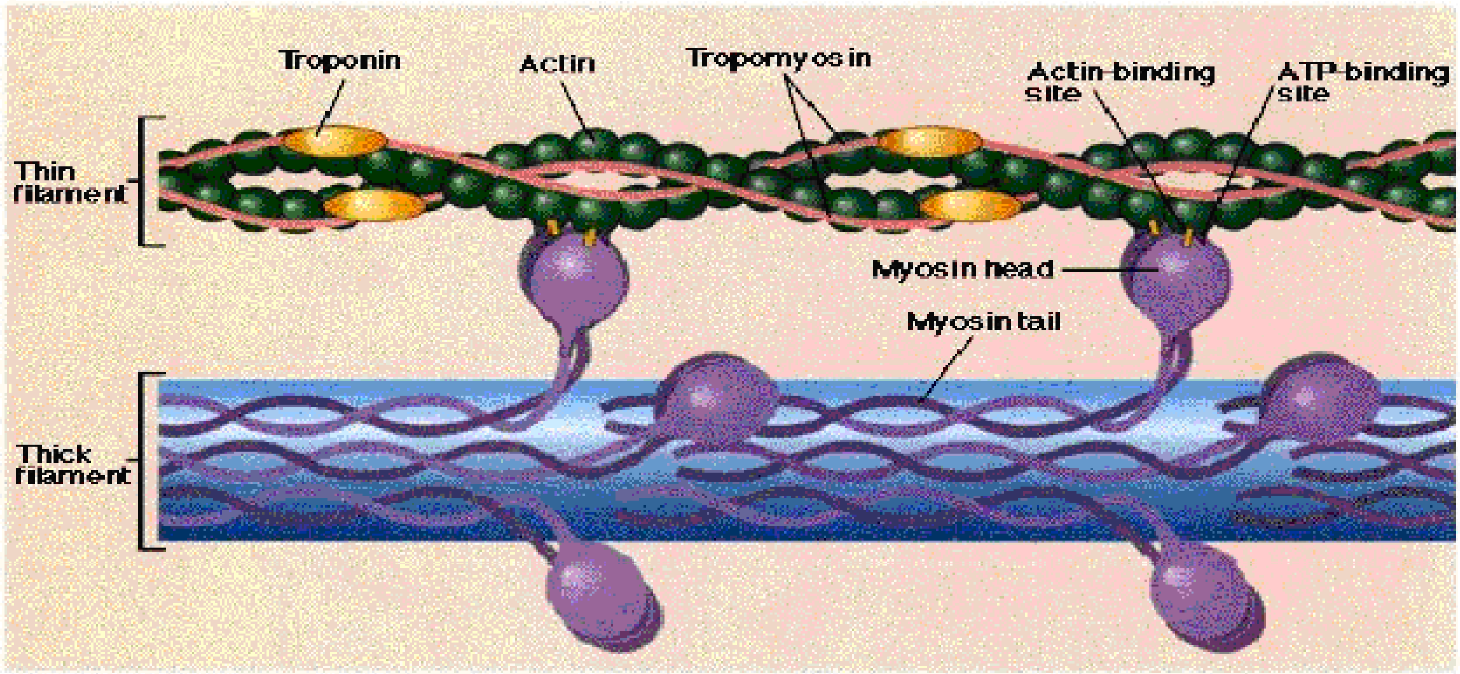
The MYOSIN HEAD : has ATP-binding sites and ACTIN-binding sites
it has a "hinge"at the point where it leaves the core of the thick myofilament.
This allows the head to swivel back and forth, and the "swivelling" is, what actually causes muscle contraction.

Thin filament



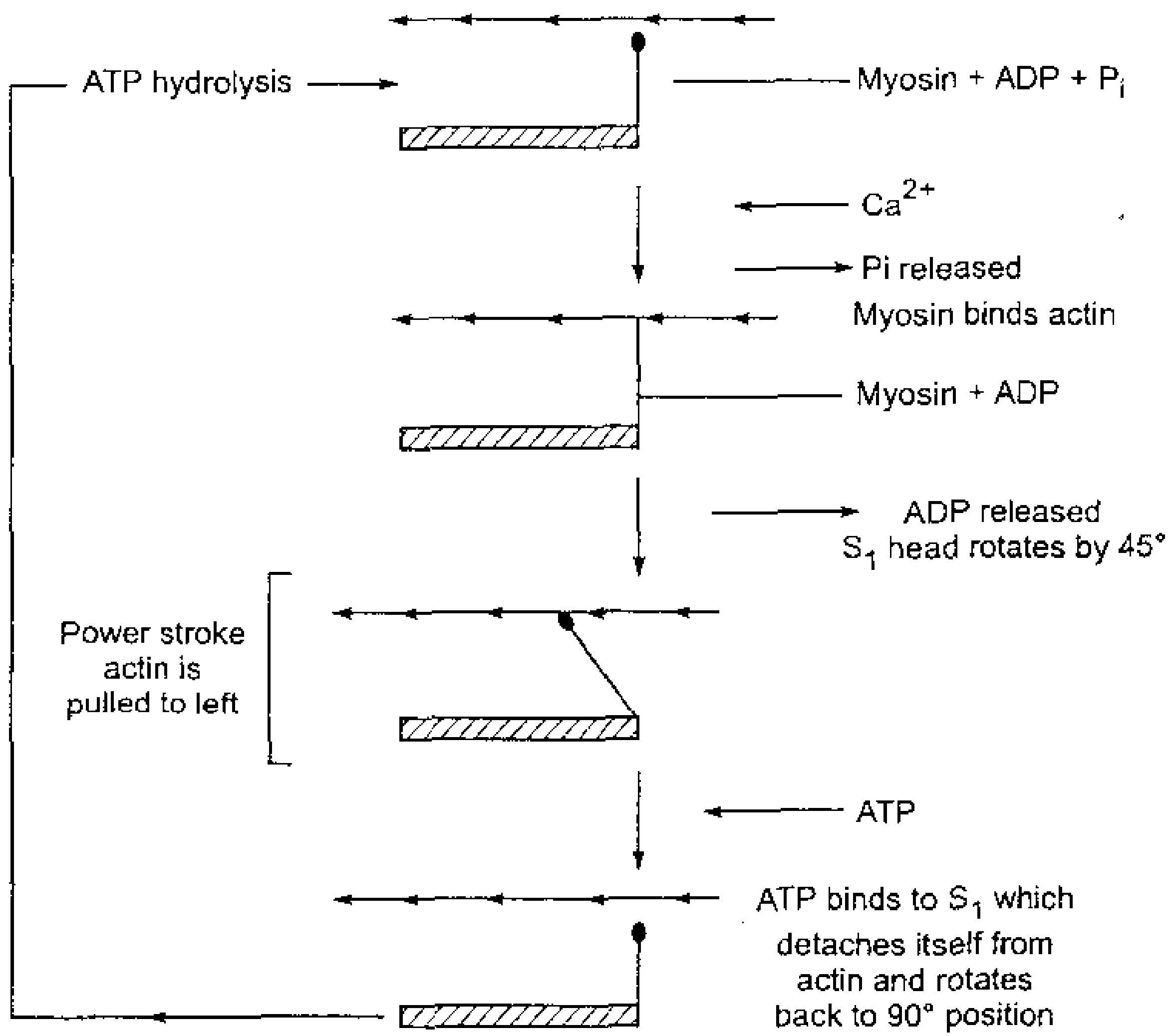
The actin molecules (or G-actin) are spherical and form long chains. Each thin myofilament contains two such chains that coil around each other. TROPOMYOSIN molecules are long, thin molecules that wrap around the chain of ACTIN. At the end of each tropomyosin is an TROPONIN molecule. The TROPOMYOSIN and TROPONIN molecules are connected to each other. Each of these 3 proteins plays a key role in muscle contraction:

Thick filament and thin filament interact through the myosin



ACTIN - when actin combines with MYOSIN HEAD the ATP associated with the head breaks down into ADP +Pi. This reaction released energy that causes the MYOSIN HEAD to SWIVEL.
TROPOMYOSIN - In a relaxed muscle, the MYOSIN HEADS of the thick filament lie against TROPOMYOSIN molecules of the thin filament .
TROPONIN - Troponin molecules have binding sites for calcium ions. When a calcium ion fills this site it causes a change in the shape and position of TROPONIN. And, when TROPONIN shifts, it pulls the TROPOMYOSIN to which it is attached. When TROPOMYOSIN is moved, the MYOSIN HEAD that was touching the tropomyosin now comes in contact with an underlying ACTIN molecule.

Muscle contraction



Animation:

http://www.youtube.com/watch?v=ren_IQPOhJc&feature=related

http://www.youtube.com/watch?v=gJ309LfHQ3M&feature=related

http://www.blackwellpublishing.com/matthews/myosin.html

Muscle contraction

- 1 - contraction requires a nervous impulse. So, step 1 in contraction is when the impulse is transferred from a neuron to the SARCOLEMMA of a muscle cell.
- 2 - The impulse travels along the SARCOLEMMA and down the T-TUBULES. From the T-TUBULES, the impulse passes to the SARCOPLASMIC RETICULUM.
- 3 - As the impulse travels along the Sarcoplasmic Reticulum (SR), the calcium gates in the membrane of the SR open. As a result, CALCIUM diffuses out of the SR and among the myofilaments.
- 4 - Calcium fills the binding sites in the TROPONIN molecules. This alters the shape and position of the TROPONIN which in turn causes movement of the attached TROPOMYOSIN molecule.
- 5 - Movement of TROPOMYOSIN permits the MYOSIN HEAD to contact ACTIN.
- 6 – release of ADP and Pi - MYOSIN HEAD swivels.
- 7 - During the swivel, the MYOSIN HEAD is firmly attached to ACTIN. So, when the HEAD swivels it pulls the ACTIN (and, therefore, the entire thin myofilament) forward. (Obviously, one MYOSIN HEAD cannot pull the entire thin myofilament. Many MYOSIN HEADS are swivelling simultaneously, or nearly so, and their collective efforts are enough to pull the entire thin myofilament).
- 8 - At the end of the swivel, ATP fits into the binding site on the cross-bridge & this breaks the bond between the cross-bridge (myosin) and actin. The MYOSIN HEAD is released from actin and swivels back. As it swivels back, the ATP breaks down to ADP & P and the cross-bridge again binds to an actin molecule.
- 9 - As a result, the HEAD is once again bound firmly to ACTIN. However, because the HEAD was not attached to actin when it swivelled back, the HEAD will bind to a different ACTIN molecule (i.e., one further back on the thin myofilament). Once the HEAD is attached to ACTIN, the cross-bridge again swivels, SO STEP 7 IS REPEATED

Energetics of muscle contraction

- The essence of contraction mechanism is the cyclic change in the conformation of myosin molecule, driven by the energy released from hydrolysis of ATP molecule to ADP + Pi (30.6 kJ/mole)
- ATP must be continuously supplied to sustain muscle contraction,
- ATP is produced in resting muscle, the amount of it in muscle is enough for 10 contractions (less than 1 s). For extended muscle activity an extra source of ATP is required (creatine phosphate and hydrolysis of glucose)
- Creatine phosphate has higher phosphoryl transfer potential than ATP and is present at higher amount, ATP is produced during hydrolysis of creatine phosphate, [ATP]=4mM, [CP]=25mM, this is enough for 4 min.

$$\text{Creatine Phosphate} + \text{H}_2\text{O} \rightarrow \text{Creatine} + \text{P}_i \qquad \Delta\text{G}^\circ = -43.2\text{kJ/mole}$$

$$\text{ADP} + \text{P}_i \rightarrow \text{ATP} + \text{H}_2\text{O} \qquad \Delta G^\circ = +30.6\text{kJ/mole}$$

$$\text{Creatine Phosphate} + \text{ADP} \rightarrow \text{ATP} + \text{Creatine} \Delta G^\circ = -12.6\text{kJ/mole}$$