PLANT FUNCTIONAL BIOLOGY

6 Sem BSc Botany
Providence Women's College, Kozhikode

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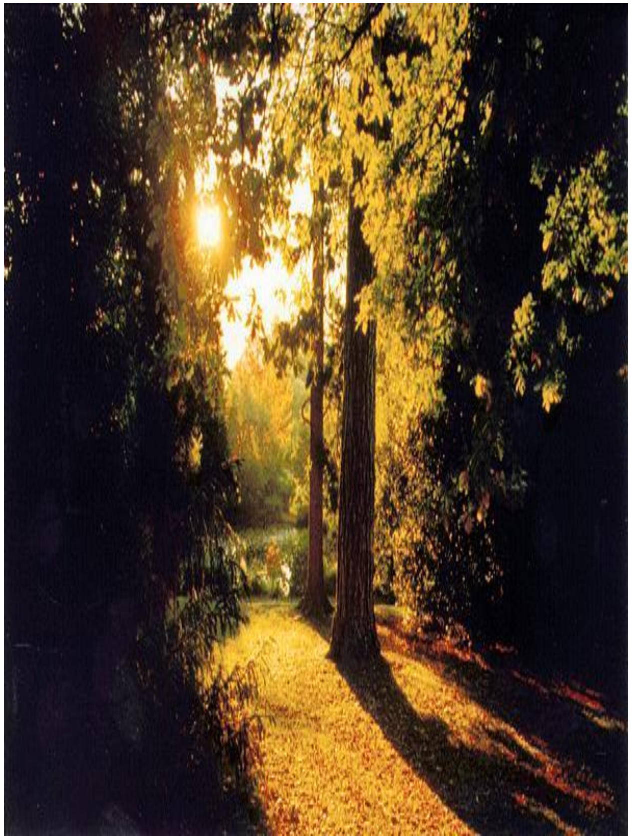
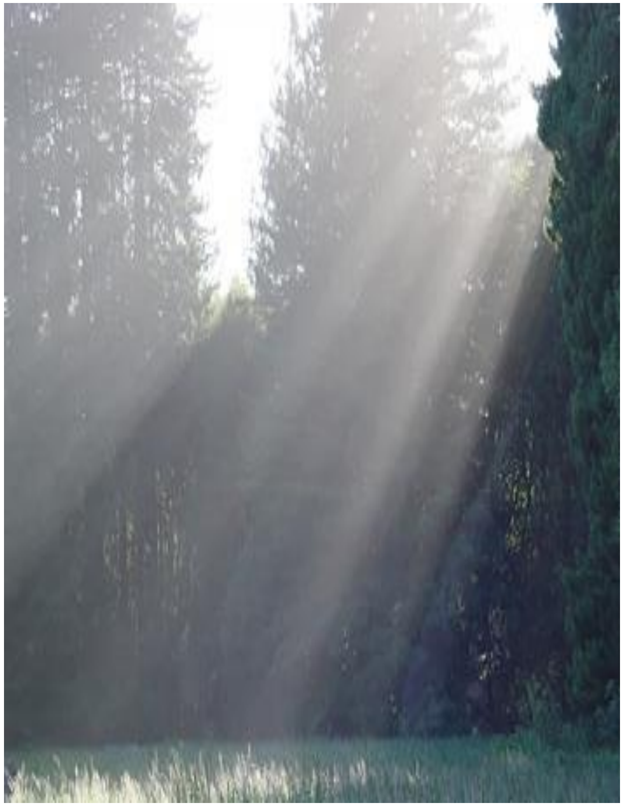
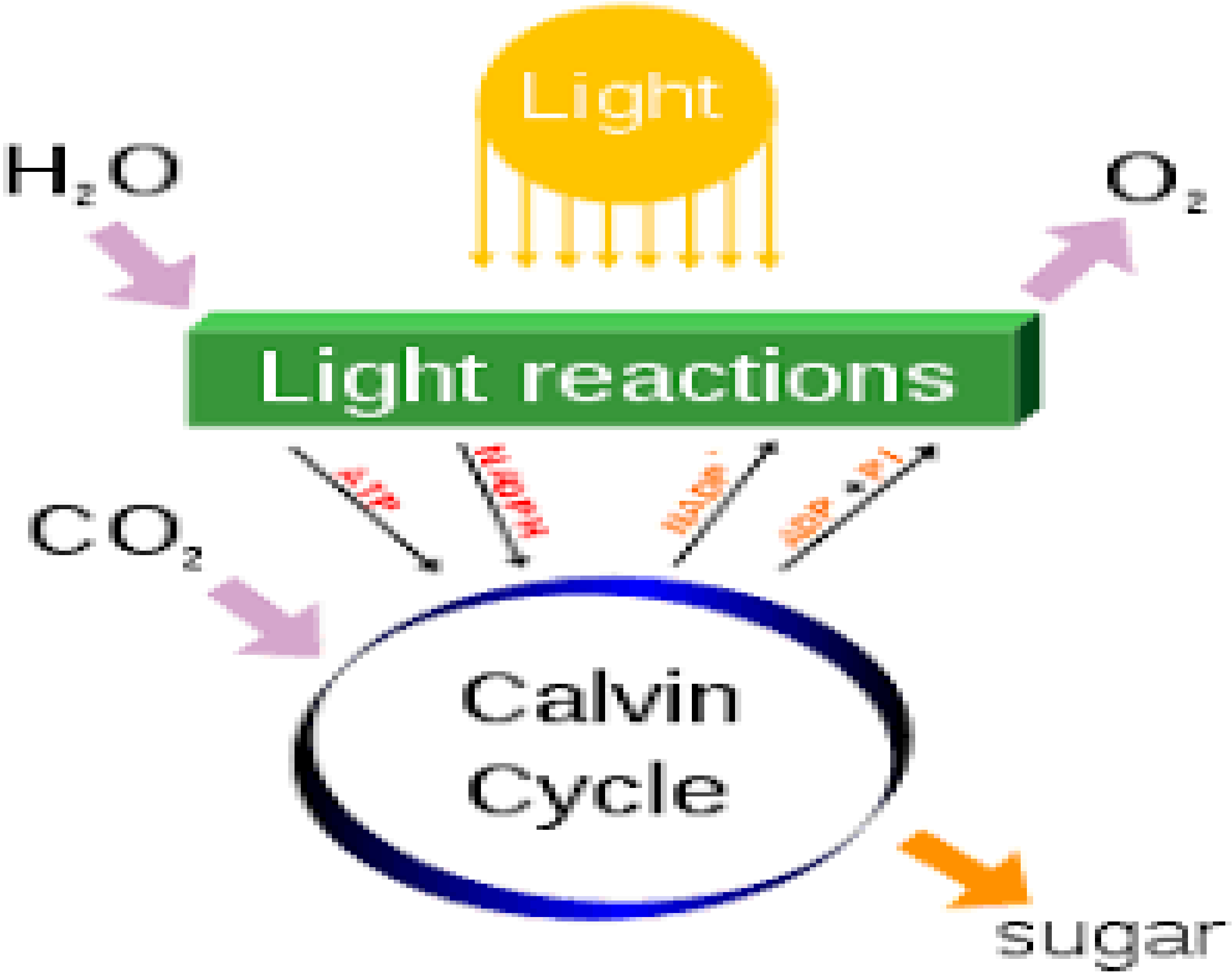
Main source of energy for life on earth



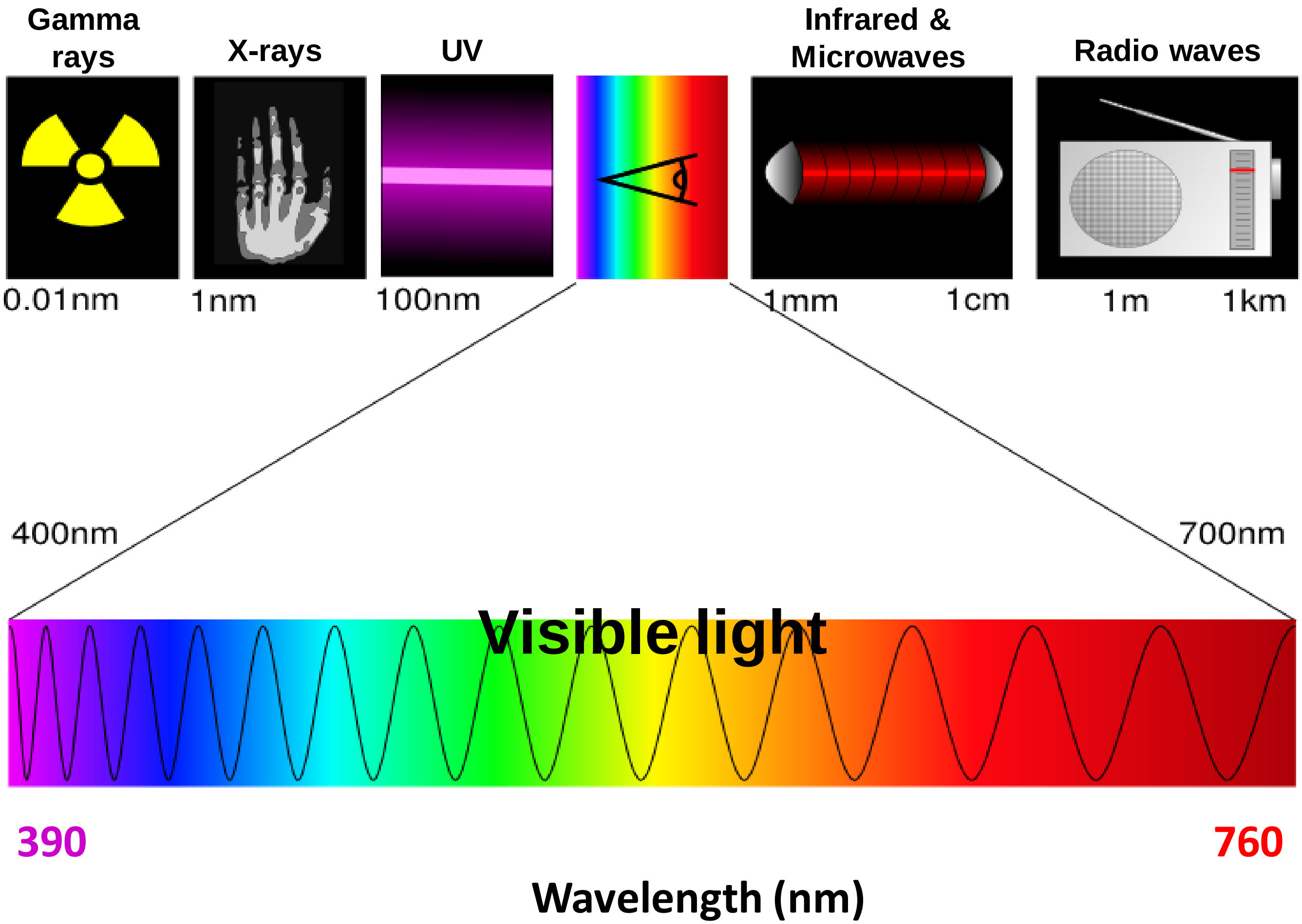
SUN



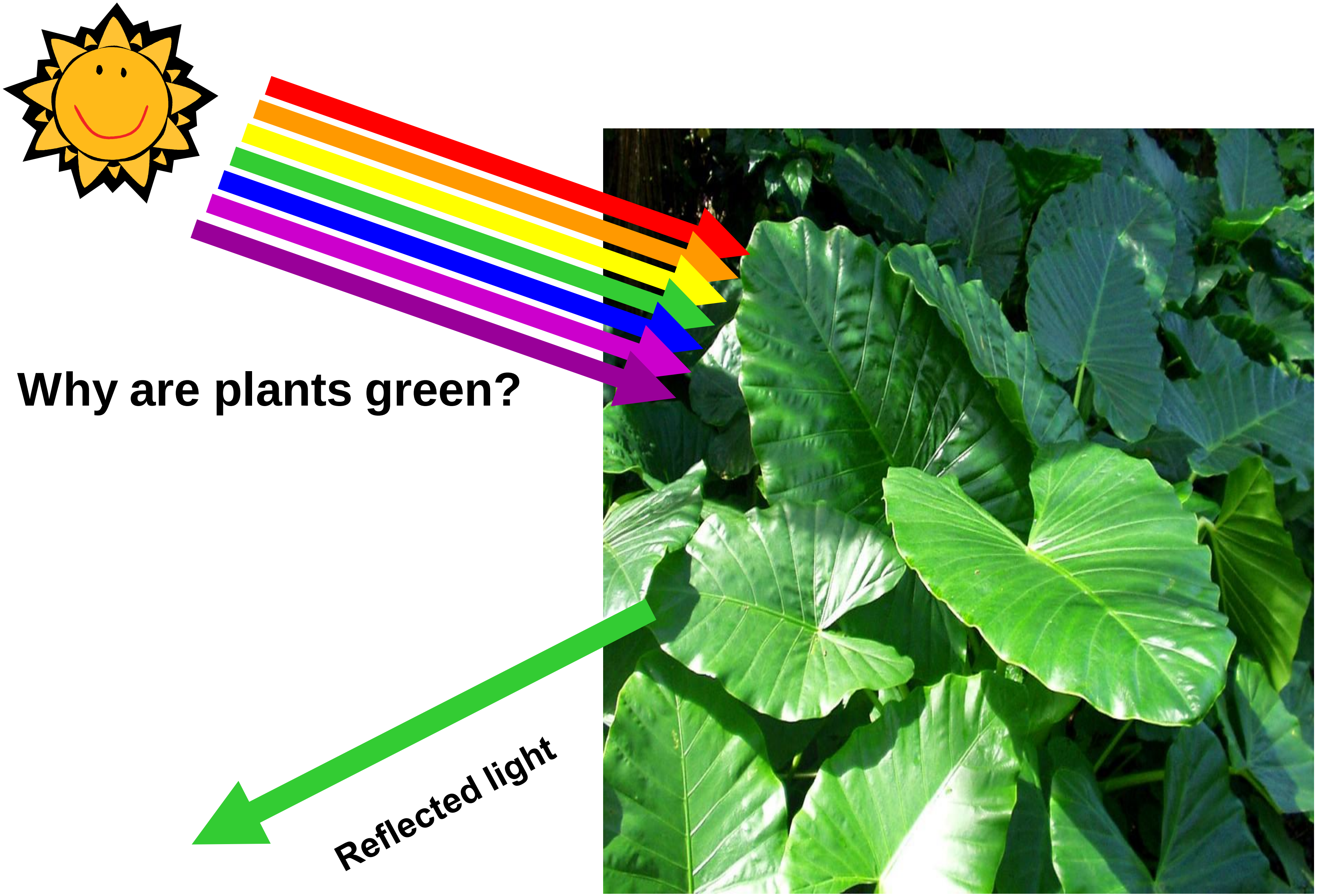
PHOTOSYNTHESIS



Electromagnetic Spectrum and Visible Light



Why are plants green?



Reflected light

Chloroplast Pigments

- Chloroplasts contain several pigments
  - Chlorophylls a, b, c, d, e, baceriochlorophyll
  - Carotenoids yellow, orange, brown, red

Figure 7.7

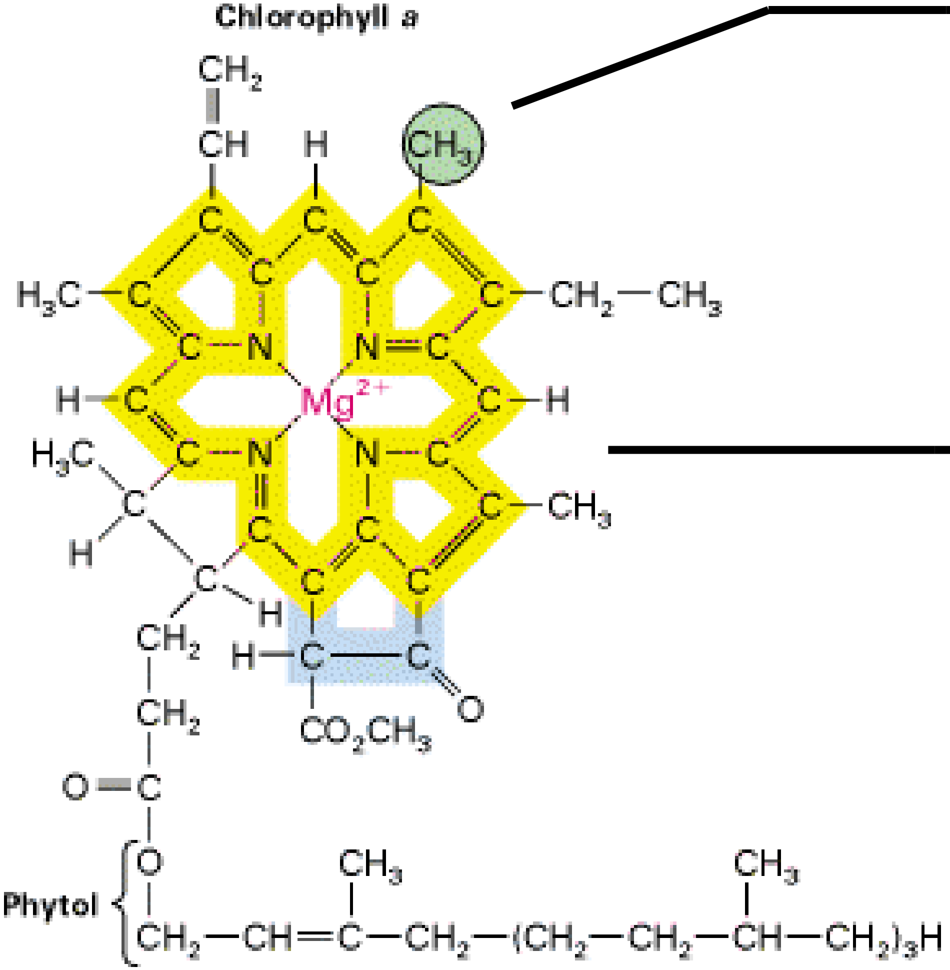
Chlorophylls

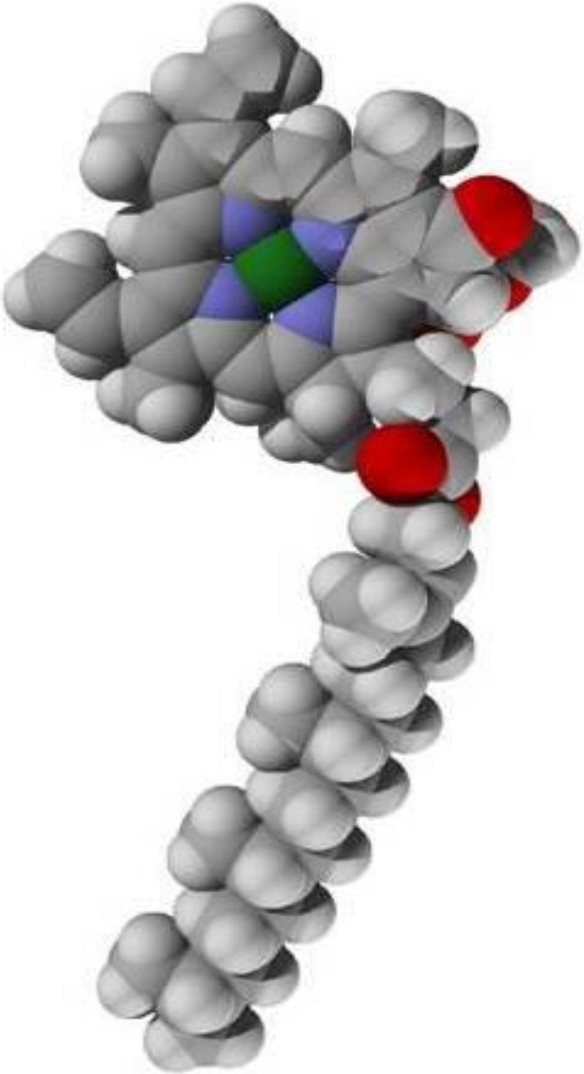
- Principal pigment
- Photochemical reaction only in **chl a**
- Magnesium porphyrin derivatives
- Pyrole head(hydrophobic), phytol tail (hydrophilic)
- Tetrapyrole ring/ porphyrin ring
- **a** $C_{55}H_{72}O_5N_4Mg$
- **b** $C_{55}H_{70}O_6N_4Mg$

Carotenoids

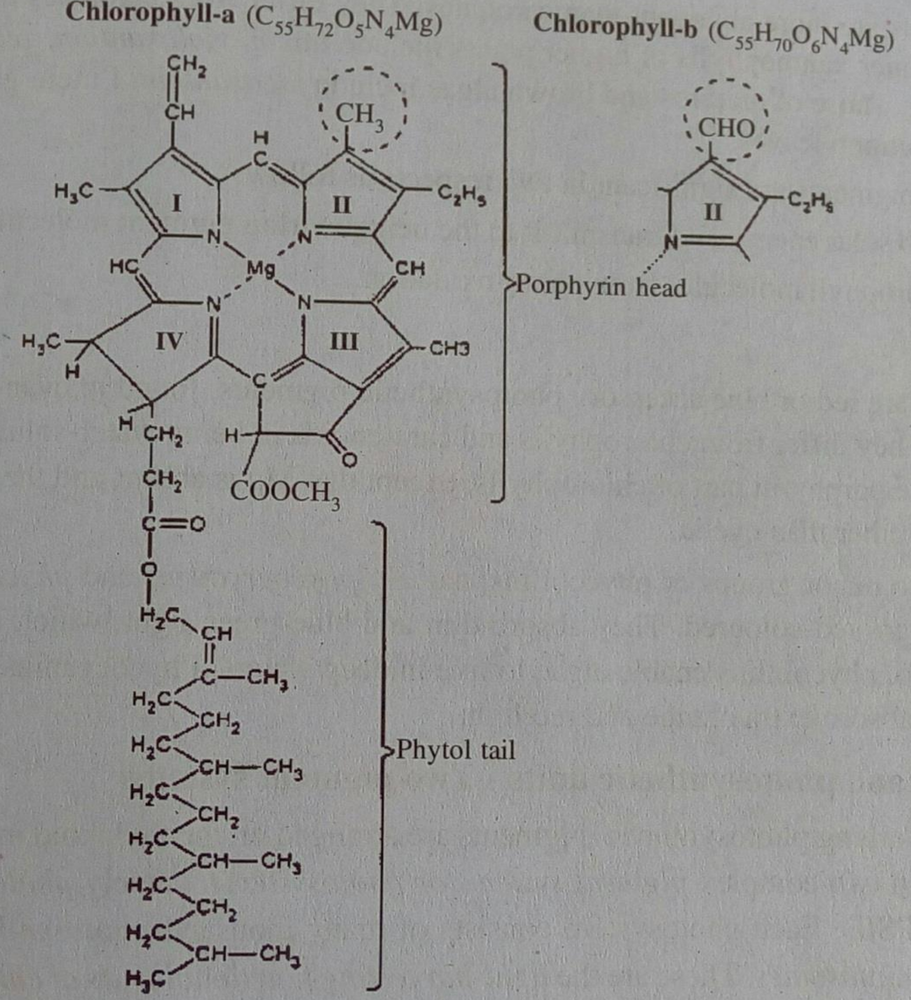
- Accessory pigments
- Carotenes $C_{40}H5_6$ Aalpha, beta, gamma, phytotene, lycopene, neurosporene
- Xanhophylls $C_{40}H_{56}O_2$ lutein, violaxanthin, zeaxanthin, neoxanthin
-

Chlorophyll a & b





Phytol tail

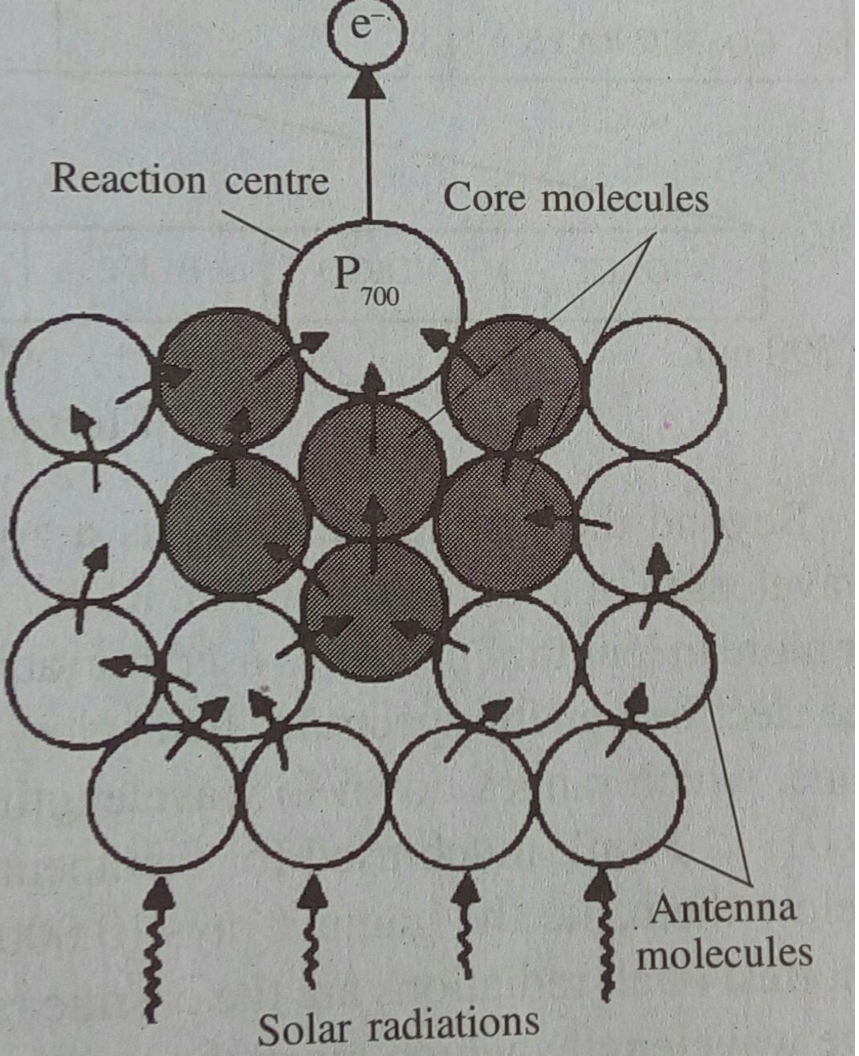


Chlorophyll-a ($C_{55}H_{72}O_5N_4Mg$)

Chlorophyll-b ($C_{55}H_{70}O_6N_4Mg$)

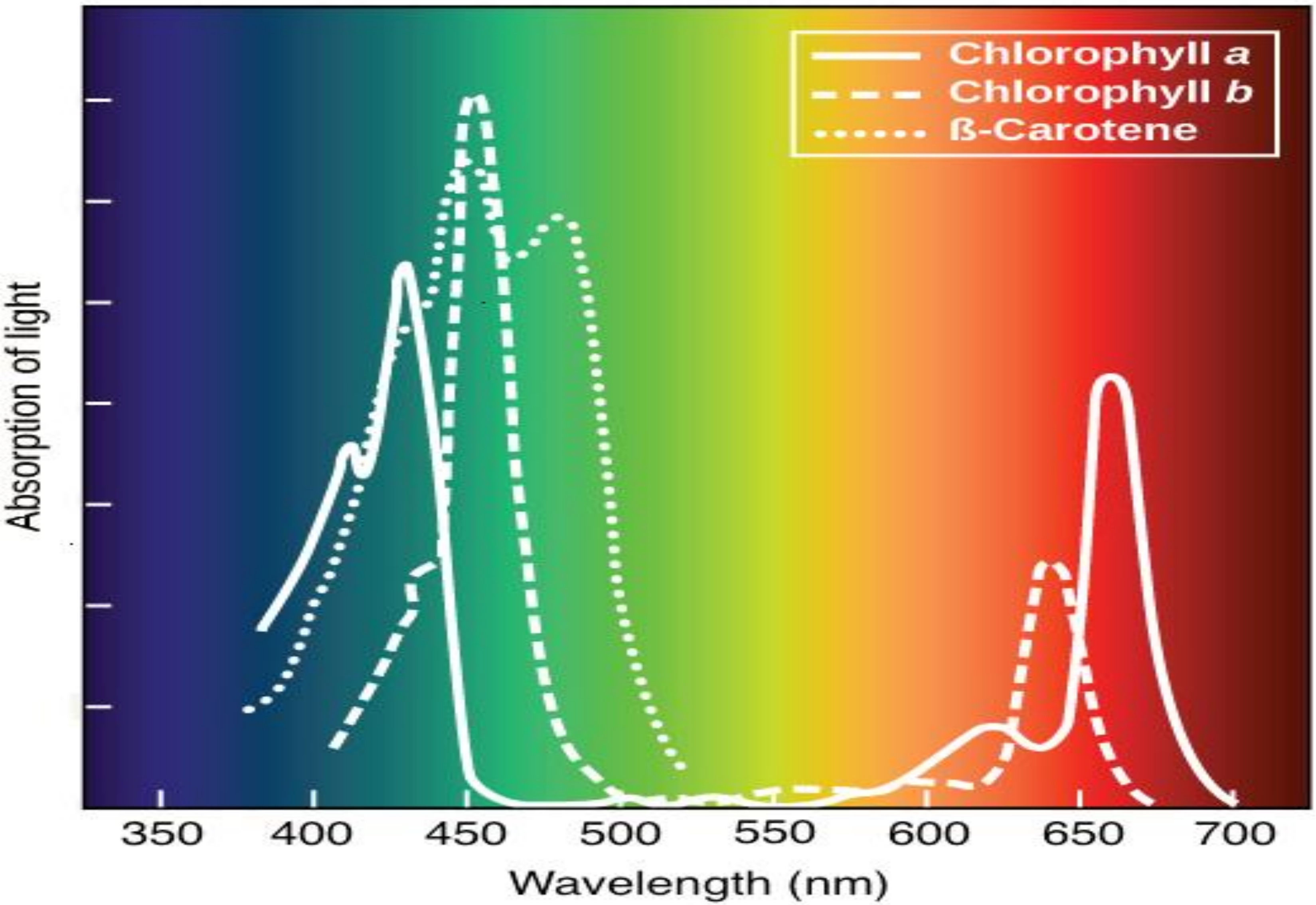
Structural formulae of chlorophyll-a & b

Some major photosynthetic pigments			
Category	*Name*	*Status*	*Distribution*
A. Chlorophylls	(i) Chlorophyll -a ($C_{55}H_{72}O_5N_4Mg$)	Principal	All photosynthetic plants
	(ii) Chlorophyll - b ($C_{55}H_{70}O_6N_4Mg$)	Accessory	Plants, green algae
	(iii) Chlorophyll - c ($C_{35}H_{32}O_5N_4Mg$)	,,	Brown algae, diatoms, dinoflagellates
	(iv) Chlorophyll - d ($C_{35}H_{70}O_6N_4Mg$)	,,	Some red algae
	(v) Bacteriochlorophyll ($C_{55}H_{74}O_6N_4Mg$)	Principal	Purple & green bacteria
	(vi) Chlorobium chlorophyll (Bacterioviridin)	,,	Green bacteria
B. Carotenoids	(i) Carotenes	Accessory	Photosynthetic plants
	(ii) Xanthophylls	Accessory	,,
C. Phycobilins	(i) Phycoerythrin	Accessory	Red algae & Cyanobacteria
	(ii) Phycocyanin	,,	,,
D. Rhodopsin	Bacteriorhodopsin	Principal	Halobacteria

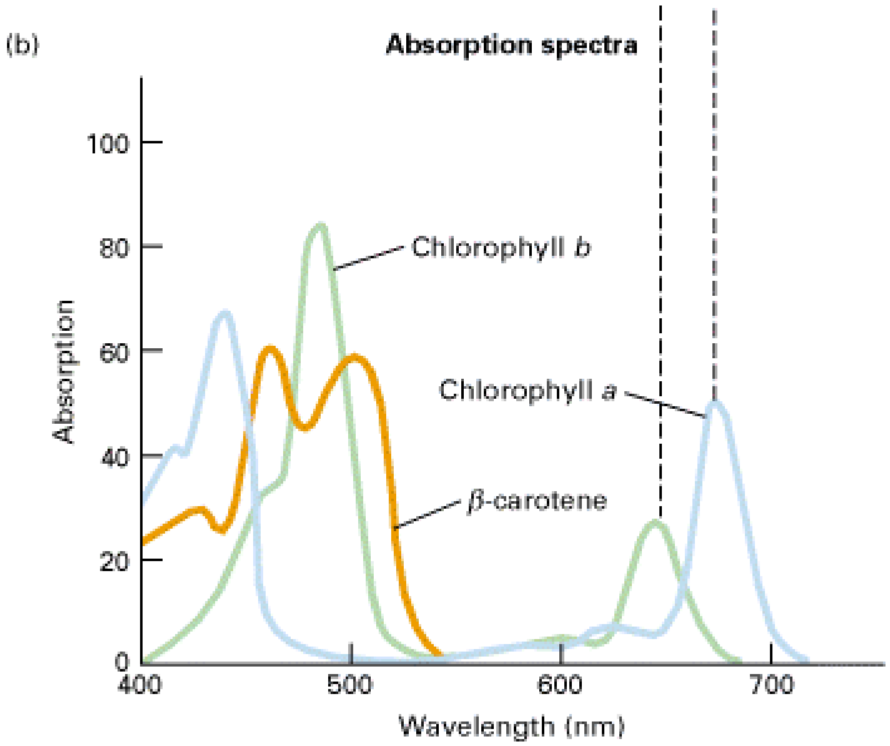


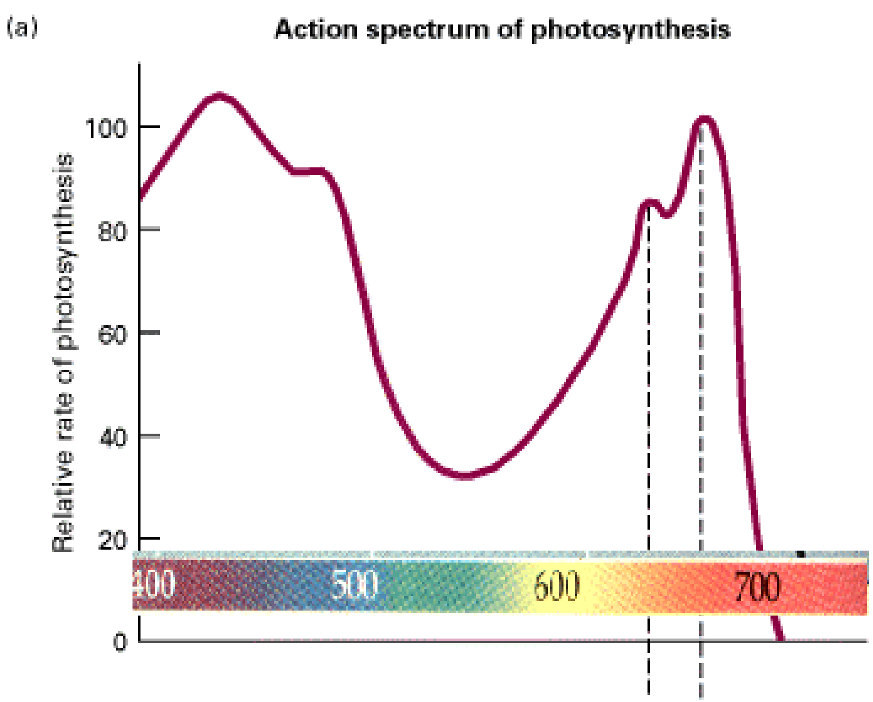
Photosynthetic unit

Absorption Spectra of Pigments

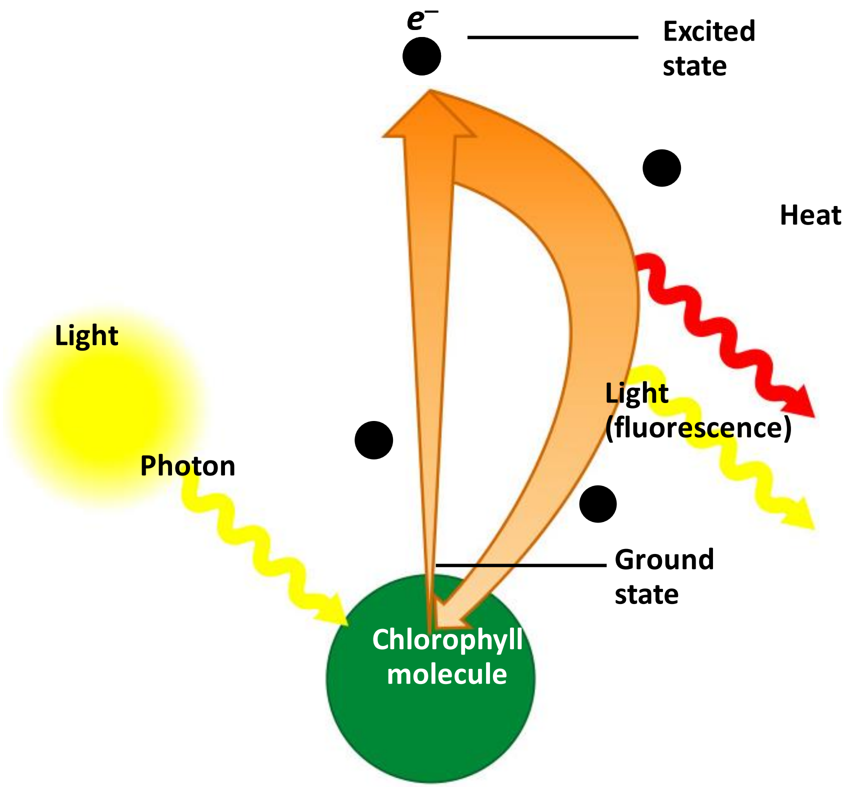


Different pigments absorb light differently



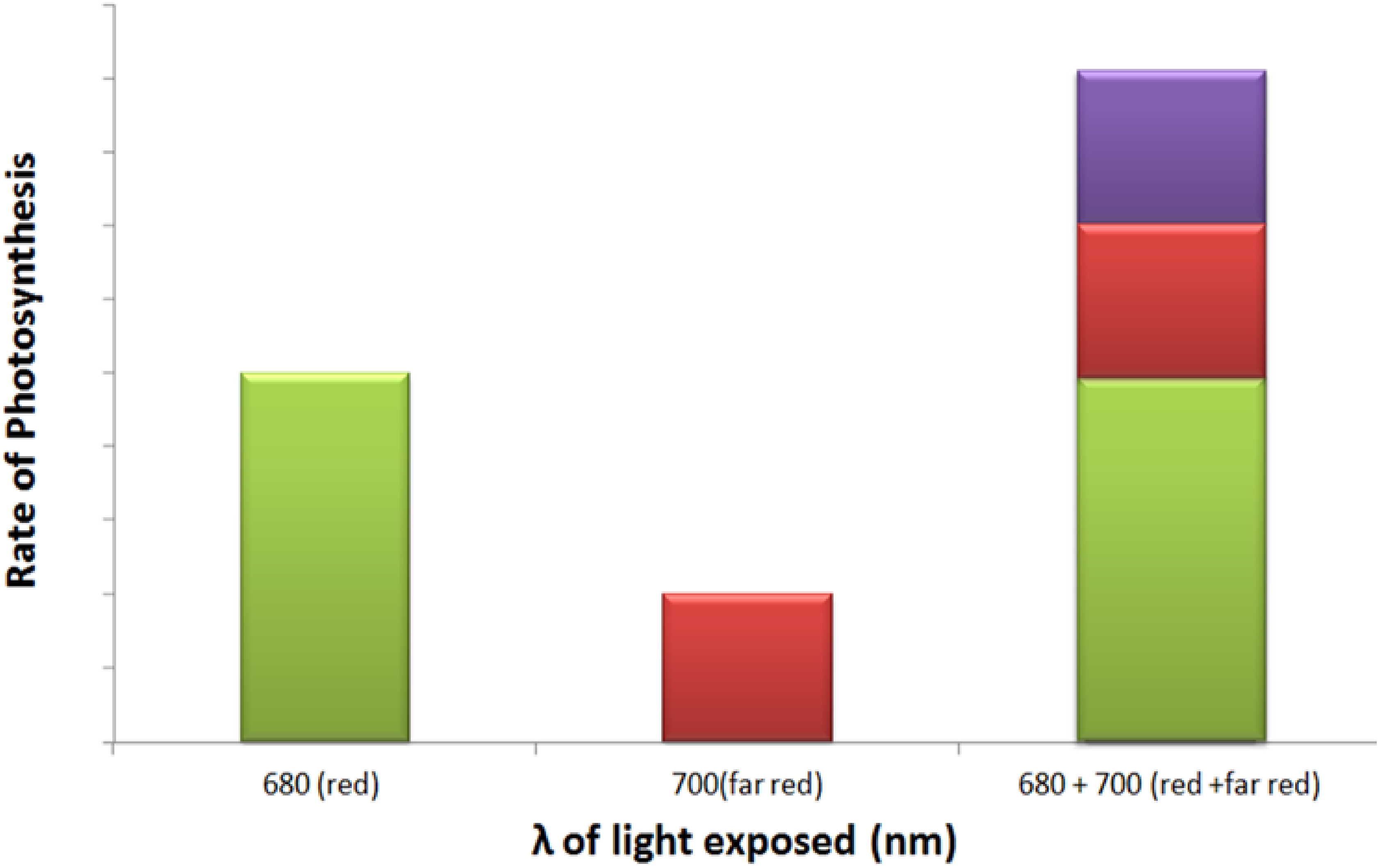


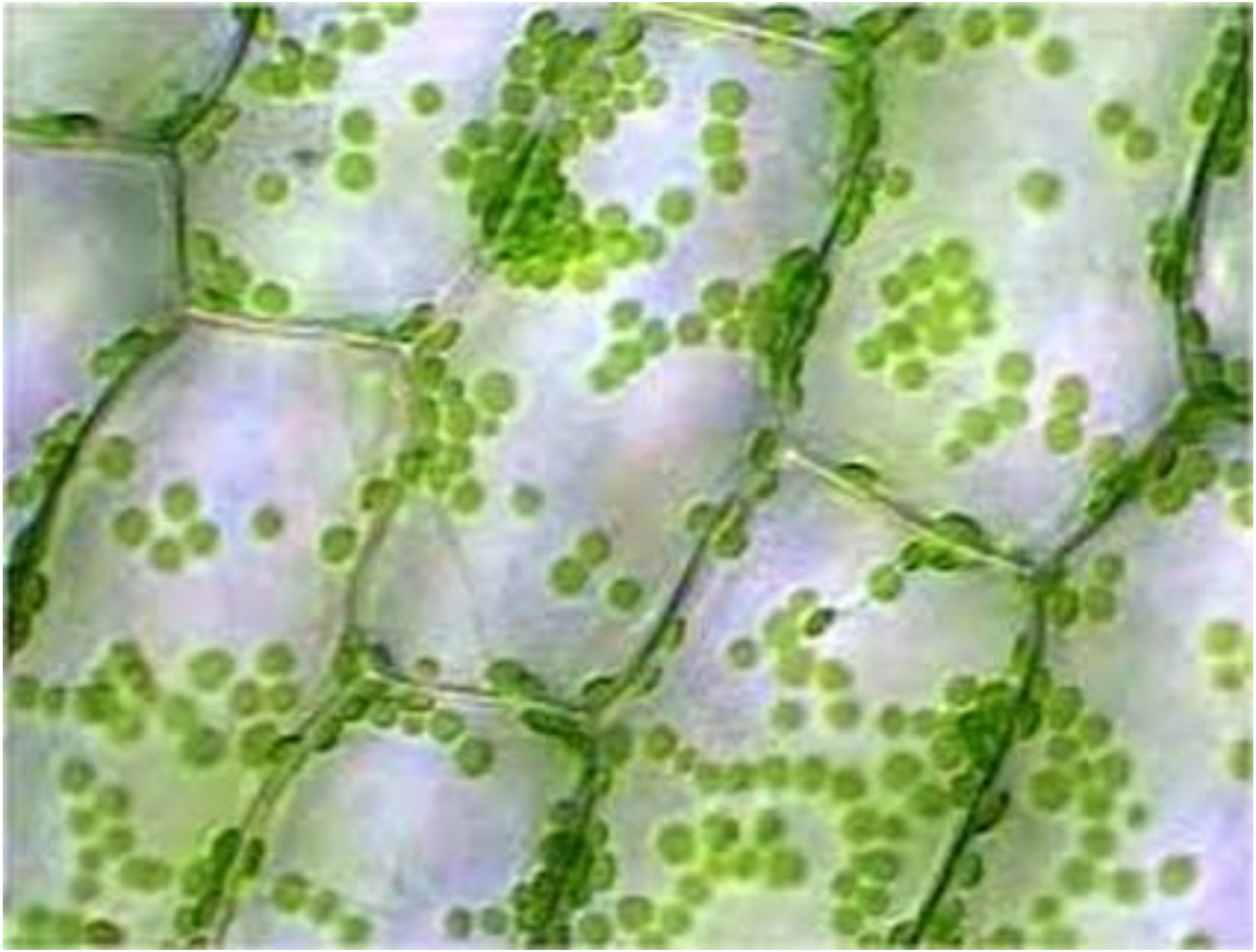
Excitation of chlorophyll in a chloroplast

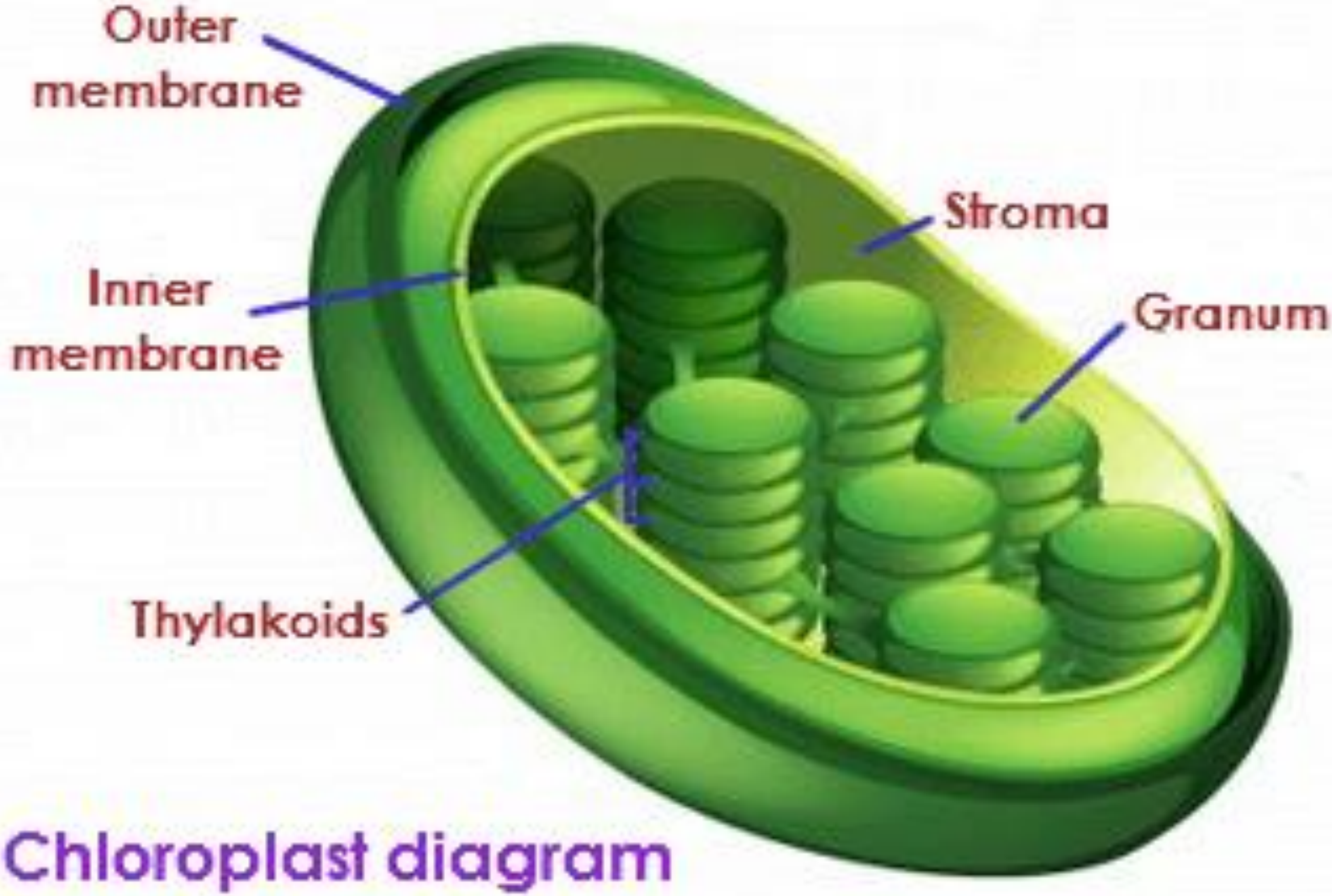


(a) Absorption of a photon

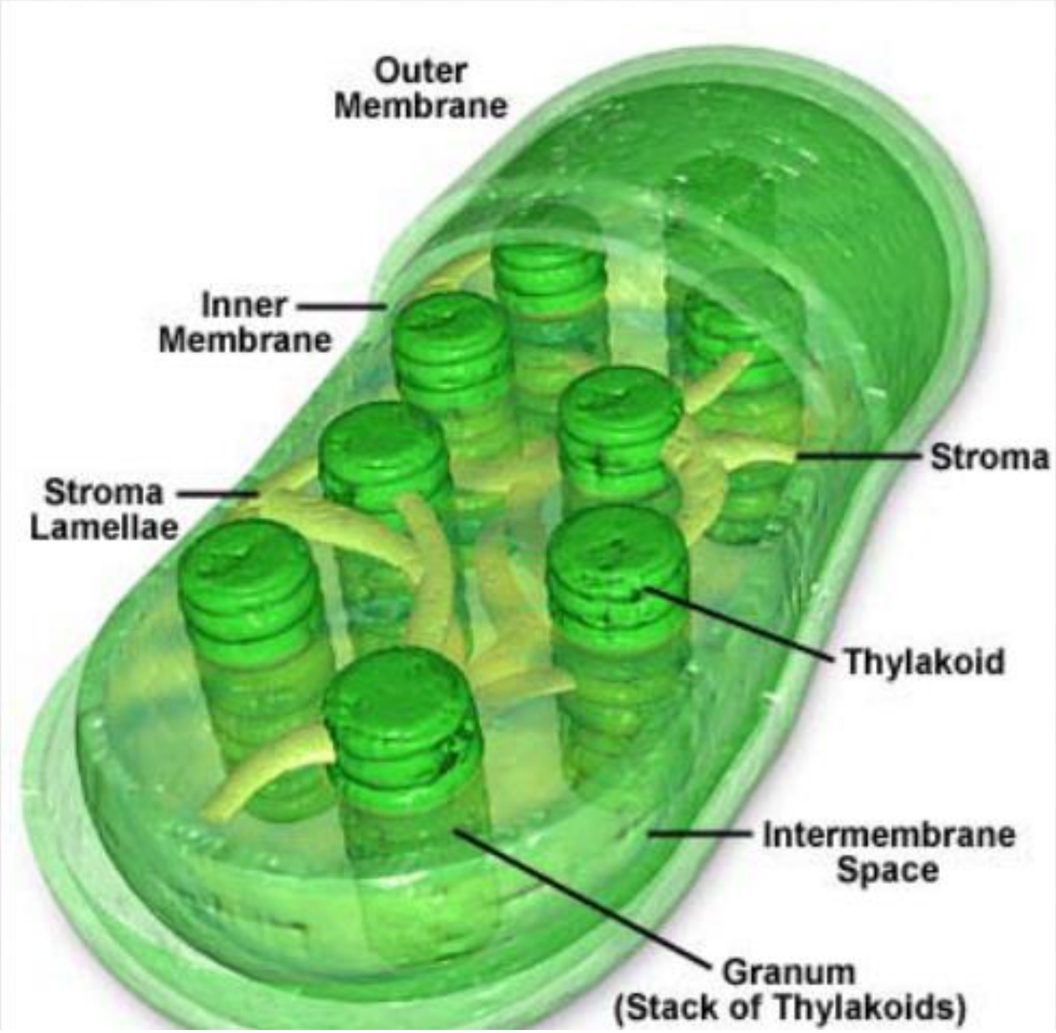
Emerson Red Drop and Enhancement Effect

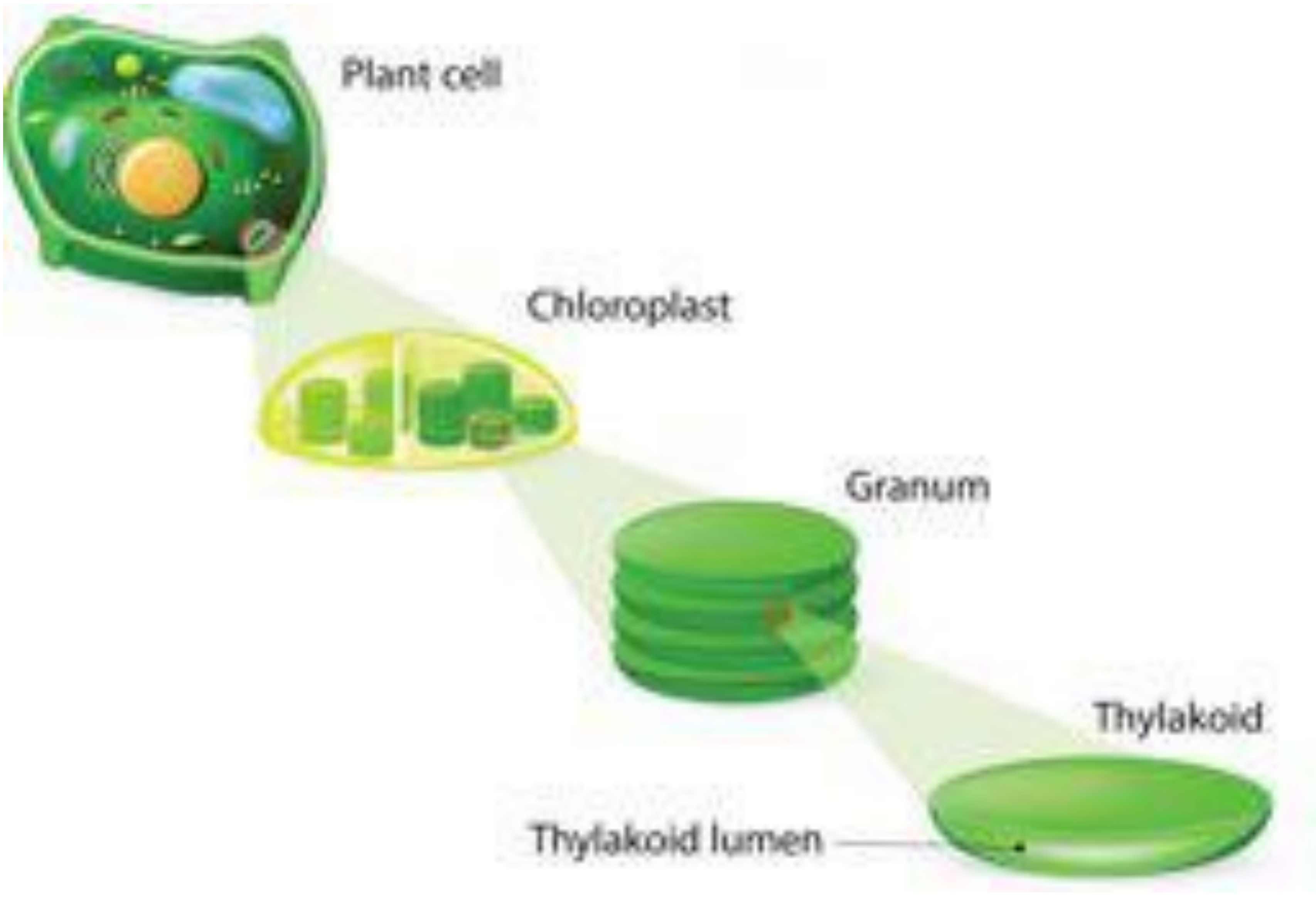


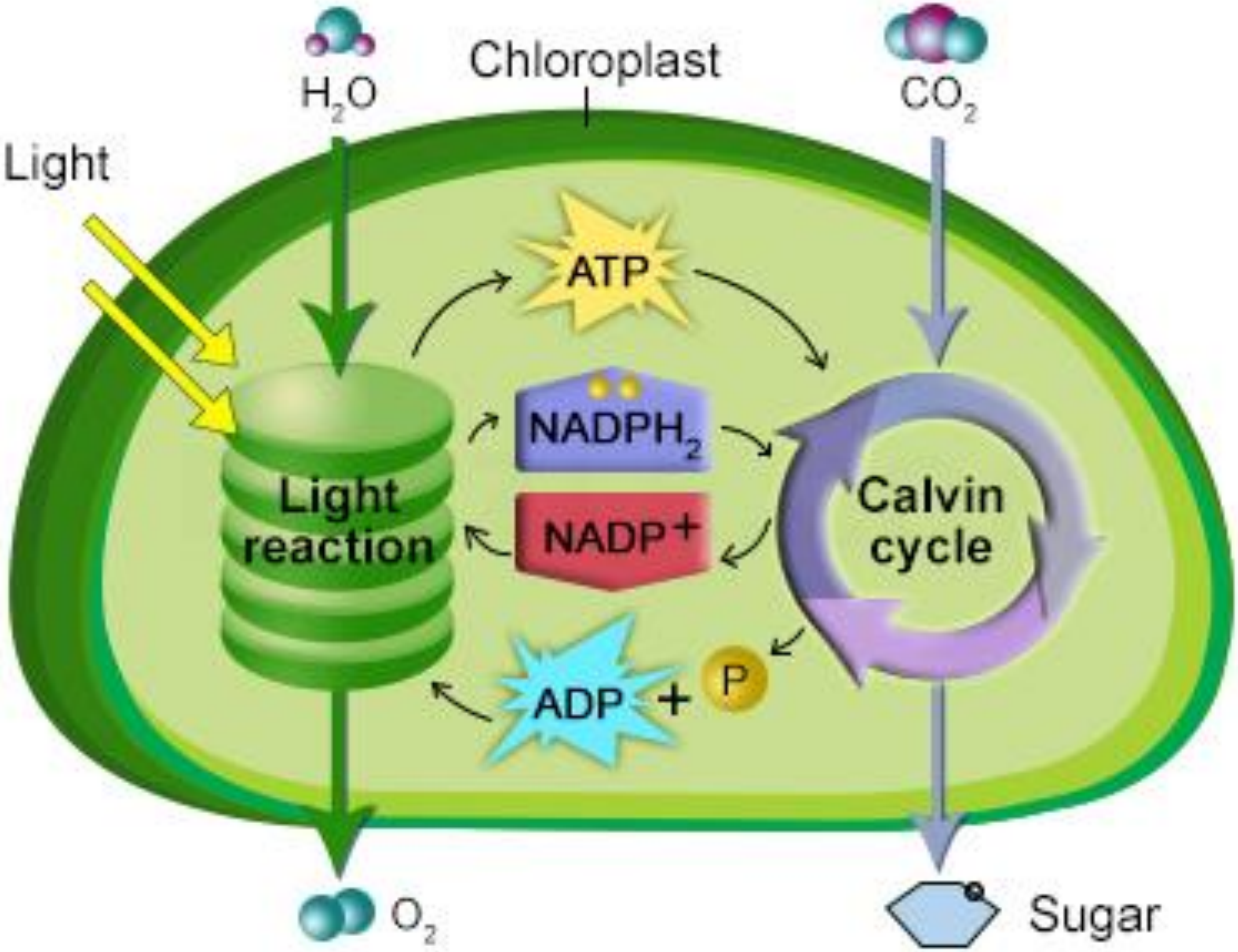




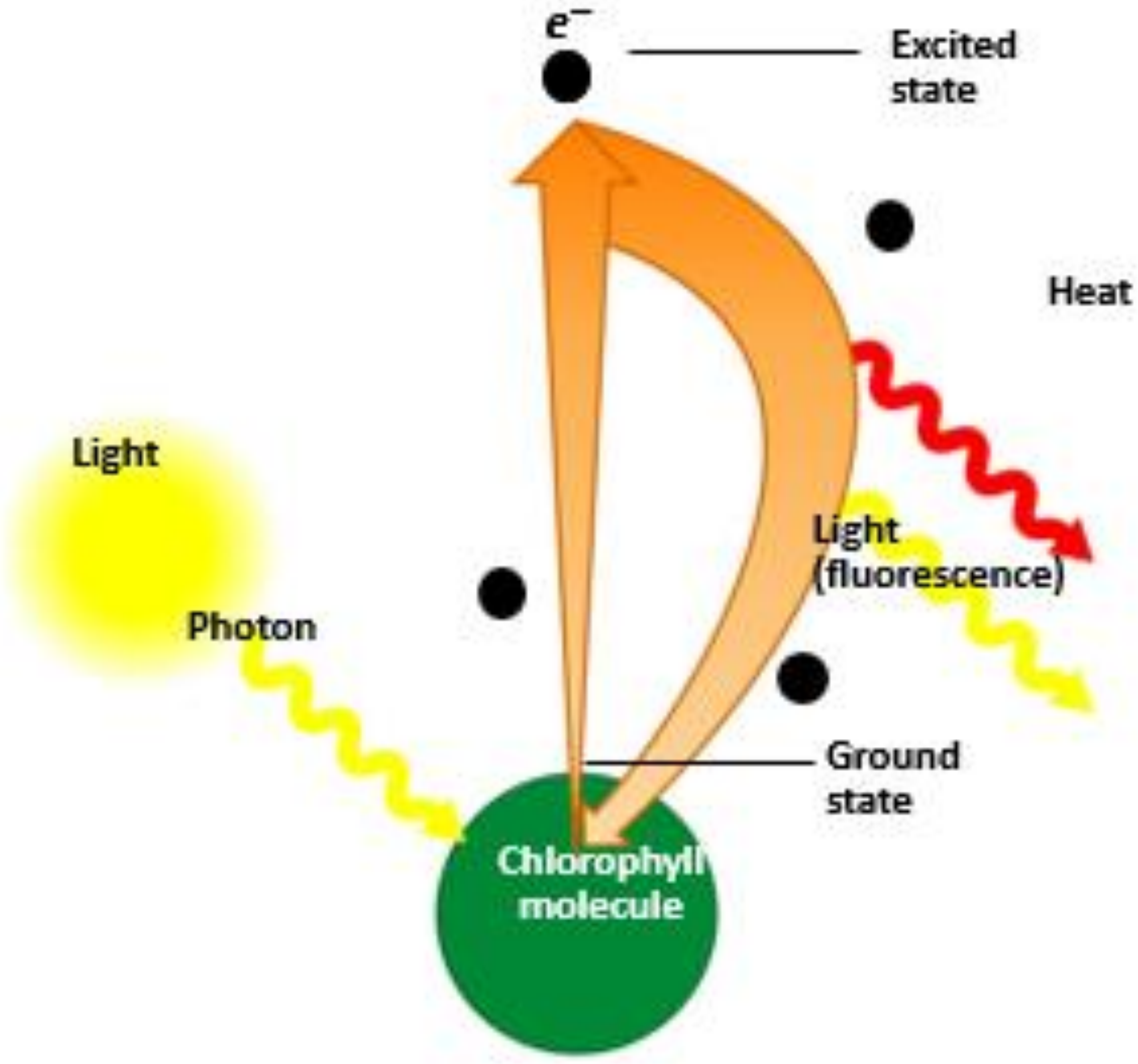
Chloroplast diagram


Outer Membrane
Inner Membrane
Stroma
Stroma Lamellae
Thylakoid
Intermembrane Space
Granum (Stack of Thylakoids)


Plant cell
Chloroplast
Granum
Thylakoid
Thylakoid lumen

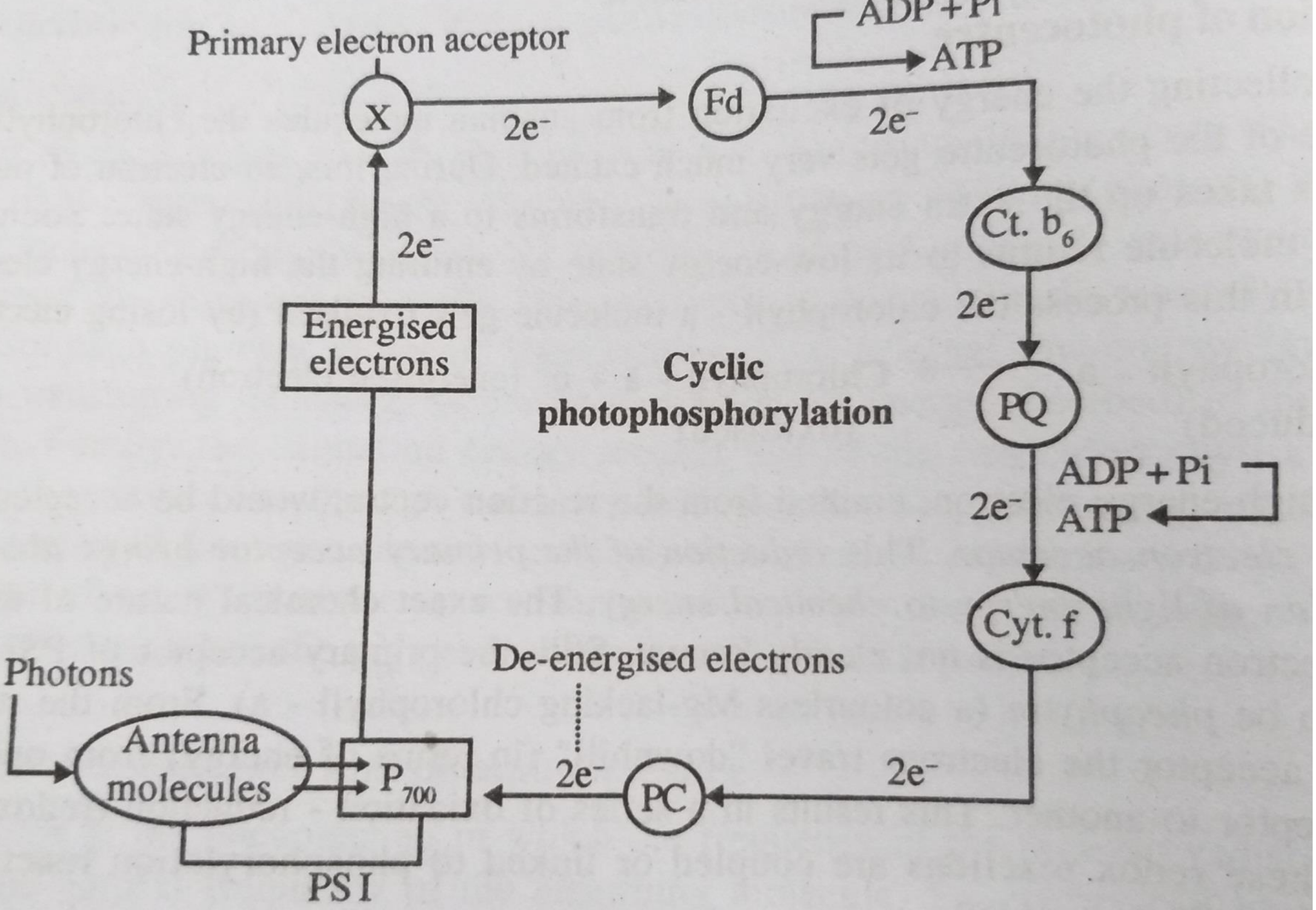

H_2O
Chloroplast
CO_2
Light
ATP
$NADPH_2$
Light reaction
$NADP^+$
Calvin cycle
ADP + P
O_2
Sugar

Excitation of chlorophyll in a chloroplast



(a) Absorption of a photon

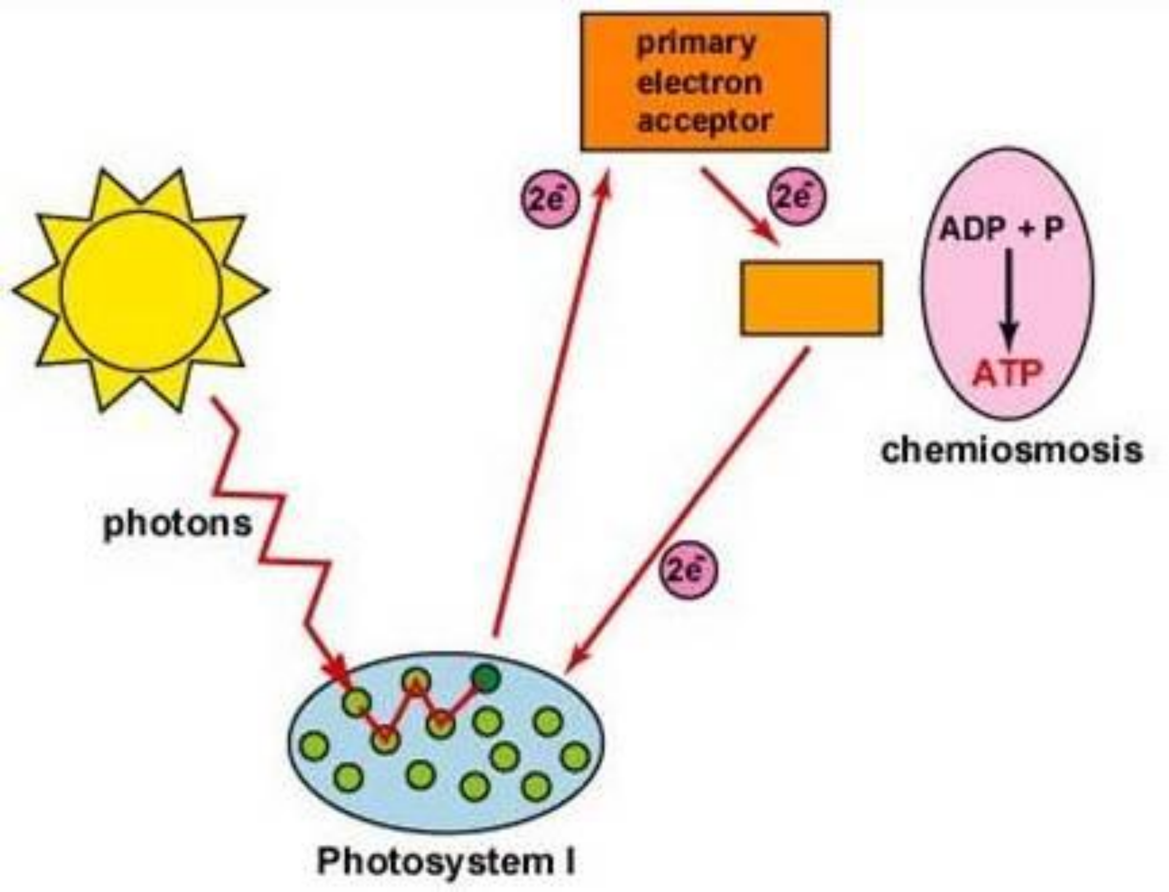
ectrons move to a *primary acceptor* (

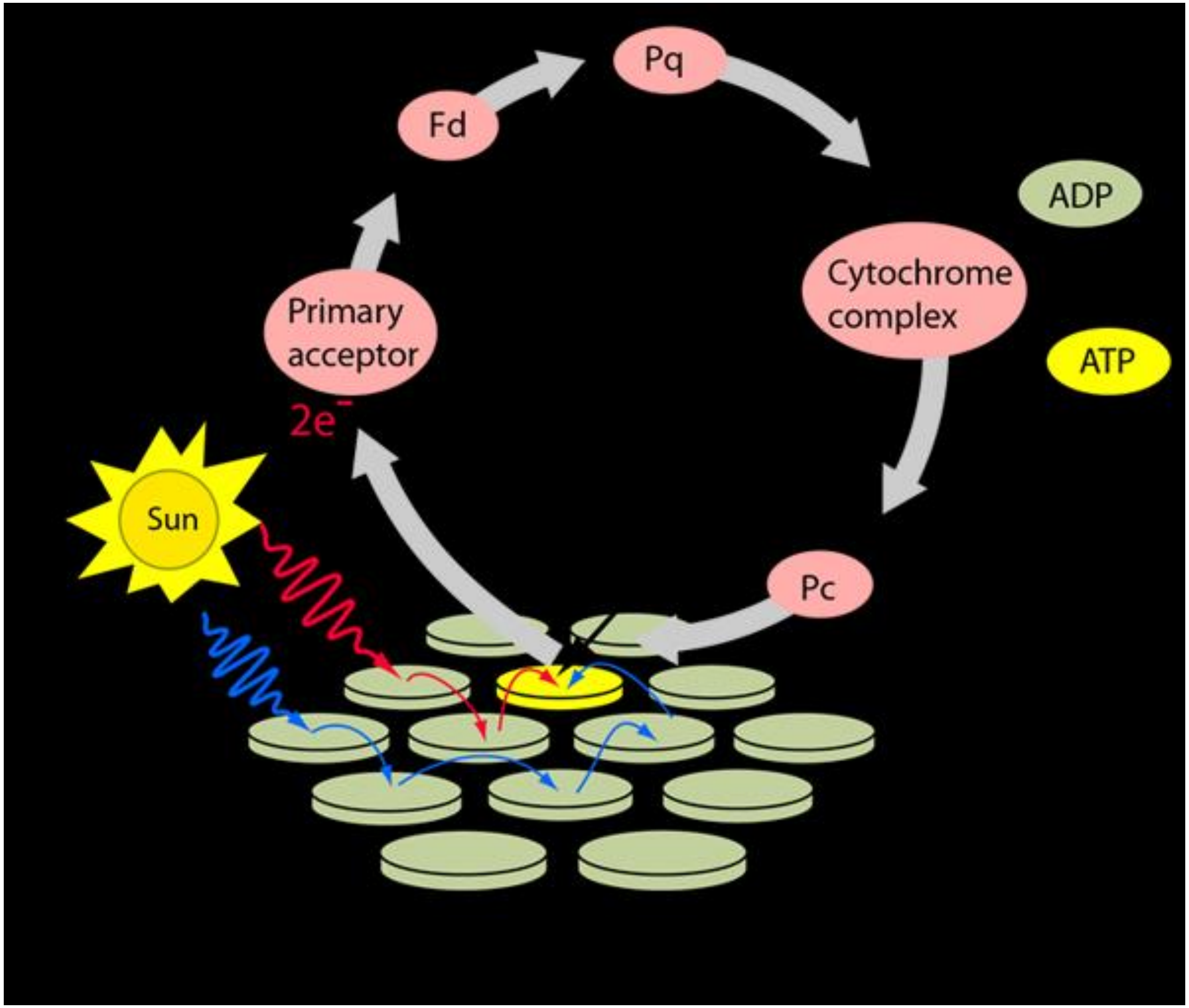


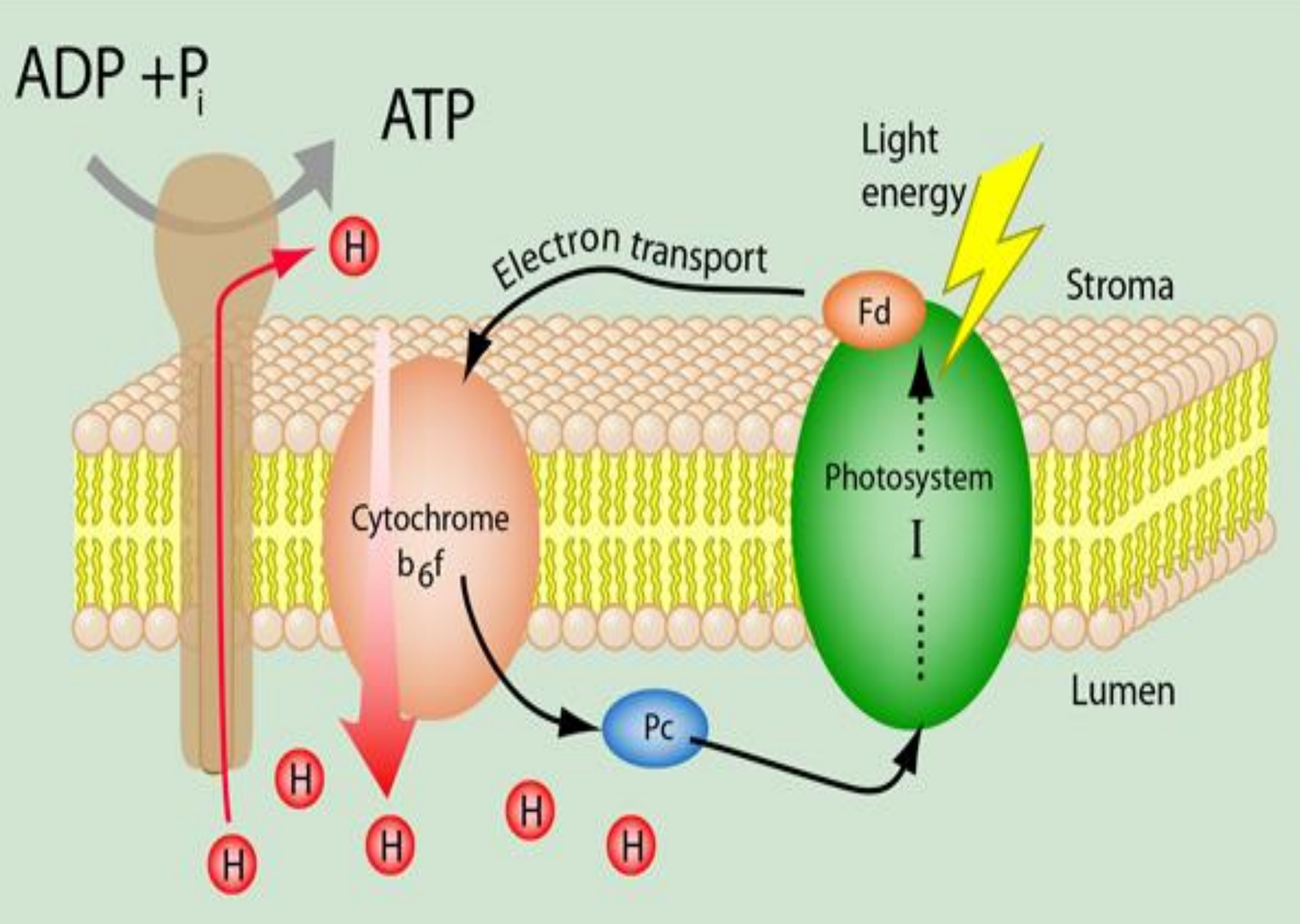
Cyclic photophosphorylation

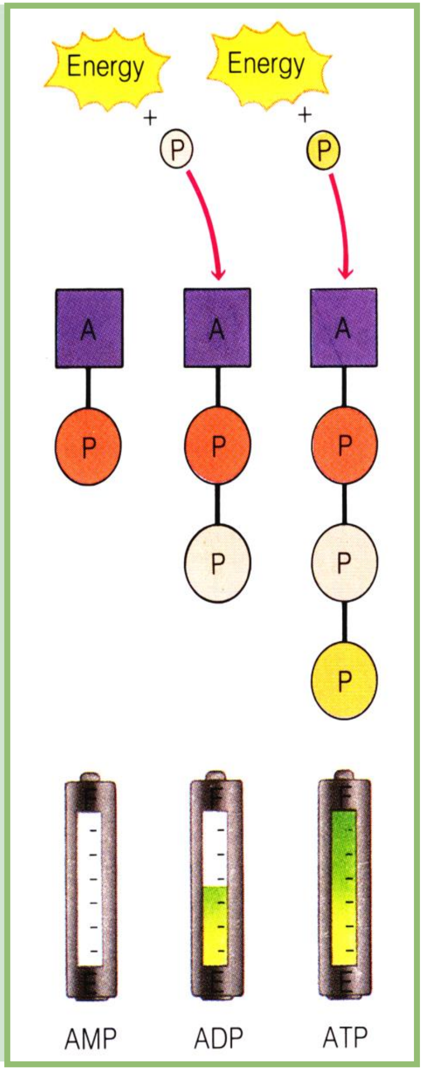
Cyclic Photophosphorylation

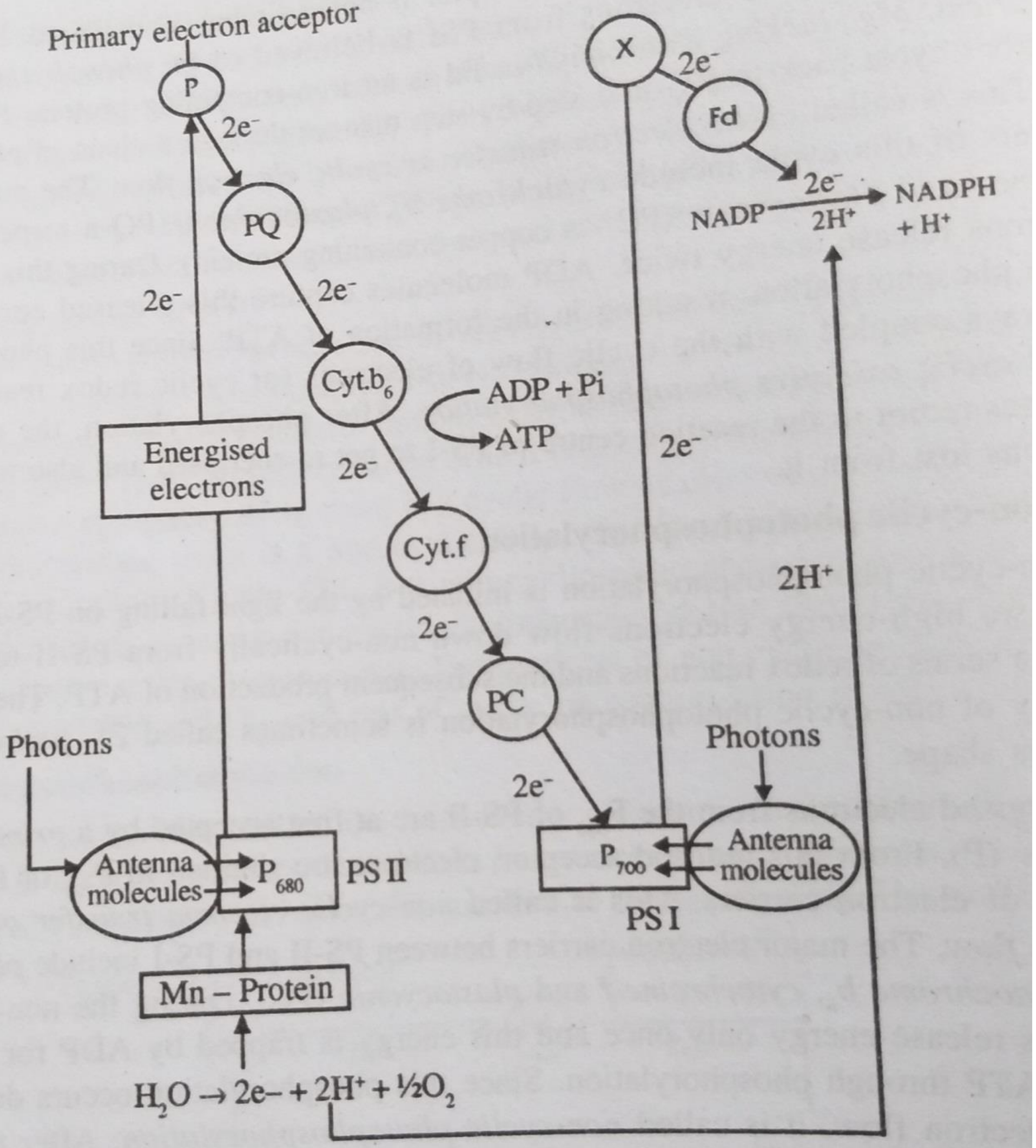
- Process for ATP generation associated with some Photosynthetic Bacteria
- Reaction Center => 700 nm




Pq
Fd
ADP
Cytochrome complex
Primary acceptor
ATP
2e⁻
Sun
Pc


ADP +P$_i$
ATP
Light energy
Electron transport
Fd
Stroma
Cytochrome b$_6$f
Photosystem I
Pc
Lumen
H

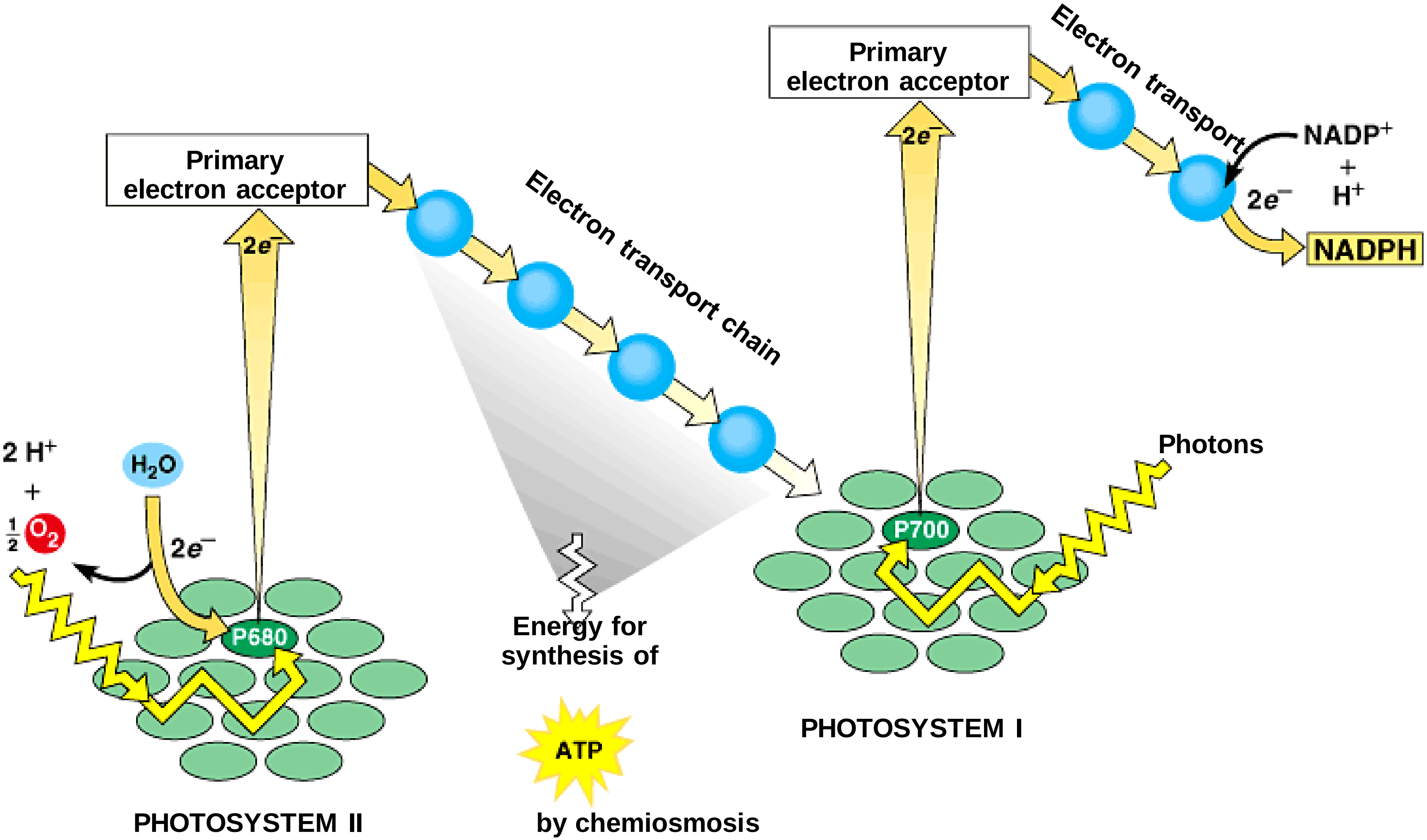

Energy
Energy
+
+
P
P
A
A
A
P
P
P
P
P
P
AMP
ADP
ATP



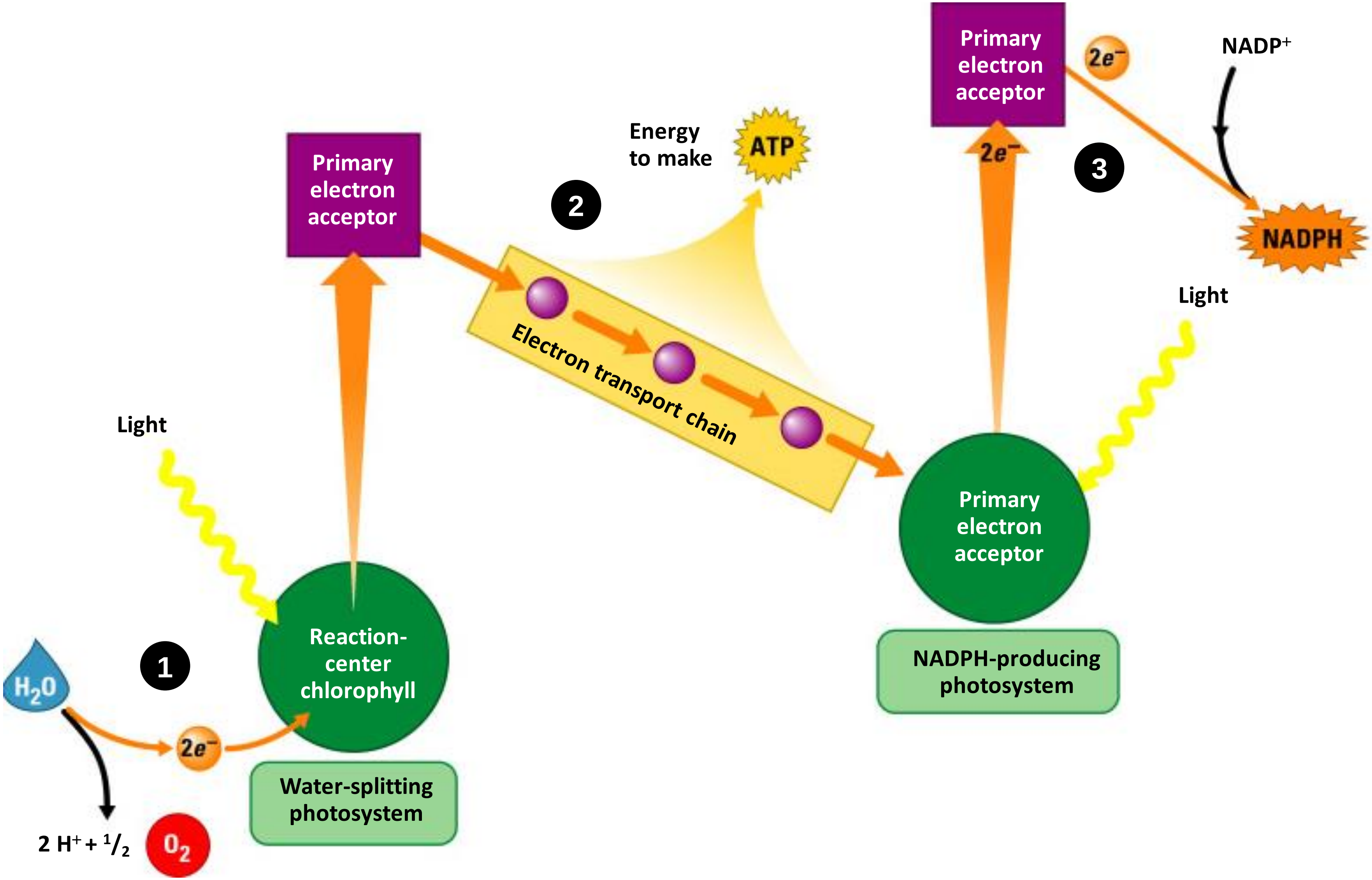
Non-cyclic photophosphorylation and reduction of NADP

Noncyclic Photophosphorylation

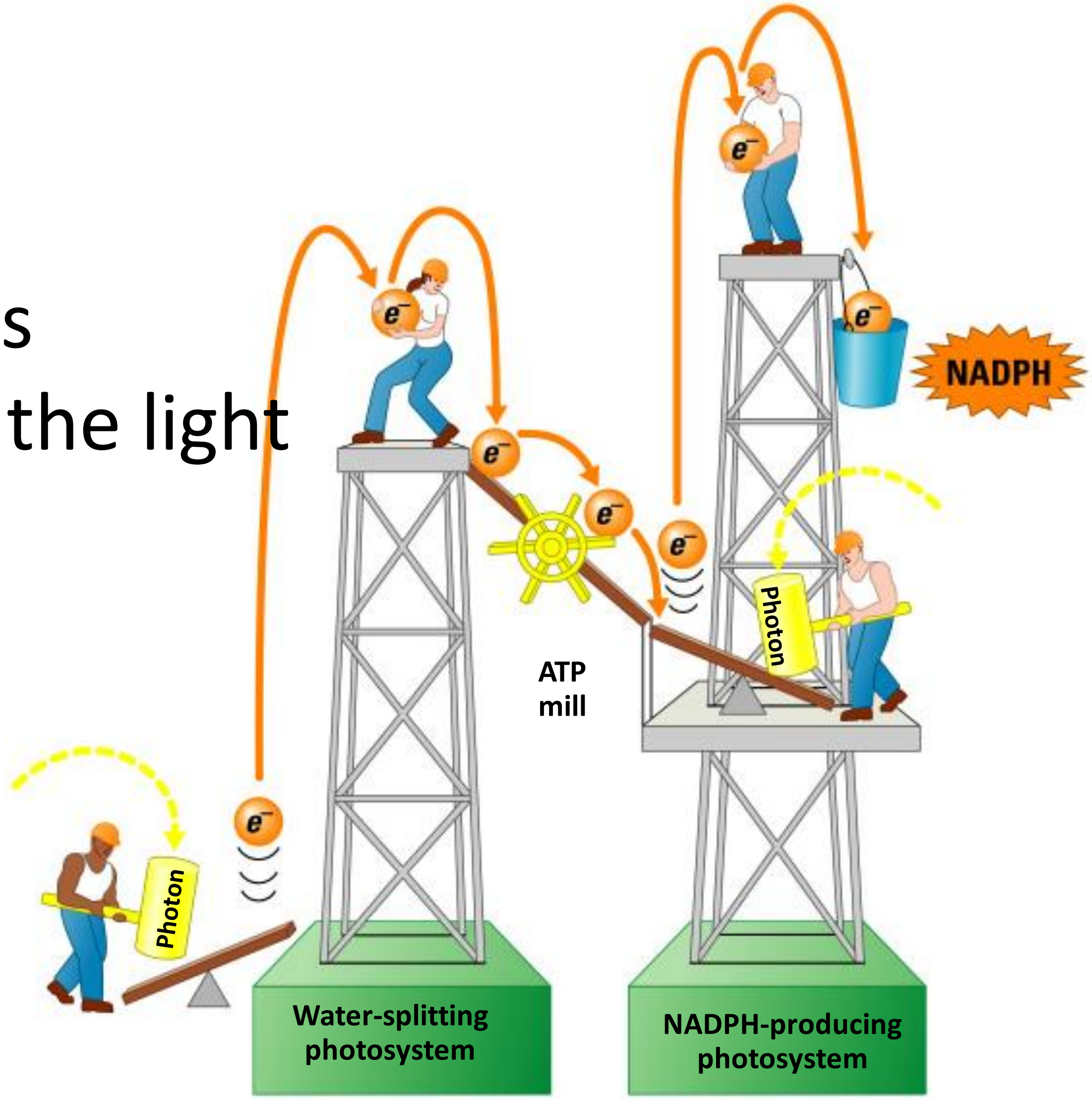
- Photosystem II regains electrons by splitting water, leaving O_2 gas as a by-product

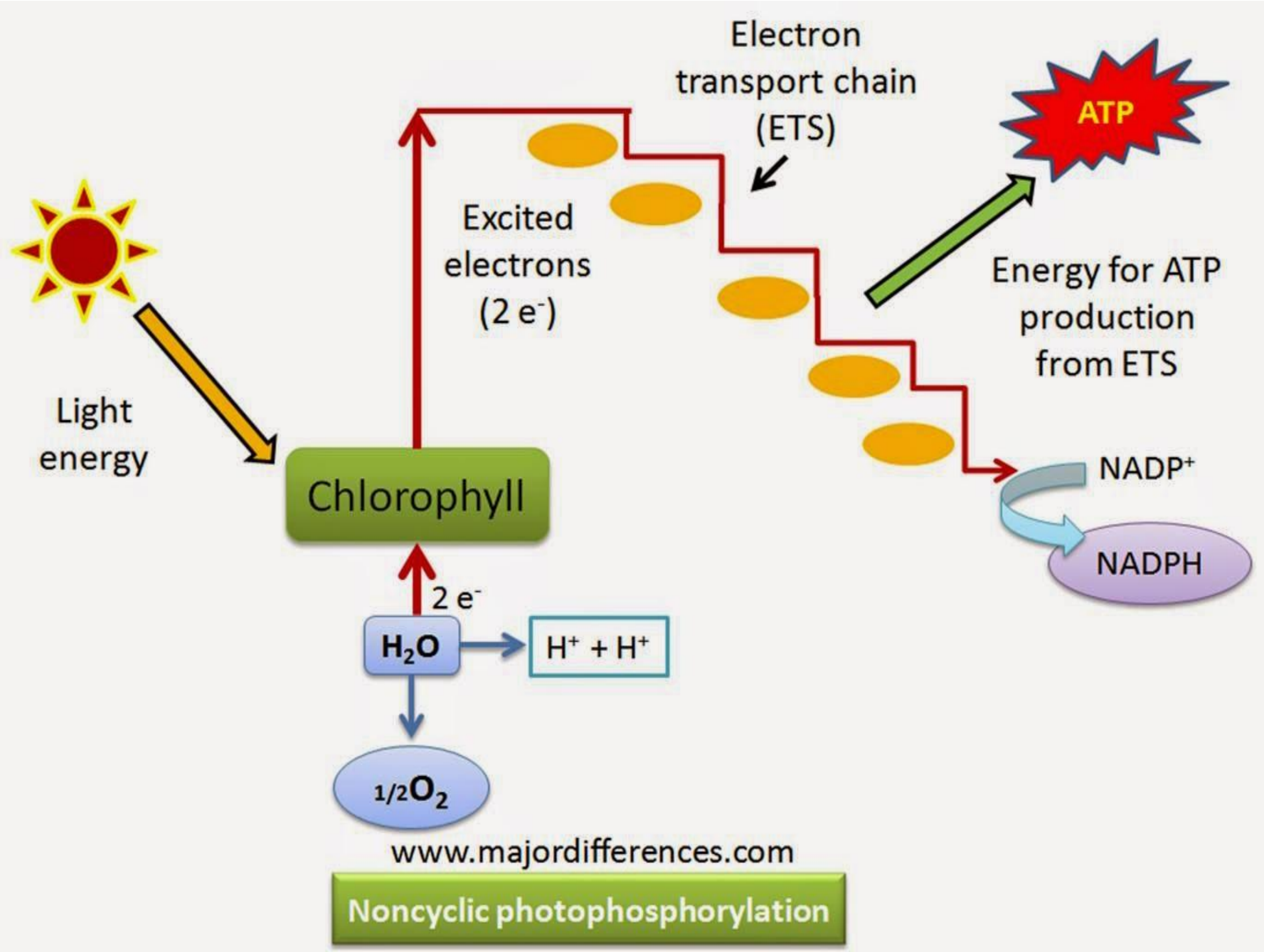


How the Light Reactions Generate ATP and NADPH



- Two types of photosystems cooperate in the light reactions





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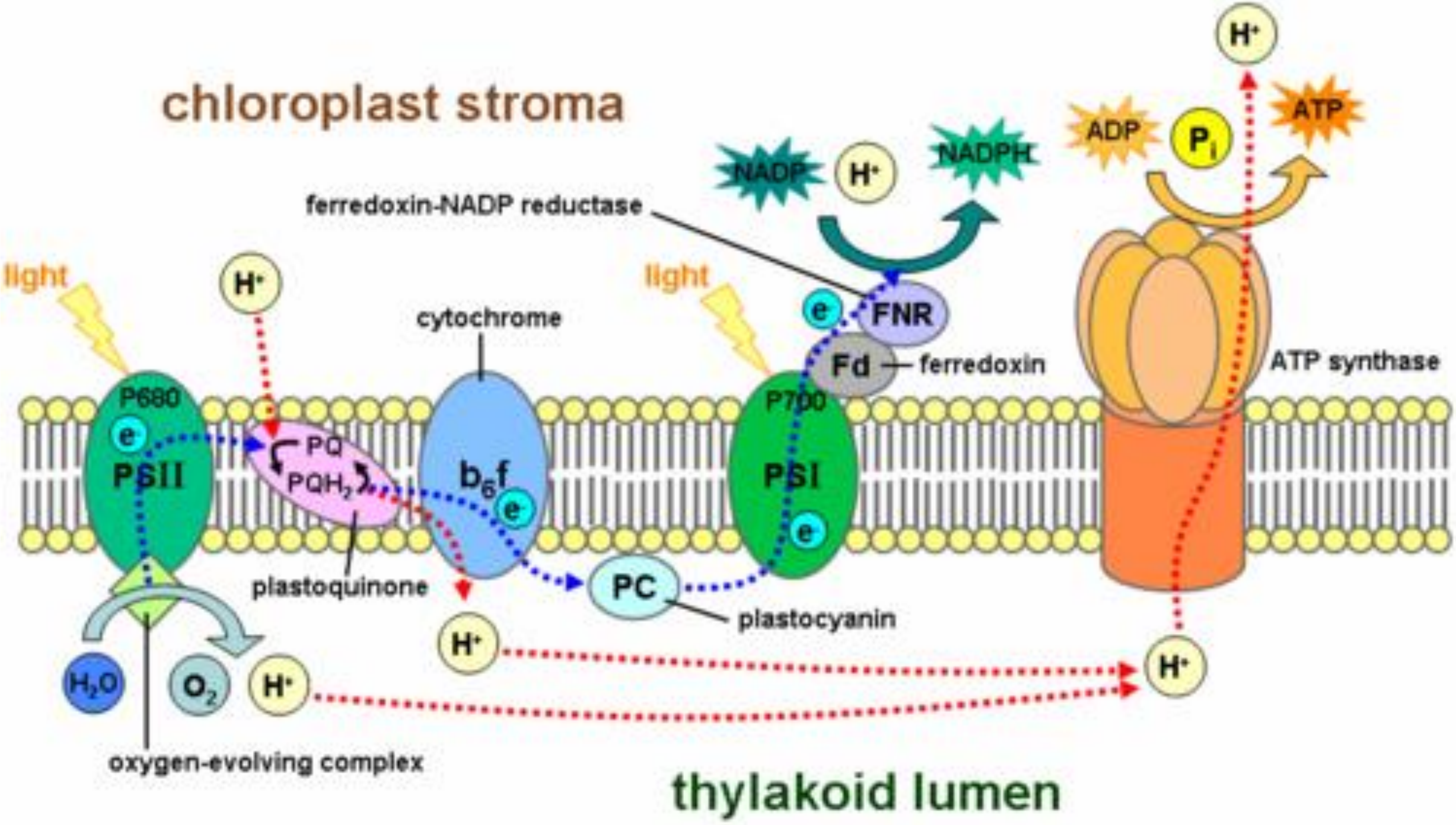
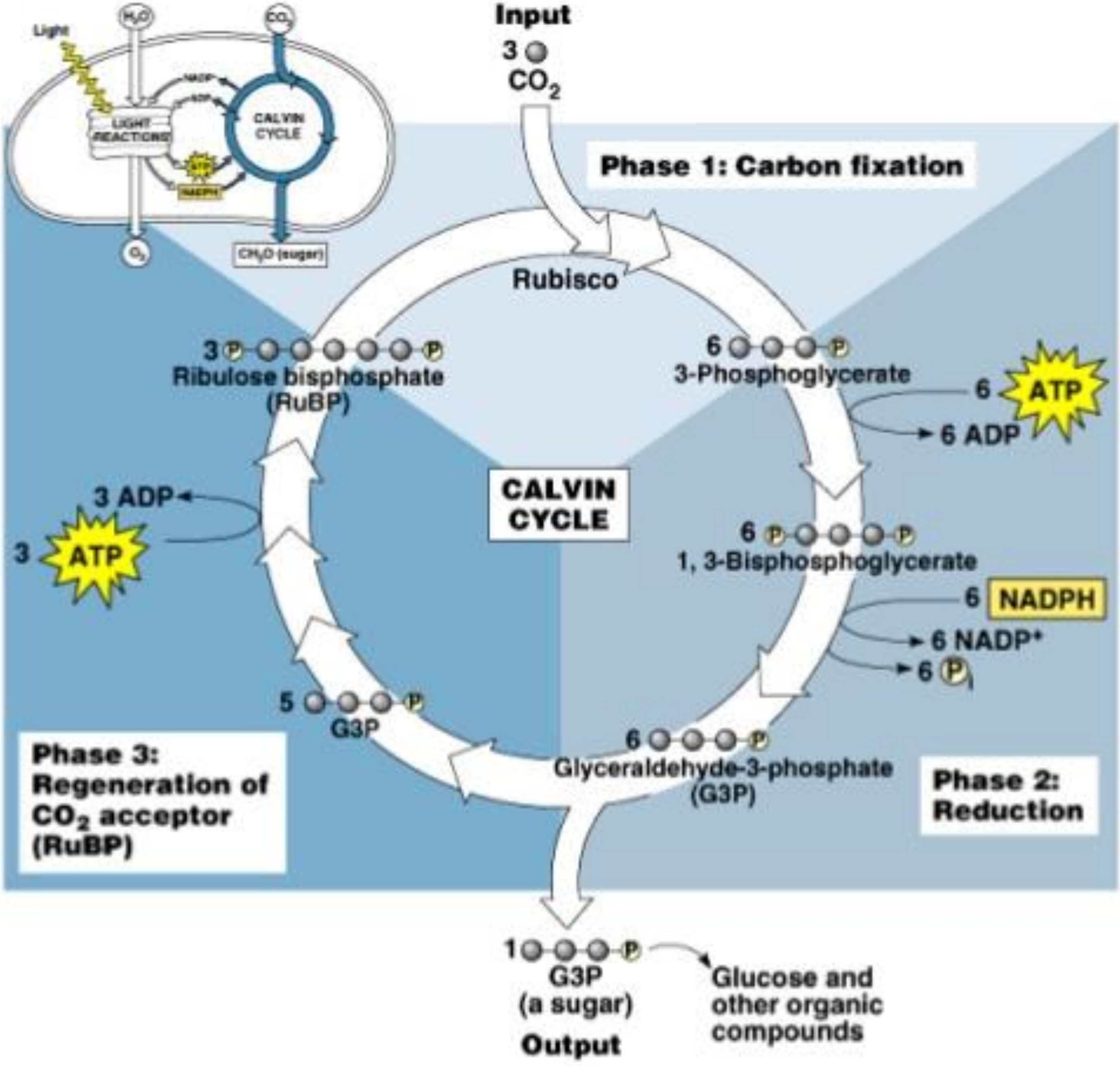
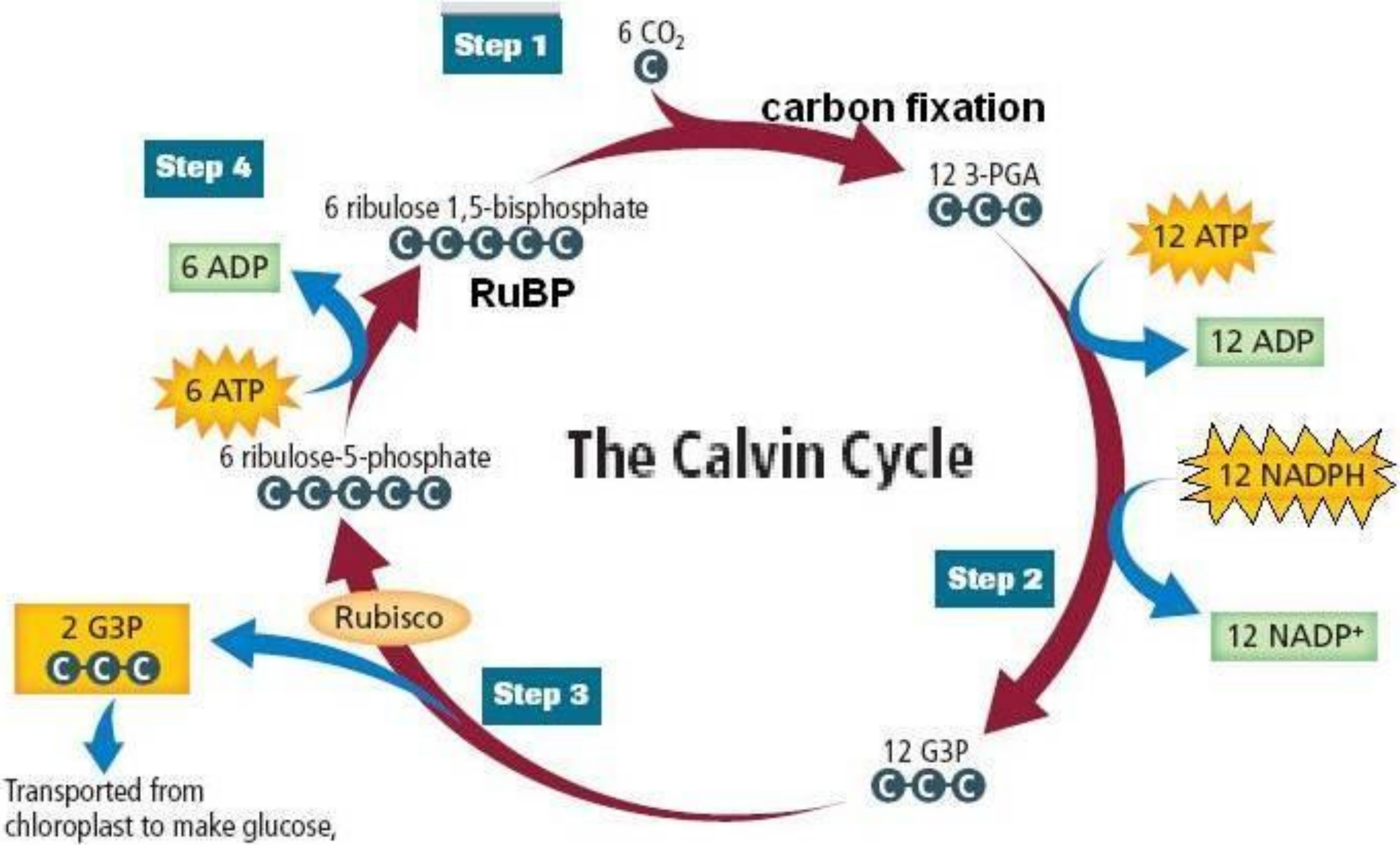
Noncyclic photophosphorylation

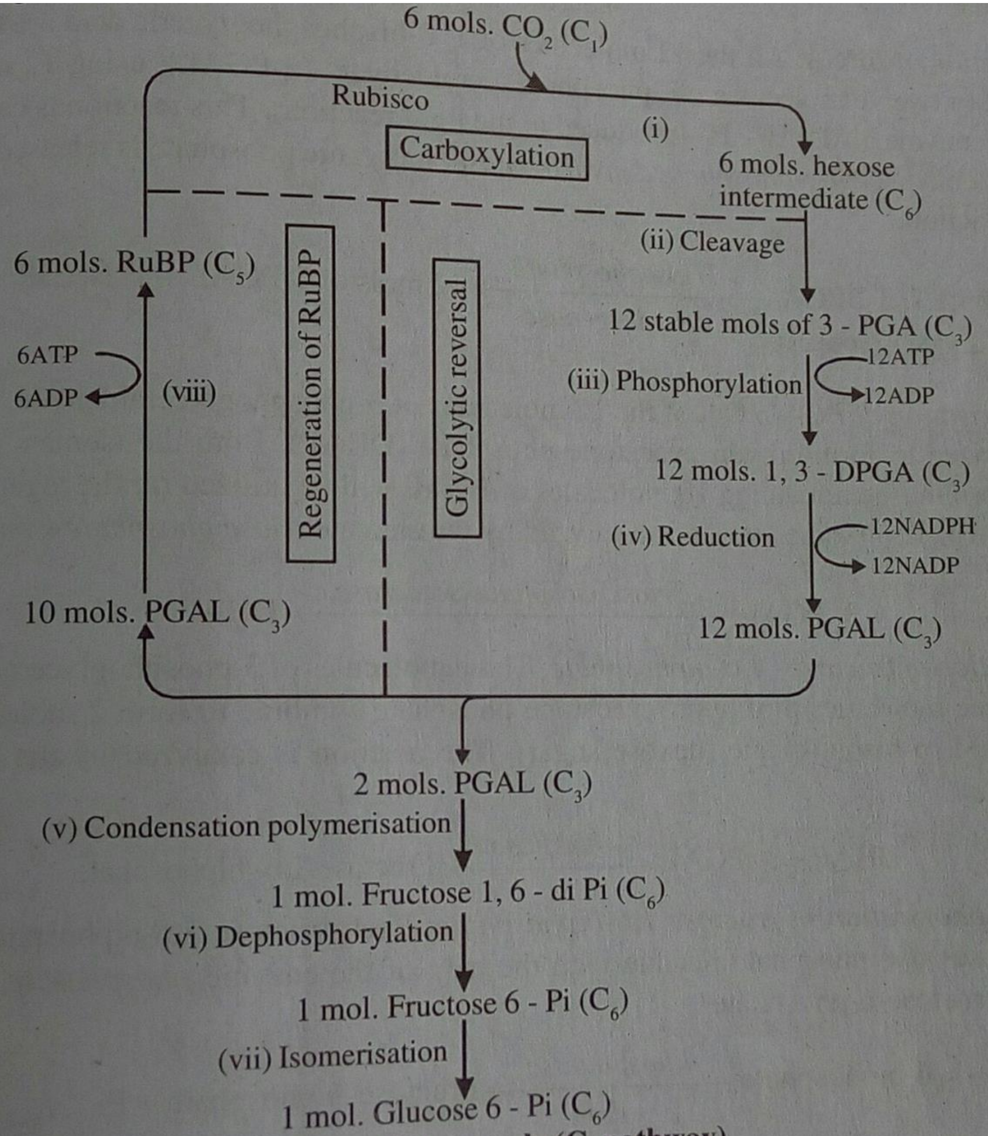

chloroplast stroma
H+
ADP
Pi
ATP
NADP
H+
NADPH
ferredoxin-NADP reductase
light
H+
cytochrome
light
e-
FNR
Fd
ferredoxin
ATP synthase
P680
e-
PQ
PQH2
PSII
b6f
e-
P700
PSI
e-
plastoquinone
PC
plastocyanin
H+
H+
H2O
O2
H+
oxygen-evolving complex
thylakoid lumen

Plants produce O_2 gas by splitting H_2O

- The O_2 liberated by photosynthesis is made from the oxygen in water (H^+ and e^-)


Light
H₂O
CO₂
NADP⁺
ADP
LIGHT REACTIONS
CALVIN CYCLE
ATP
NADPH
O₂
CH₂O (sugar)
Input
3 CO₂
Phase 1: Carbon fixation
Rubisco
3 Ribulose bisphosphate (RuBP)
6 3-Phosphoglycerate
6 ATP
6 ADP
CALVIN CYCLE
6 1, 3-Bisphosphoglycerate
6 NADPH
6 NADP⁺
6 Pᵢ
3 ADP
3 ATP
5 G3P
6 Glyceraldehyde-3-phosphate (G3P)
Phase 2: Reduction
Phase 3: Regeneration of CO₂ acceptor (RuBP)
1 G3P (a sugar)
Output
Glucose and other organic compounds


Step 1
6 CO_2
C
carbon fixation
12 3-PGA
C-C-C
12 ATP
12 ADP
12 NADPH
12 NADP+
Step 2
12 G3P
C-C-C
Step 3
Rubisco
2 G3P
C-C-C
Transported from
chloroplast to make glucose,
6 ribulose-5-phosphate
C-C-C-C-C
6 ATP
6 ADP
Step 4
6 ribulose 1,5-bisphosphate
C-C-C-C-C
RuBP
The Calvin Cycle



Calvin cycle (C$_3$ pathway)

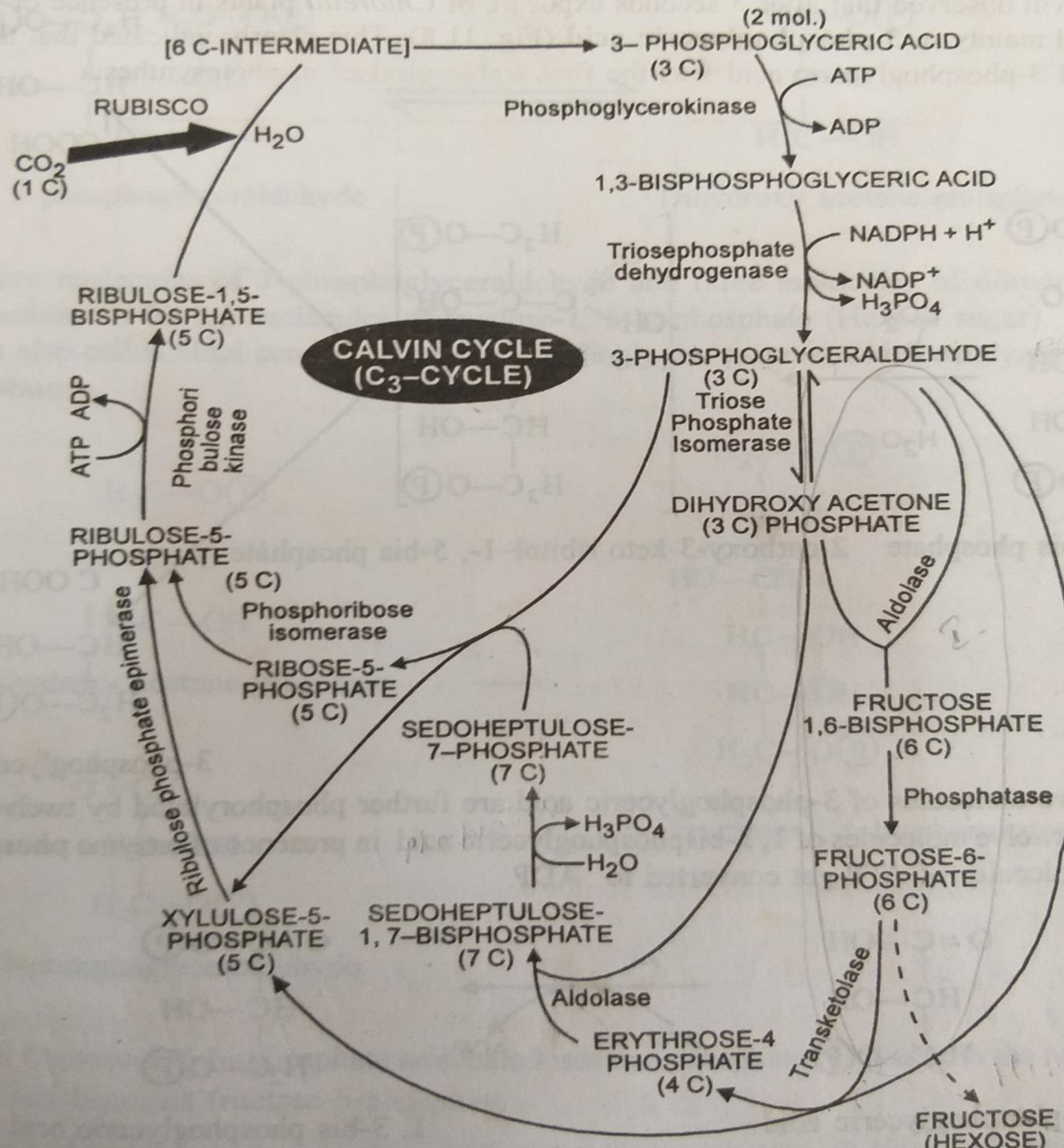


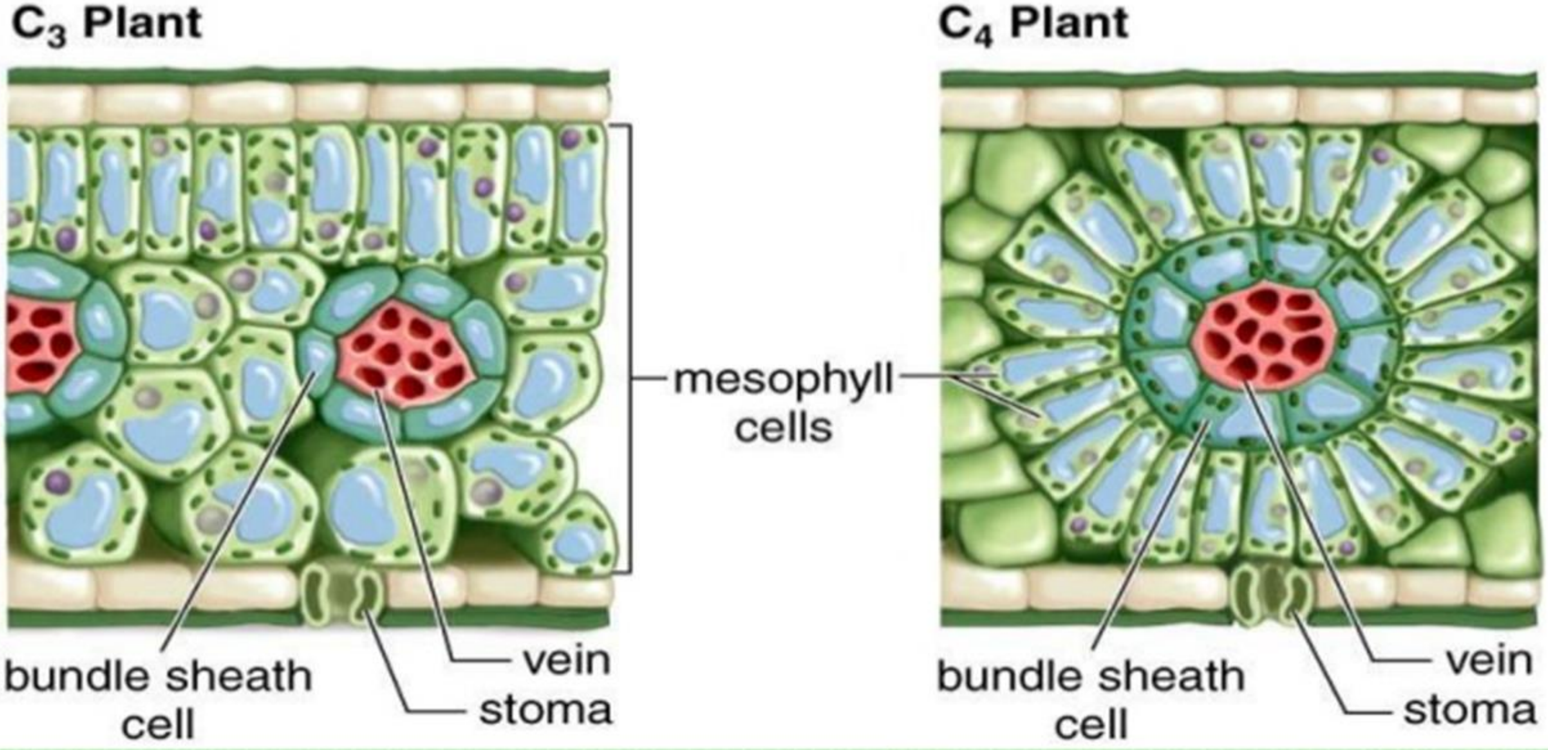
FIGURE 11.9. The Calvin cycle (The C_3 pathway).

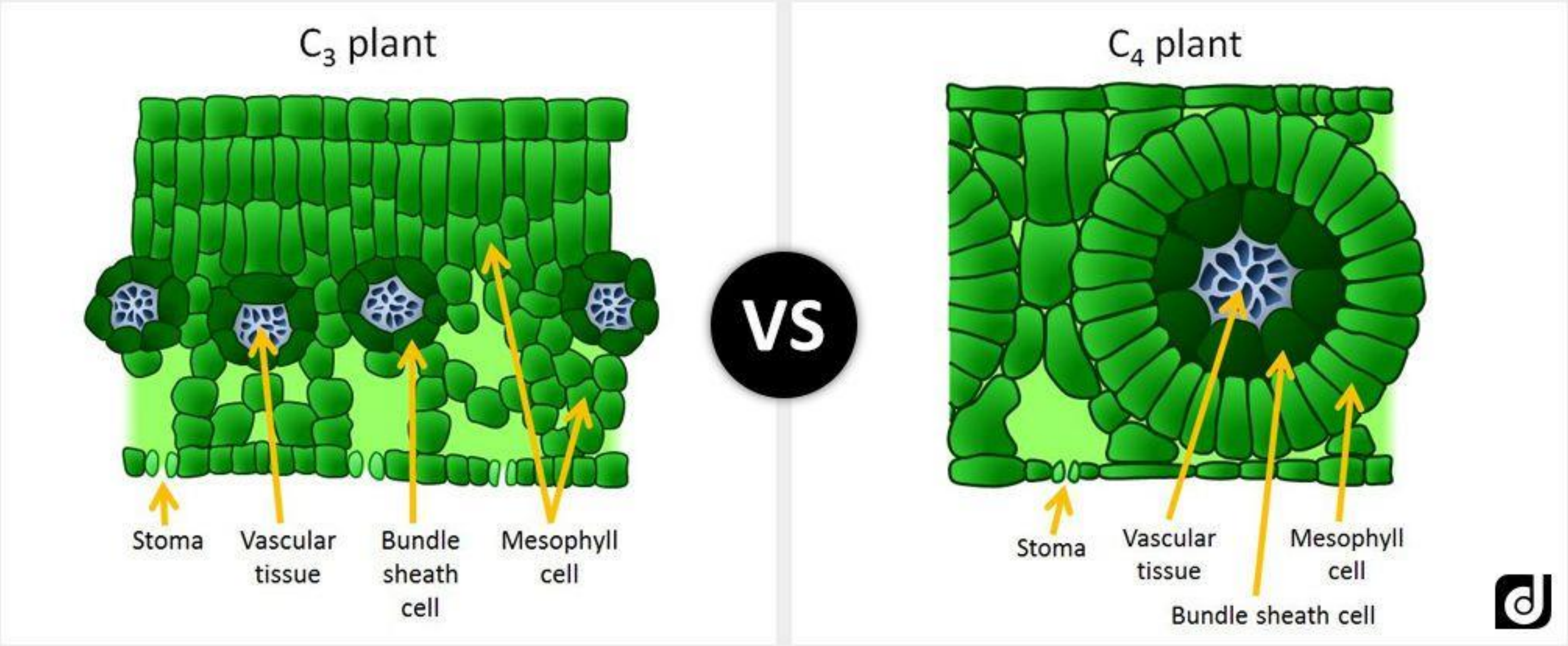
- At lower light levels and temperature, C4 plants will utilize the traditional C3 pathway.

- C4 plants occur largely in tropical regions because they grow faster under hot and sunny conditions.

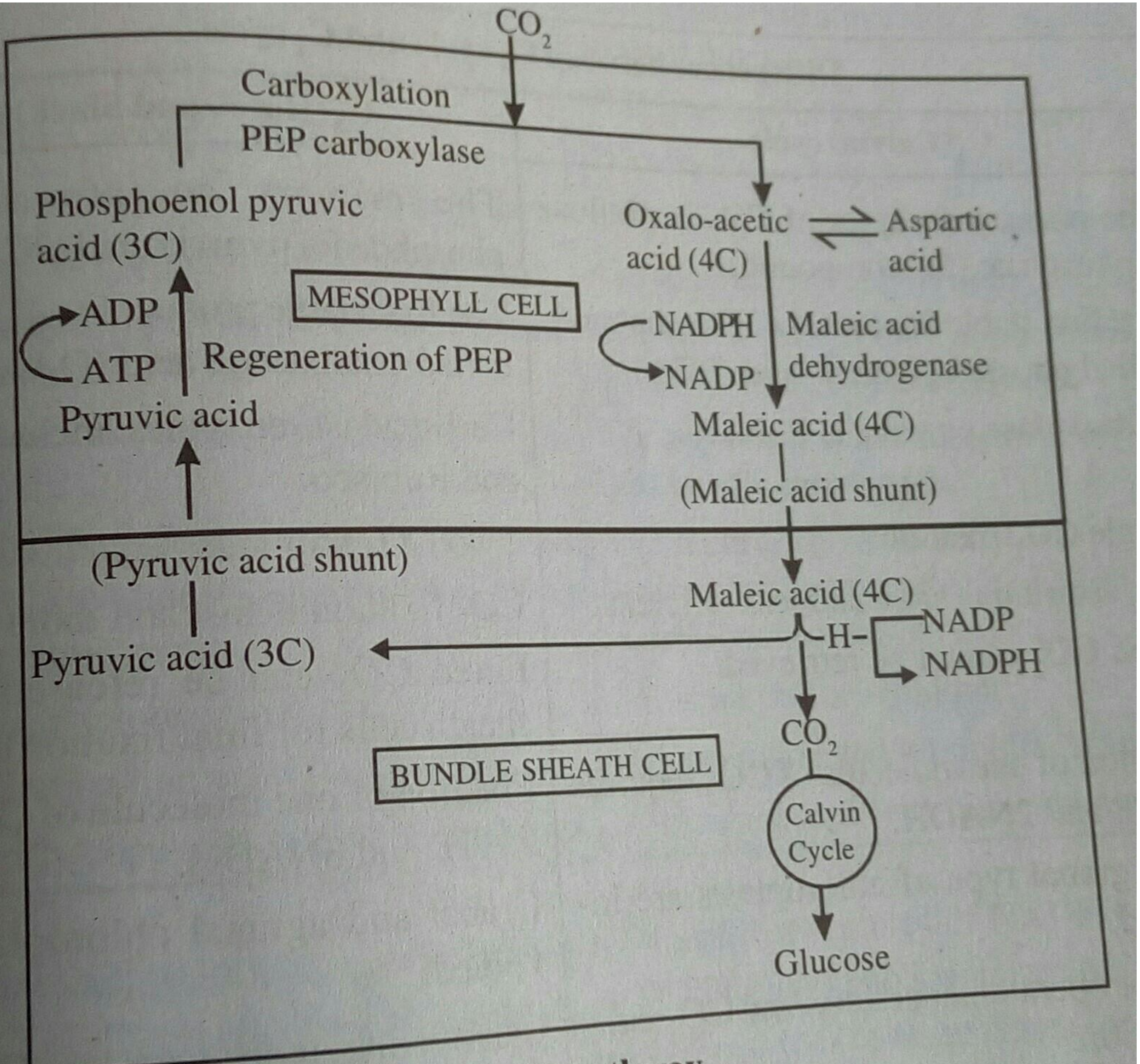
  C3 plants live in cooler climates where photorespiration is less of a burden and less ATP is required to fix carbon.

Chloroplast distribution in C_4 vs. C_3 Plants





C3 Plants vs. C4 Plants


CO_2
Carboxylation
PEP carboxylase
Phosphoenol pyruvic acid (3C)
Oxalo-acetic acid (4C)
Aspartic acid
MESOPHYLL CELL
ADP
ATP
Regeneration of PEP
NADPH
NADP
Maleic acid dehydrogenase
Pyruvic acid
Maleic acid (4C)
(Maleic acid shunt)
(Pyruvic acid shunt)
Maleic acid (4C)
-H-
NADP
NADPH
Pyruvic acid (3C)
CO_2
BUNDLE SHEATH CELL
Calvin Cycle
Glucose

C_4 pathway

Differences between C_3 cycle and C_4 cycle

C_3 (Calvin) cycle	C_4 (Hatch and Slack) cycle
1. The primary acceptor of CO_2 is ribulose biphosphate (5C compound).	The primary acceptor of CO_2 is phosphoenol pyruvic acid (3C compound).
2. The first stable product is a 3C compound, called phosphoglyceric acid (PGA).	The first stable product is a 4C compound, called oxaloacetic acid (OAA).
3. Carboxylase enzyme is Rubisco.	Carboxylase enzymes include PEPCase and Rubisco.
4. Single CO_2 fixation.	Two CO_2 fixations.
5. CO_2 fixation is slow and less efficient.	CO_2 fixation is fast and more efficient
6. Fixed CO_2 cannot be retrieved	Fixed CO_2 can be released to bundle sheath cells for final fixation by C_3 cycle.
7. Fixation of one molecule of CO_2 requires 3 ATP and 2NADH.	Fixation of one molecule of CO_2 requires 5 ATP and 3NADH.
8. Only granal type of chloroplasts are involved.	Granal and agranal chloroplasts are involved.
9. Cannot operate under very low CO_2 concentration.	Can operate under very low CO_2 concentration.
10. Operates in all plants.	Operates only in C_4 plants.

Differences between C_3 plants and C_4 plants

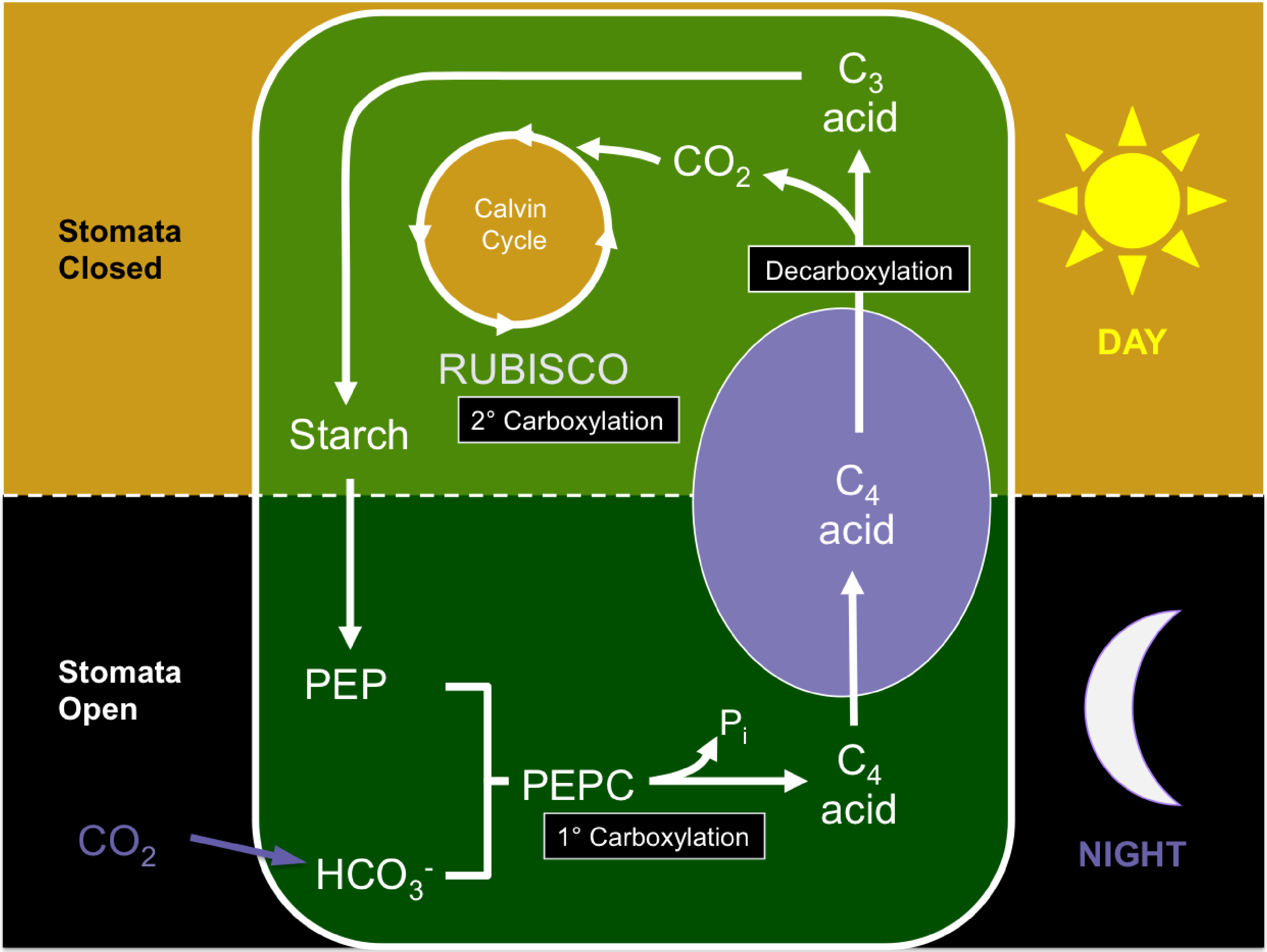
	C_3 plants	*C_4 plants*
(i)	Include most crop plants, cereals, to bacco, beans, etc.	Include maize, millets, sorghum, sugarcane, etc.
(ii)	Only C_3 pathway is present.	Both C_3 and C_4 pathways present.
(iii)	Do not possess knanz anatomy.	Possess krans anatomy.
(iv)	Chloroplasts are monomorphic and granal.	Chloroplasts are dimorphic, with granal and agranal types.
(v)	Photosystems I & II present.	PSII is absent in krans type chloroplasts.
(vi)	Primary CO_2 acceptor is RuBP.	Primary CO_2 acceptor is PEP.
(vii)	CO_2 fixing enzyme is RuBP carboxylase.	CO_2 fixing enzyme is PEP carboxylase.
(viii)	Carboxylase has moderate affinity to CO_2.	Carboxylase has high affinity to CO_2.
(ix)	The first stable product of photosynthesis is the 3-carbon PGAL.	The first stable product of photosynthe sis is the 4-carbon oxaloacetic acid.
(x)	Photosynthetic cells include only mesophyll cells.	Photosynthetic cells include mesophyll cells and bundle sheath cells.
(xi)	Optimum temperature for photosynthesis is lower. So, photosynthetic rate is lesser at warmer temperature.	Optimum temperature for photosynthesis is higher. So, photosynthetic rate is higher at warmer temperature.
(xii)	Maximal photorespiration.	Minimal photorespiration.
(xiii)	Transpiration and water loss greater.	Transpiration and water loss lesser.
(xiv)	Can hardly cope with higher temperature.	Can easily cope with higher temperature.

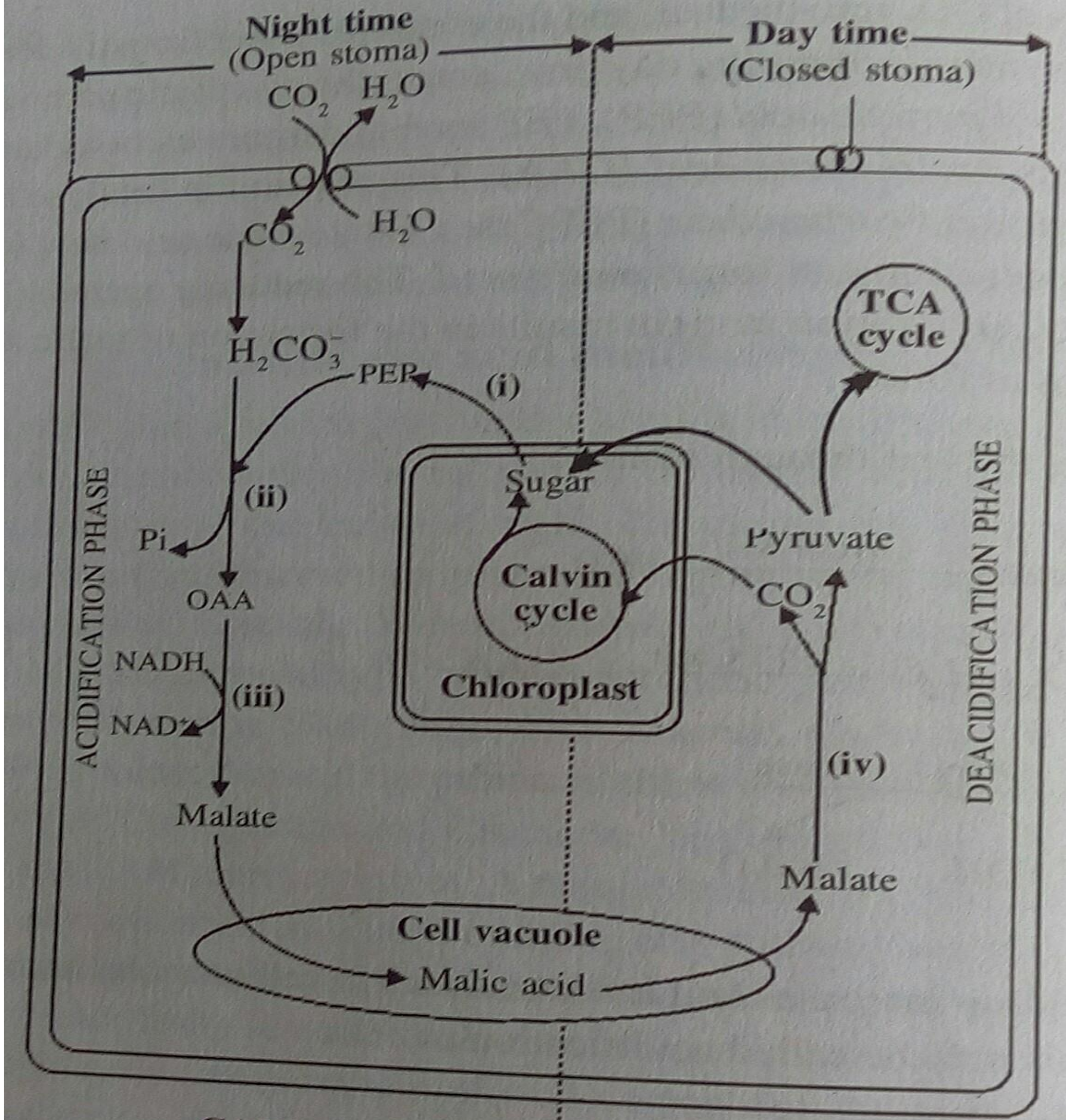








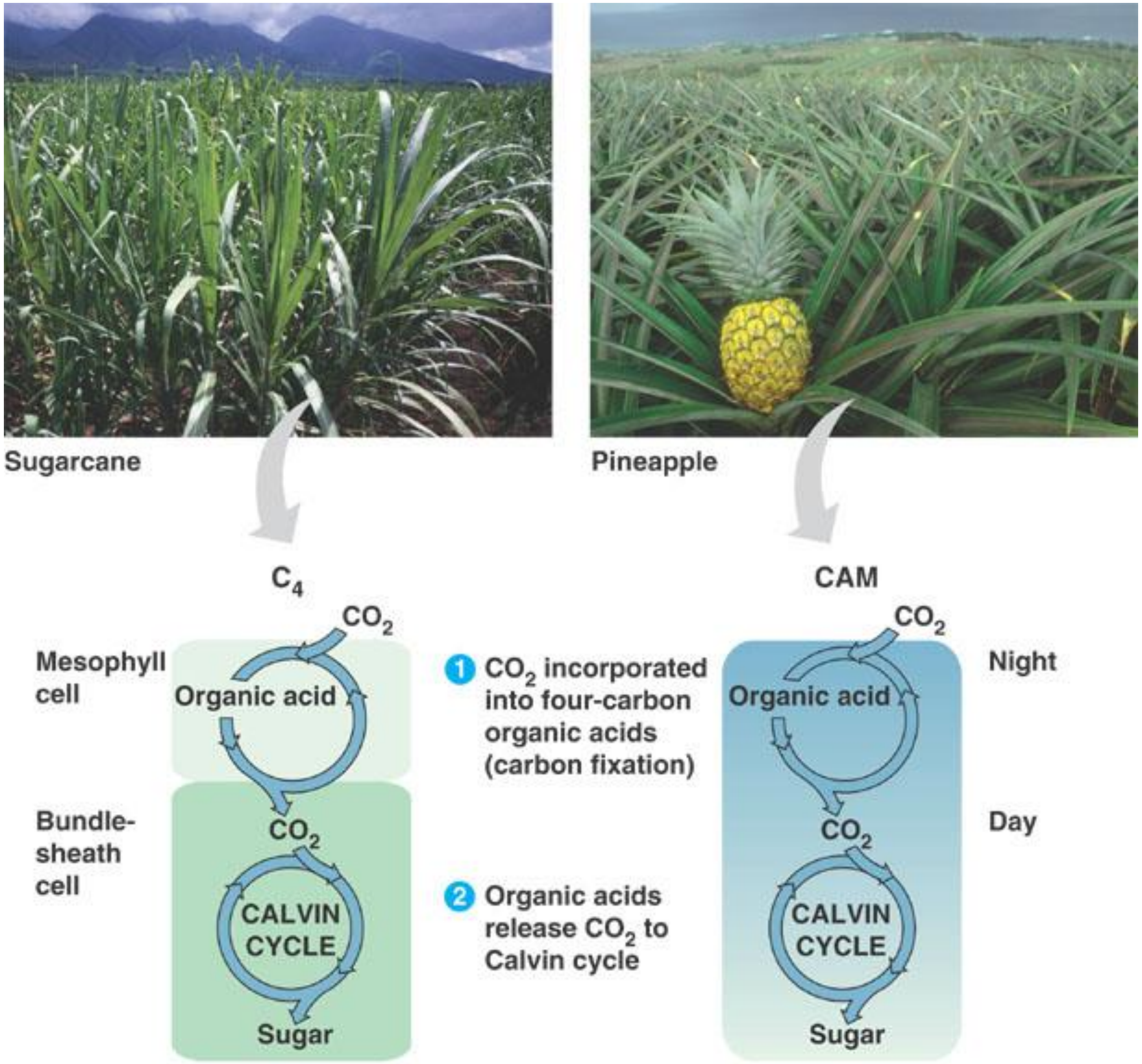

Stomata Closed
Stomata Open
DAY
NIGHT
C_3 acid
CO_2
Calvin Cycle
RUBISCO
2° Carboxylation
Decarboxylation
Starch
C_4 acid
PEP
P_i
PEPC
C_4 acid
1° Carboxylation
CO_2
HCO_3^-



CAM pathway (Diagrammatic)

C4 & CAM Plants Introduction

C_4 and CAM plants have devised mechanisms that prevent/reduce the impact of photorespiration.

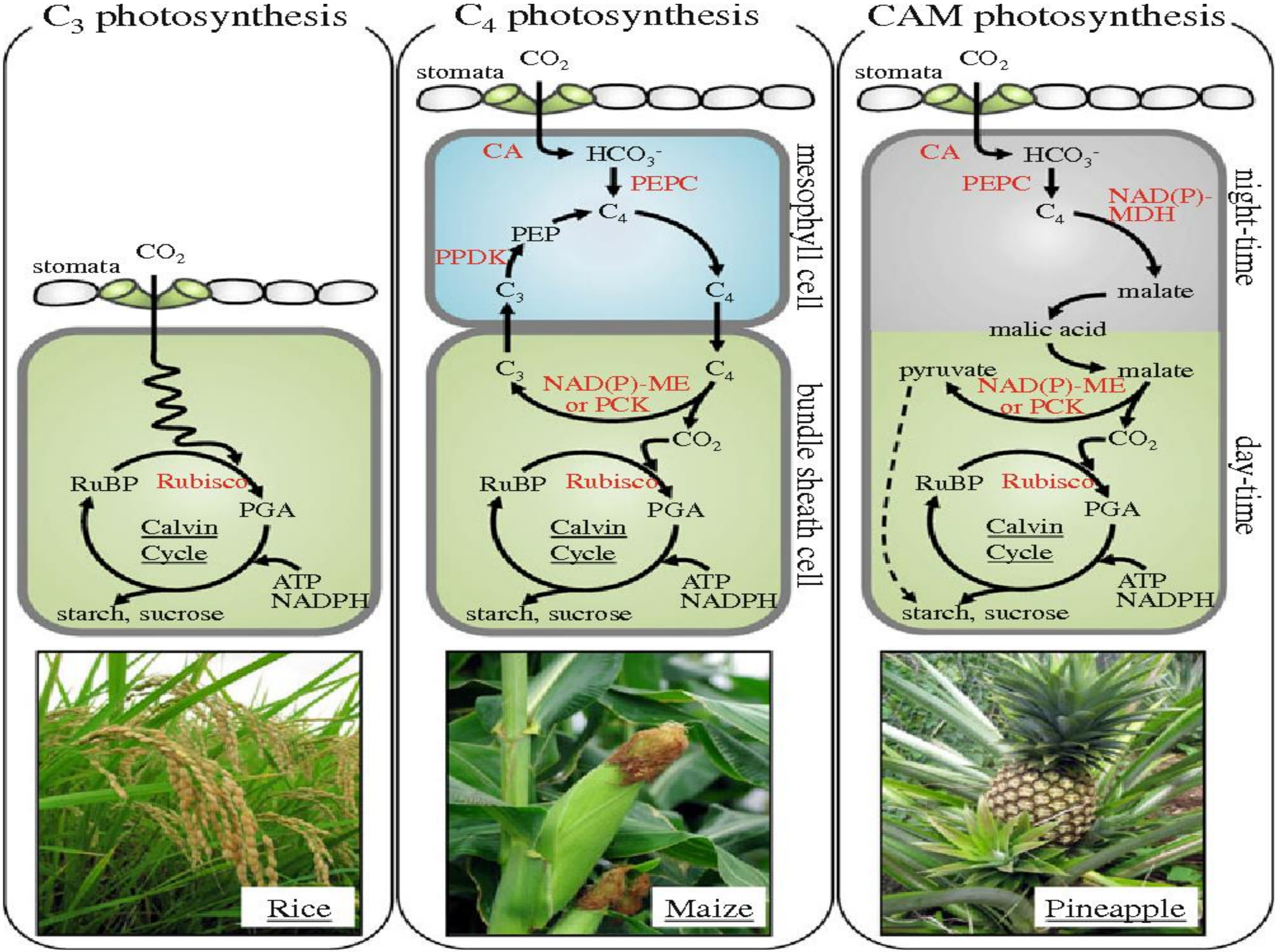


① CO_2 incorporated into four-carbon organic acids (carbon fixation)

② Organic acids release CO_2 to Calvin cycle

(a) Spatial separation of steps

(b) Temporal separation of steps


C$_3$ photosynthesis
C$_4$ photosynthesis
CAM photosynthesis
stomata
CO$_2$
CA
HCO$_3^-$
PEPC
C$_4$
PEP
PPDK
C$_3$
mesophyll cell
NAD(P)-ME or PCK
bundle sheath cell
NAD(P)-MDH
malate
malic acid
pyruvate
night-time
day-time
Rubisco
RuBP
PGA
Calvin Cycle
ATP
NADPH
starch, sucrose
Rice
Maize
Pineapple

PHOTORESPIRATION

In a very lengthy and costly process, O_2 is converted into CO_2 & 3-PGAL

Photorespiration involves the use of three organelles

- Chloroplast
- Peroxisome
- Mitochondria

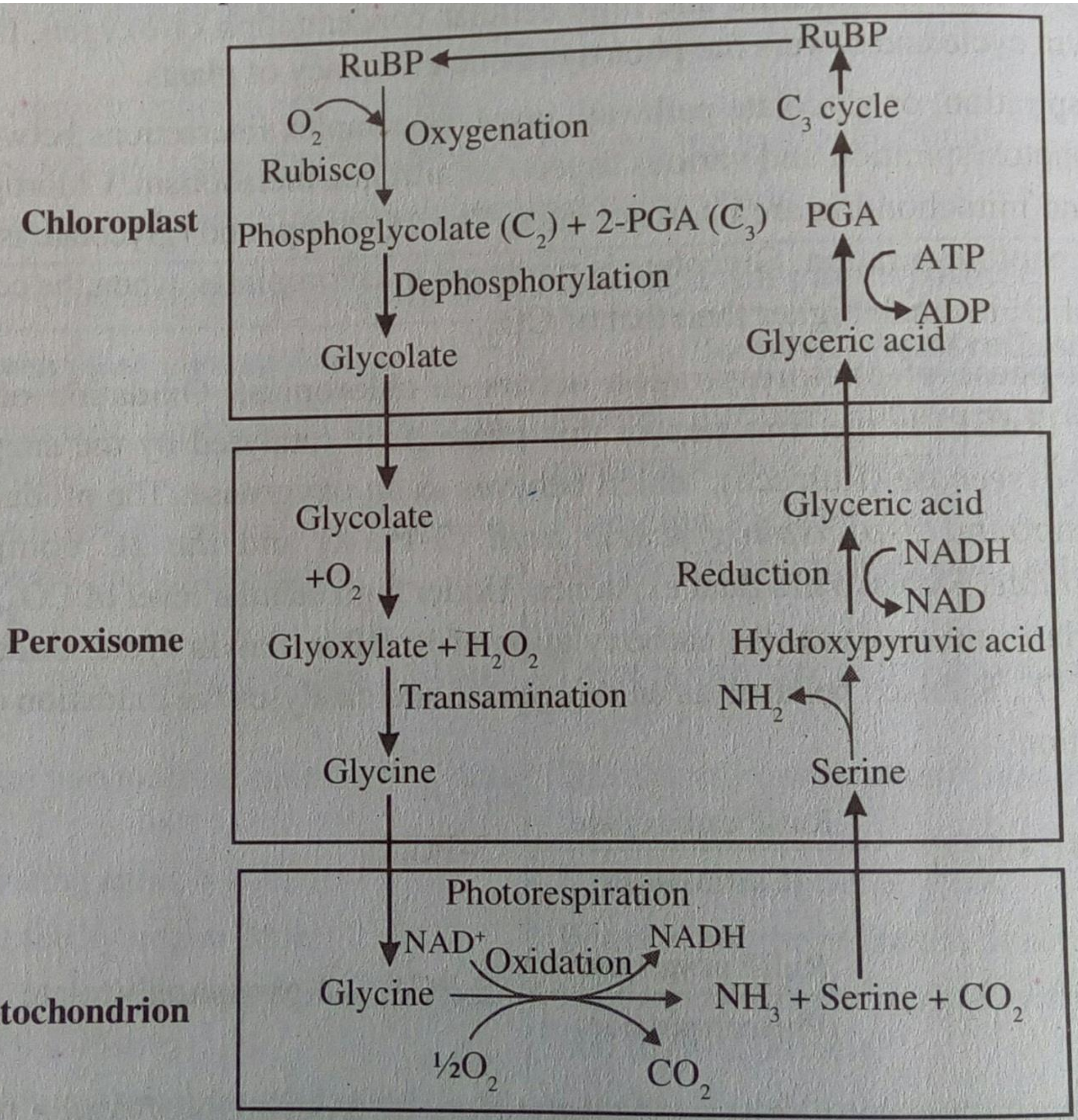
Photorespiration also requires the use of ATP and NADPH.

- Reducing the number of those molecules readily available for the Calvin cycle

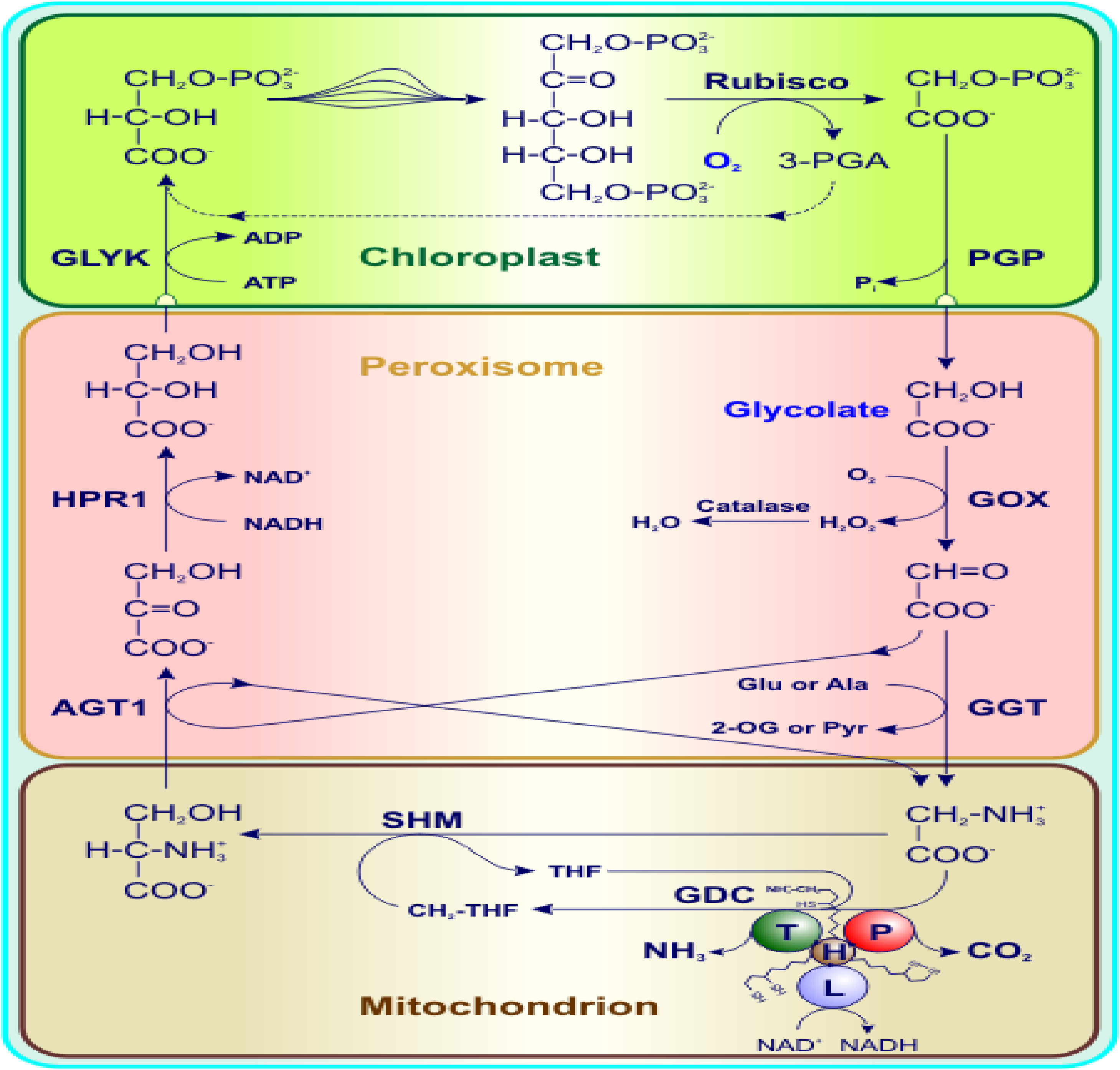
- On dry, hot days in the presence of light C_3 plants close their stomata.
- This causes the plant to use O_2 retain as much H_2O.

O_2 binds to RUBISCO and starts the series of reactions.

H_2O is retained for use in the light reactions to fill the ATP and NADPH used as a result of photorespiration.



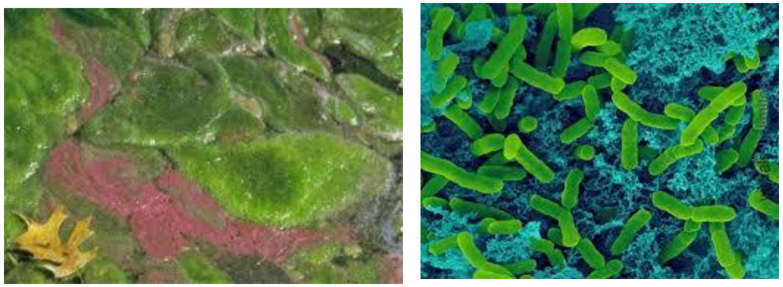
Photorespiration (C_2 cycle)


CH₂O-PO₃²⁻
H-C-OH
COO⁻
CH₂O-PO₃²⁻
C=O
H-C-OH
H-C-OH
CH₂O-PO₃²⁻
Rubisco
O₂
3-PGA
CH₂O-PO₃²⁻
COO⁻
GLYK
ADP
ATP
Chloroplast
PGP
Pᵢ
CH₂OH
H-C-OH
COO⁻
Peroxisome
Glycolate
CH₂OH
COO⁻
HPR1
NAD⁺
NADH
O₂
GOX
Catalase
H₂O
H₂O₂
CH₂OH
C=O
COO⁻
CH=O
COO⁻
AGT1
Glu or Ala
2-OG or Pyr
GGT
CH₂OH
H-C-NH₃⁺
COO⁻
SHM
CH₂-NH₃⁺
COO⁻
THF
CH₂-THF
GDC
NH-C-CH₂
HS
T
P
H
L
NH₃
CO₂
Mitochondrion
NAD⁺
NADH

Bacterial photosynthesis

- **Green sulphur bacteria** **H2S**

  (Chlorobium, Chlorobacterium)



- **Purple sulphur bacteria** **thiosulphate**

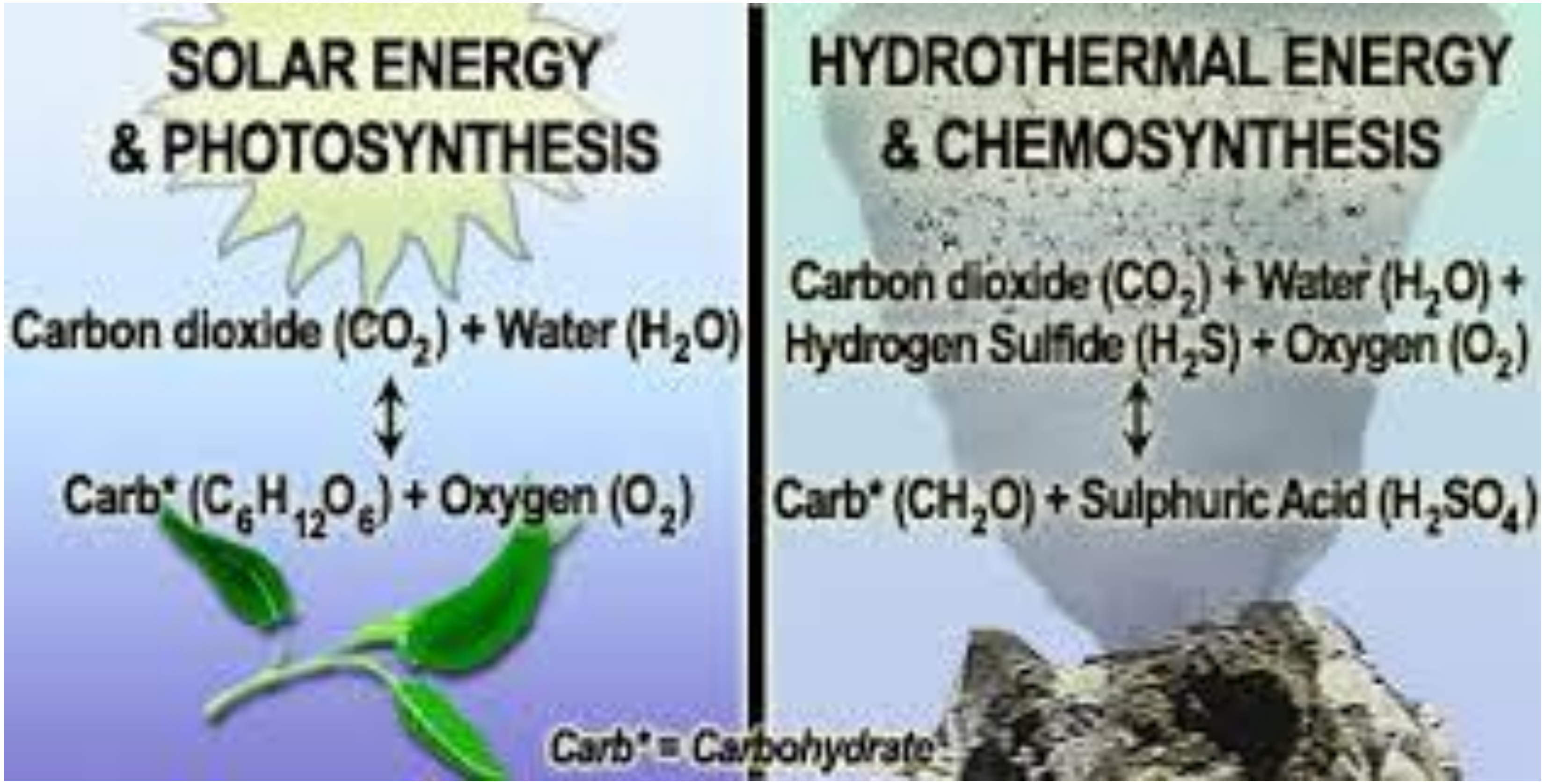
  (Chromatium)

- Non sulphur baceria **Malate, succinate, alcohol**

  (Rhodospirillum)

- Pigments (Green bacterioviridin, Reddish purple bacterial chlorophyll)
- Not oxygenic, hydrogen donor not water
- Only one pigment system, one photosystem, one reaction centre (p840/870), one photochemical reaction, two light harvesting complexes.
- Chloroplast absent, pigments located on plasma membrane
- Reducing agent NAD+
- Wavelength 870 to 1020nm
- Both cyclic and non cyclic photophosphorylation occur
-

Chemosynthesis



SOLAR ENERGY & PHOTOSYNTHESIS

Carbon dioxide (CO_2) + Water (H_2O)

↕

Carb* ($C_6H_{12}O_6$) + Oxygen (O_2)

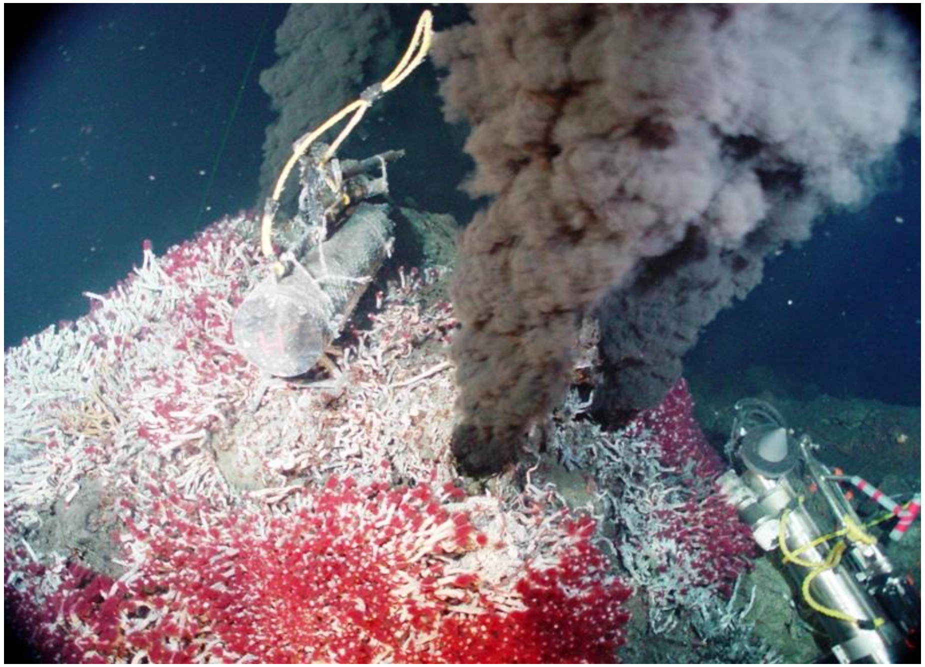
HYDROTHERMAL ENERGY & CHEMOSYNTHESIS

Carbon dioxide (CO_2) + Water (H_2O) + Hydrogen Sulfide (H_2S) + Oxygen (O_2)

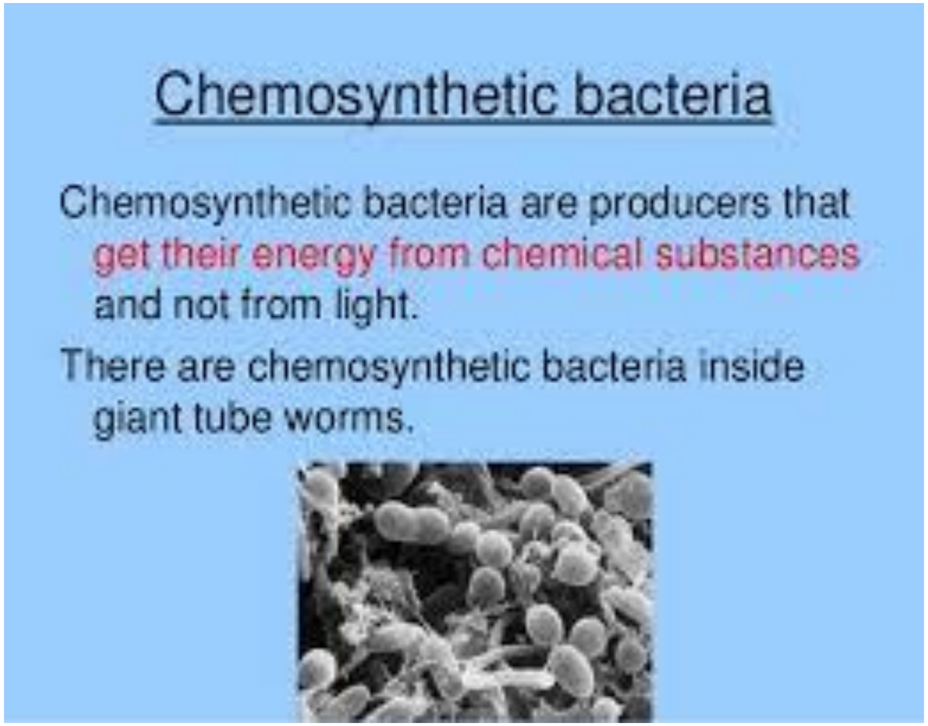
↕

Carb* (CH_2O) + Sulphuric Acid (H_2SO_4)

Carb* = Carbohydrate



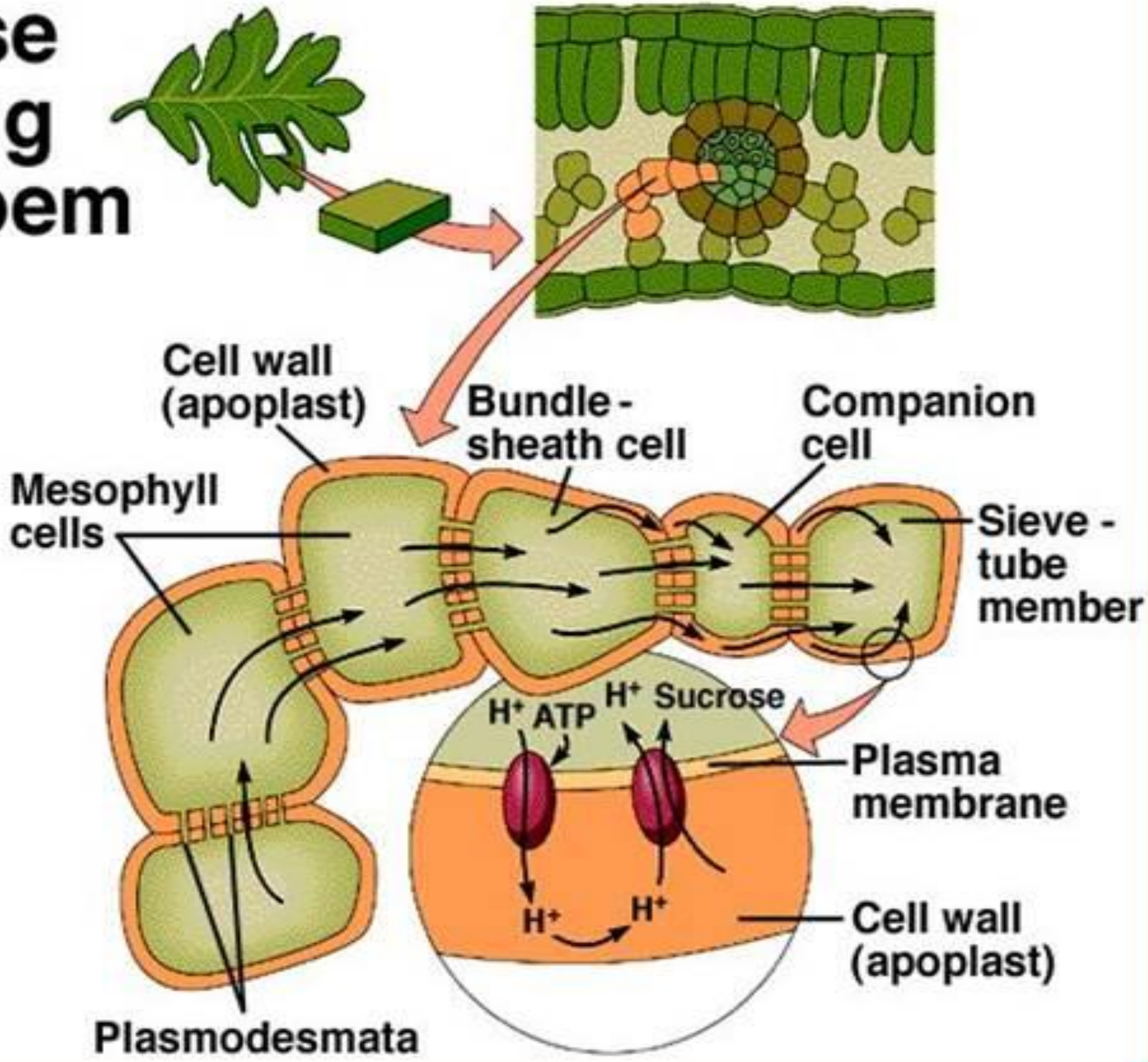
Chemosynthetic Bacteria
(commonly found in hydrothermal vents)



Chemosynthetic bacteria

- Chemosynthetic bacteria are producers that get their energy from chemical substances and not from light.
- There are chemosynthetic bacteria inside giant tube worms.

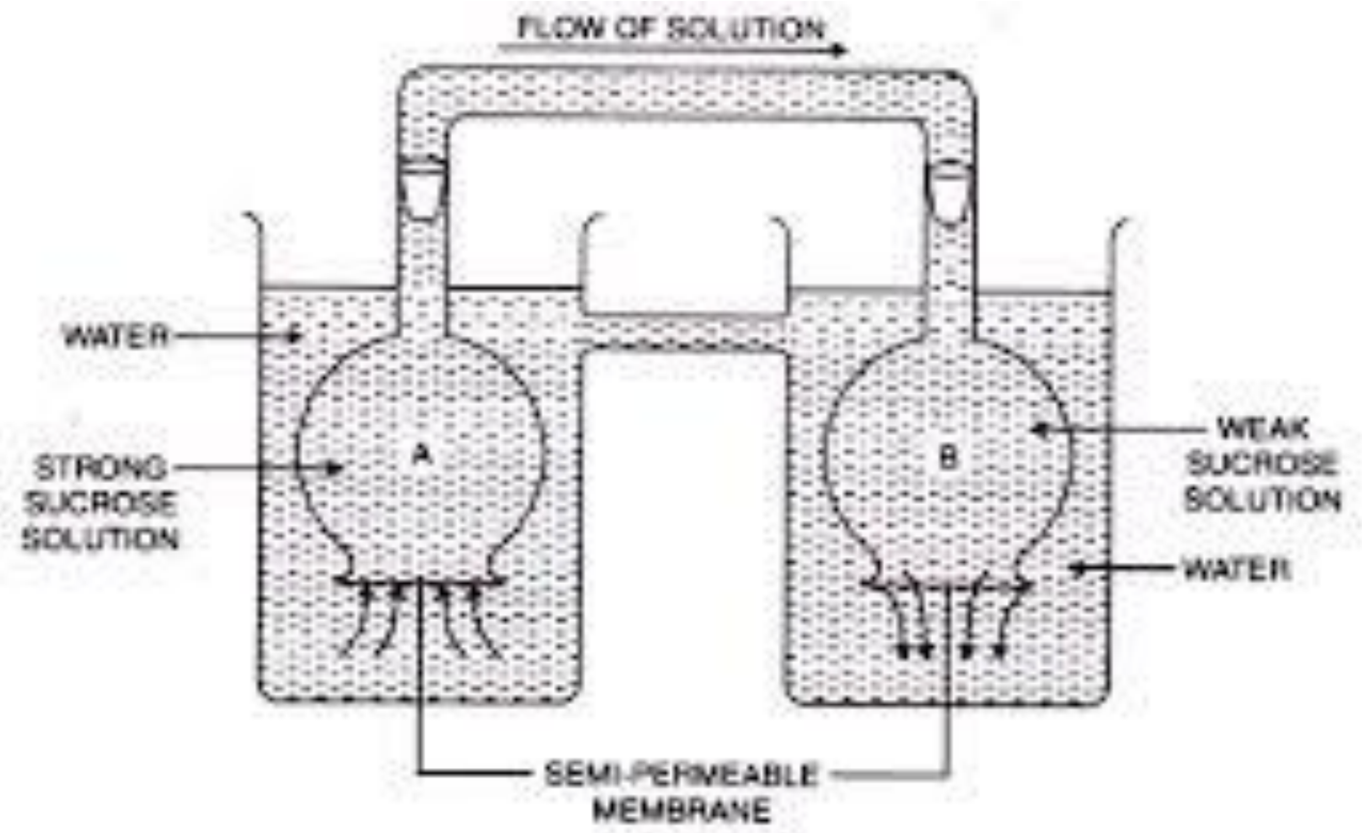
Sucrose Loading into Phloem

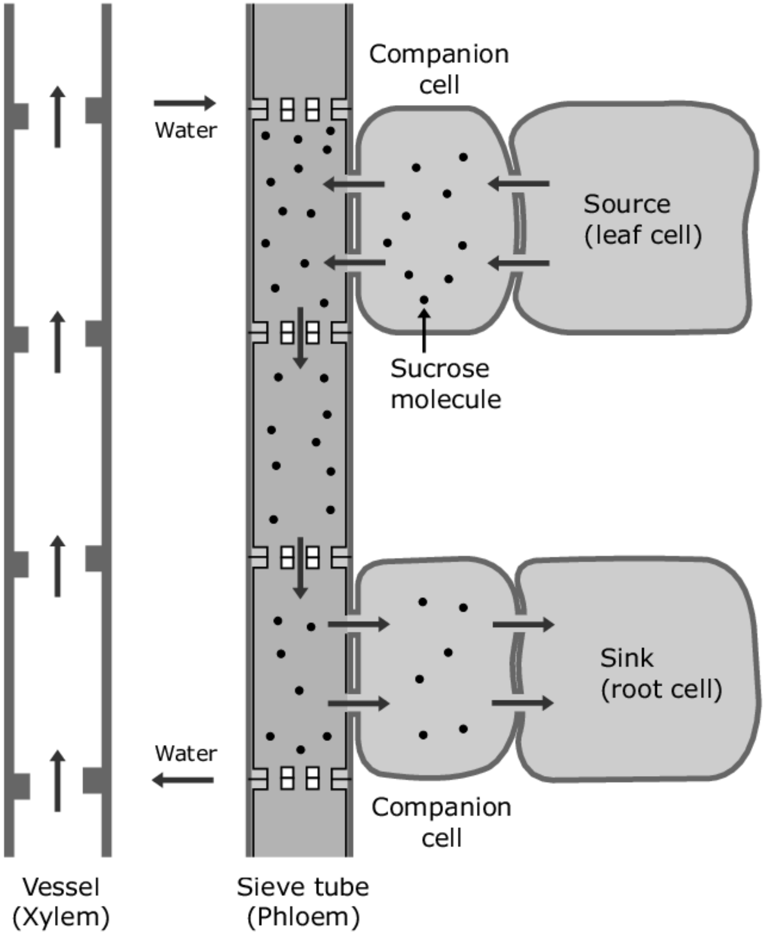


Translocation

- **Short distance translocation**
  - Protoplasmic streaming theory
  - Contractile protein hypothesis
  - Diffusion hypothesis
  - Activated diffusion theory
- **Long distance translocation**
  - Munch hypothesis / Mass flow hypothesis/ Pressure flow hypothesis

Munch hypothesis




Companion cell
Water
Source (leaf cell)
Sucrose molecule
Sink (root cell)
Water
Companion cell
Vessel (Xylem)
Sieve tube (Phloem)

- Phloem transports food molecules made by photosynthesis by a pressure-flow mechanism
  - Sugar is loaded into a phloem tube at the sugar source, raising the solute concentration inside the tube

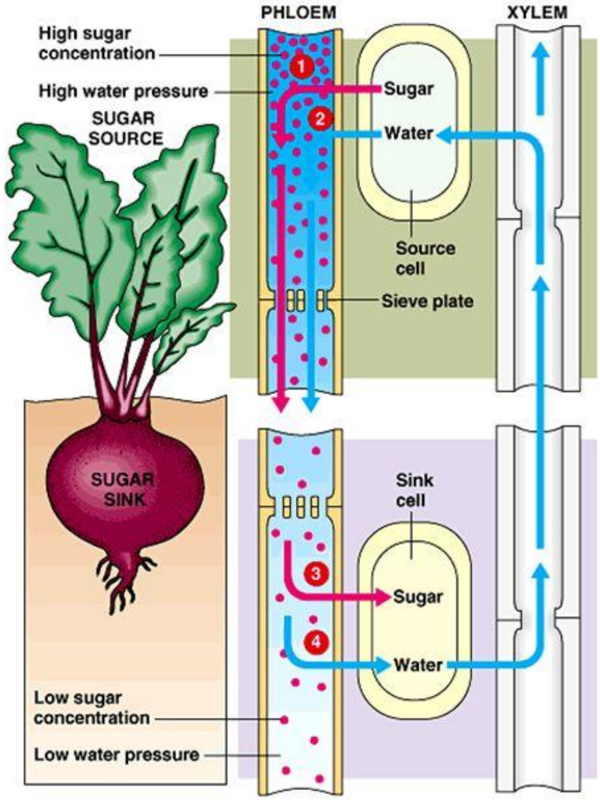
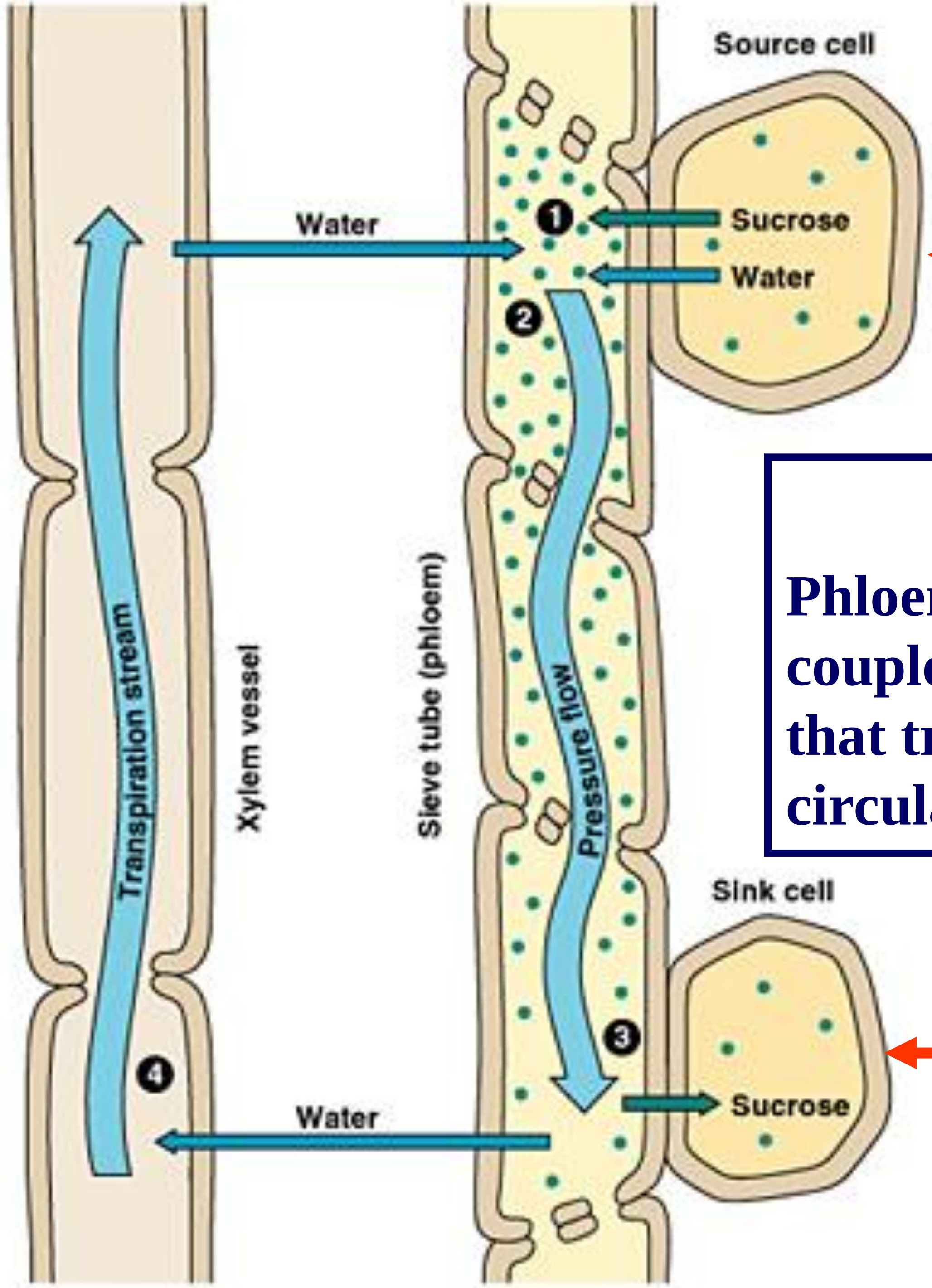


Figure 32.5B



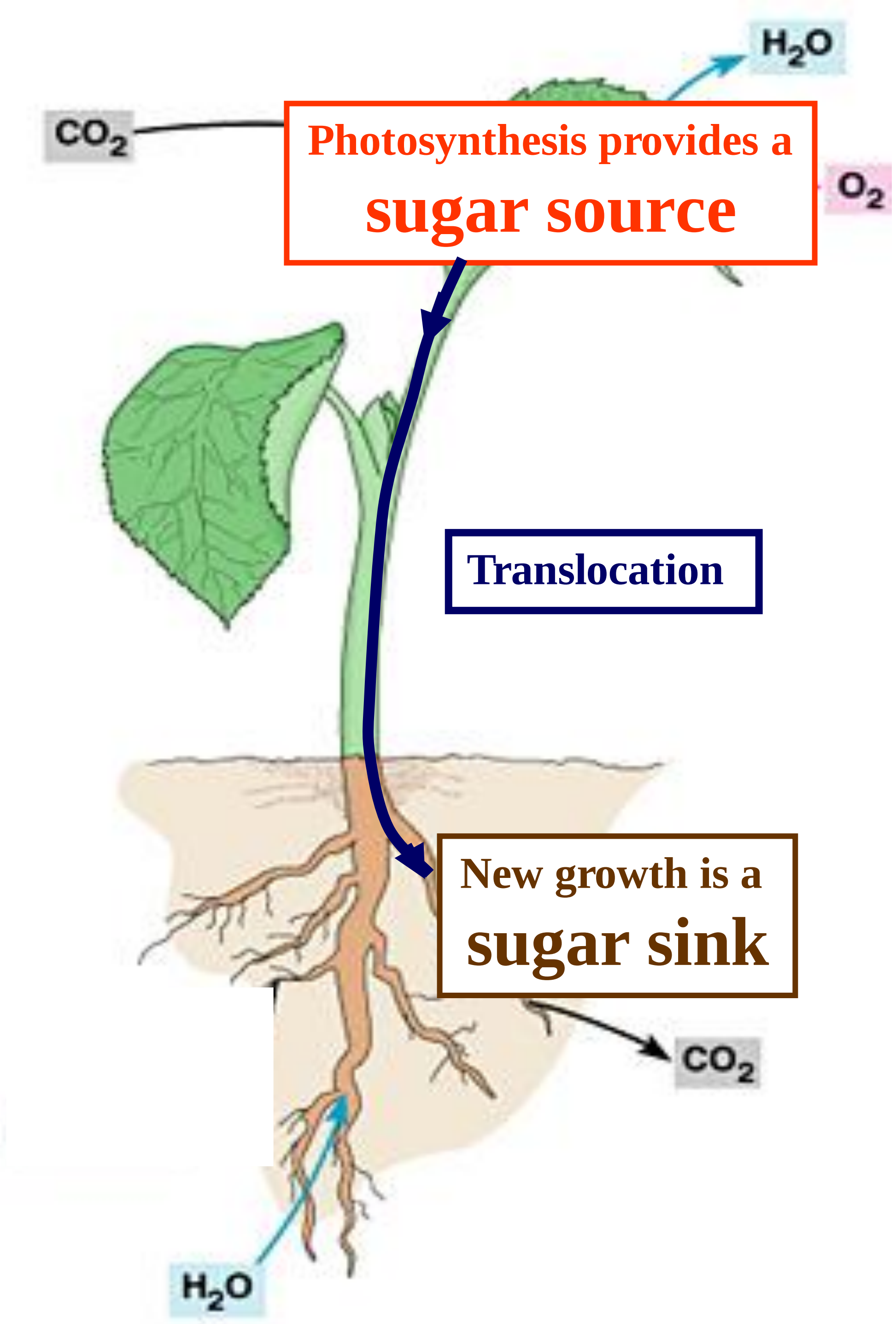
Physiological process of loading sucrose into the phloem

Pressure-flow

Phloem and xylem are coupled in an osmotic system that transports sucrose and circulates water.

Physiological process of unloading sucrose from the phloem into the sink

Sources and sinks



Photosynthesis provides a **sugar source**

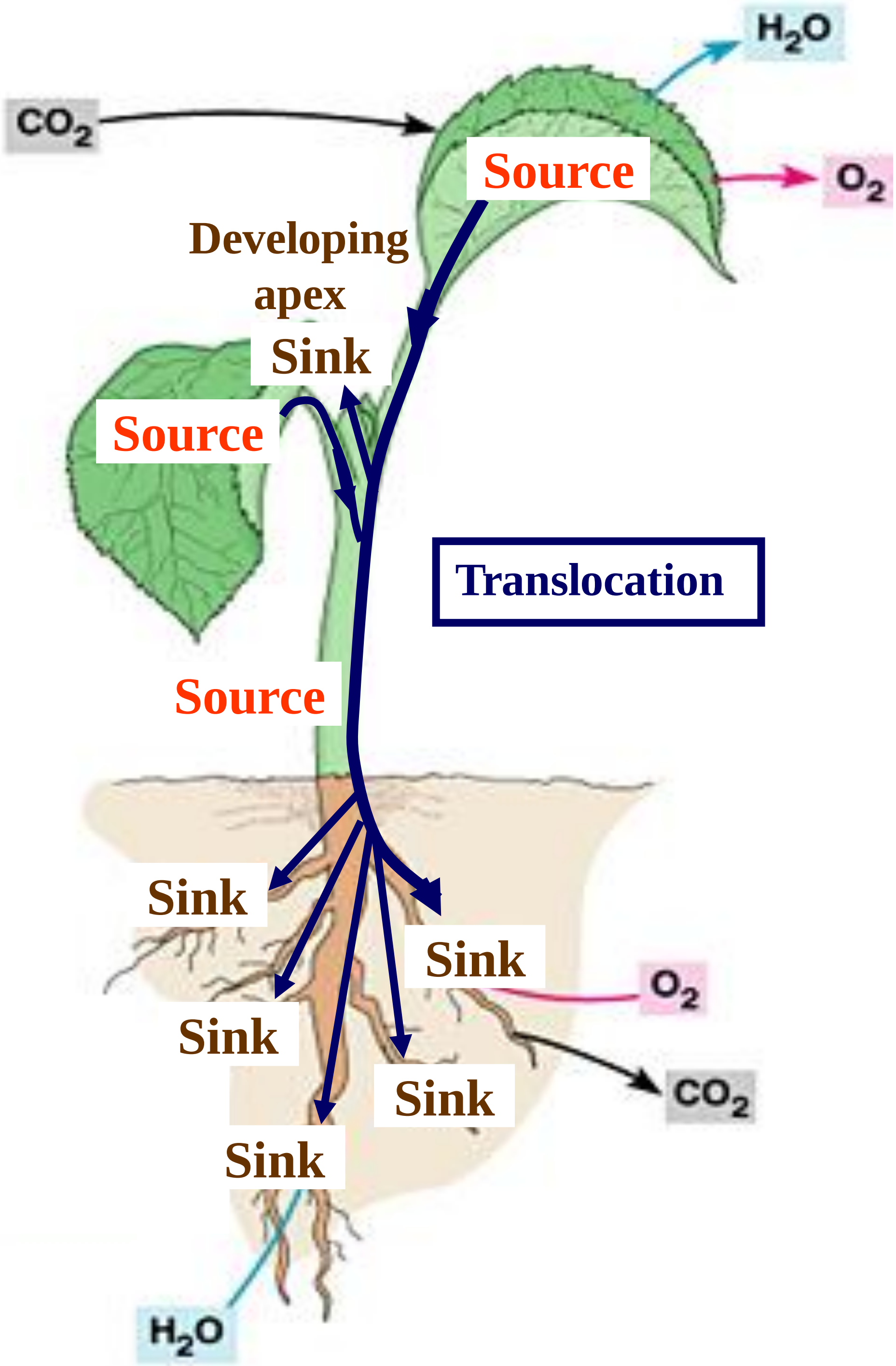
Translocation

New growth is a **sugar sink**

Direction of transport through phloem is determined by relative locations of areas of supply, sources and areas where utilization of photosynthate takes place, sinks.

Source: any transporting organ capable of mobilizing organic compounds or producing photosynthate in excess of its own needs, e.g., mature leaf, storage organ during exporting phase of development.

Sink: non photosynthetic organs and organs that do not produce enough photoassimilate to meet their own requiements, e.g., roots, tubers, develpoping fruits, immature leaves.



The flow of water in plants is almost always from roots to leaves.

Translocation of sucrose can be in any direction – depending on source and sink location and strength.

Examples:

Beta maritima (wild beet) root is a sink during the first growing season.

In the second season the root becomes a source, sugars are mobilized and used to produce a new shoot.

In contrast, in cultivated sugar beets roots are sinks during all phases of development.

What is transported in phloem?

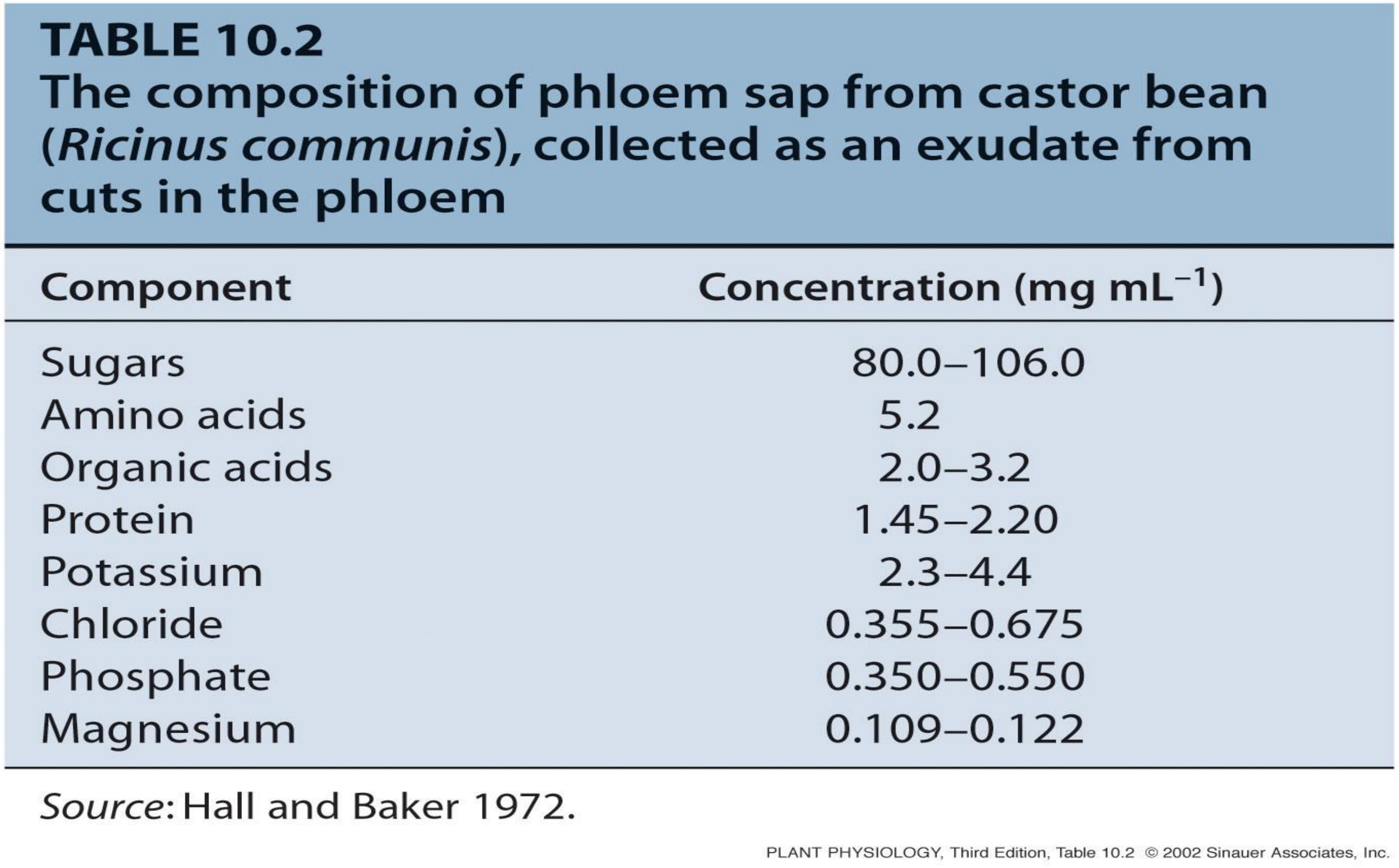


TABLE 10.2
The composition of phloem sap from castor bean (*Ricinus communis*), collected as an exudate from cuts in the phloem

Component	Concentration (mg mL^{-1})
Sugars	80.0–106.0
Amino acids	5.2
Organic acids	2.0–3.2
Protein	1.45–2.20
Potassium	2.3–4.4
Chloride	0.355–0.675
Phosphate	0.350–0.550
Magnesium	0.109–0.122

Source: Hall and Baker 1972.

PLANT PHYSIOLOGY, Third Edition, Table 10.2

Sugars that are *not generally* in phloem

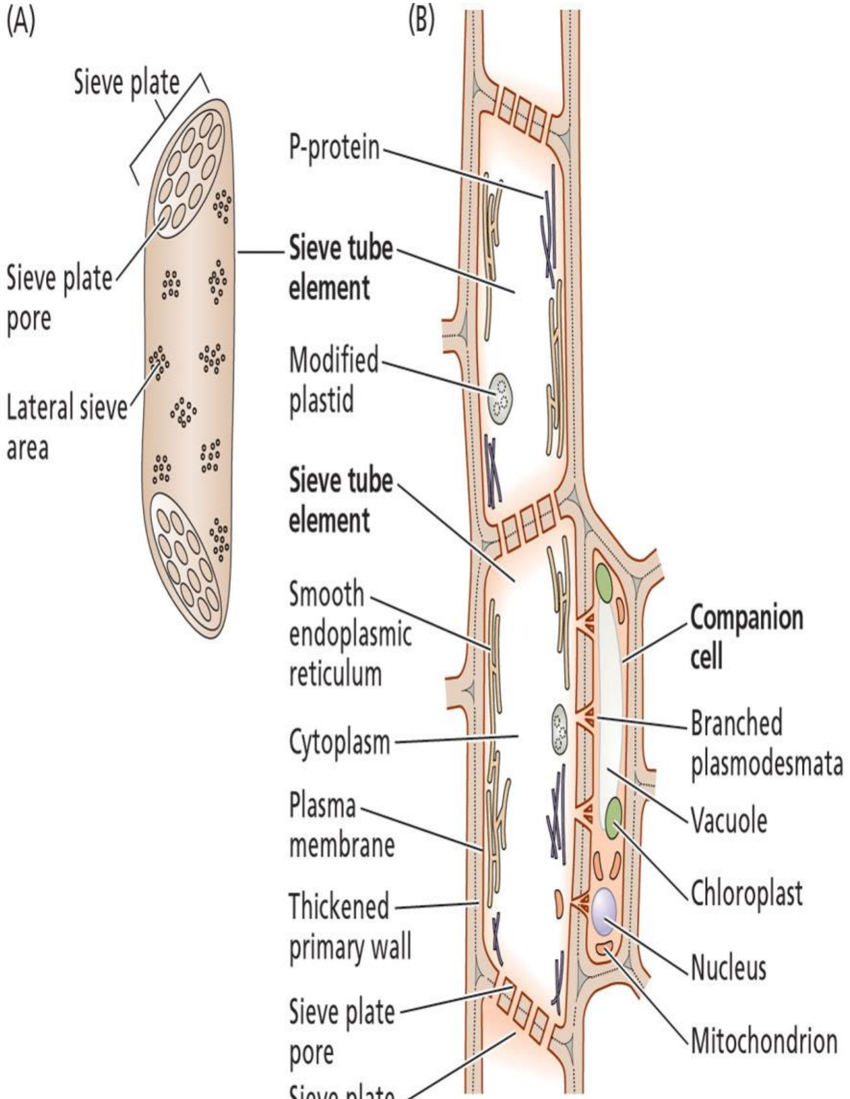
- Carbohydrates transported in phloem are all ***nonreducing*** sugars.
  - ***This is because they are less reactive***
- Reducing sugars, such as ***Glucose***, ***Mannose*** and ***Fructose*** contain an exposed aldehyde or ketone group
  - ***Too chemically reactive to be transported in the phloem***

Sugars that are in phloem (polymers)

- The most common transported sugar is **sucrose**.
  - *Made up from glucose & Fructose*
- This is a reducing sugar
  - ***The ketone or aldehyde group is combined with a similar group on another sugar***
  - ***Or the ketone or aldehyde group is reduced to an alcohol***
    - **D-Mannitol**
- Most of the other mobile sugars transported contain Sucrose bound to varying numbers of *Galactose* units

Phloem transport requires specialized, living cells

- *Companion cells*:
  - Role in transport of photosynthesis products from producing cells in mature leaves to sieve plates of the small vein of the leaf
  - Synthesis of the various proteins used in the phloem
  - Contain many, many mitochondria for cellular respiration to provide the cellular energy required for active transport
  - There ate three types
    - Ordinary companion cells
    - Transfer cells
    - Intermediary cells



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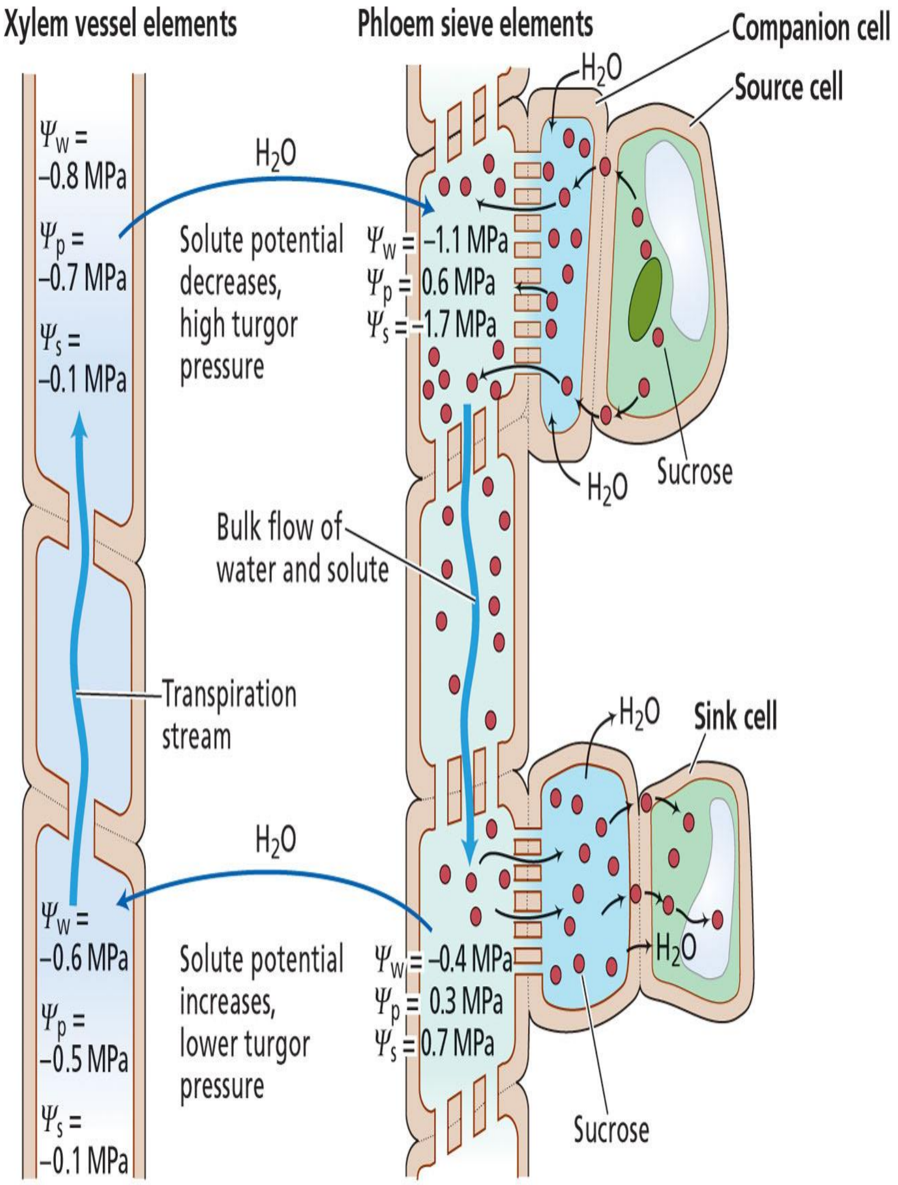
The Pressure-Flow Model

Translocation is thought to move at 1 meter per hour

  - *Diffusion too slow for this speed*

- The flow is driven by an osmotically generated pressure gradient between the ***source*** and the ***sink***.
- **Source**
  - Sugars (red dots) is actively loaded into the sieve element-companion cell complex
    - *Called phloem loading*
- **Sink**
  - Sugars are unloaded
    - *Called phloem unloading*



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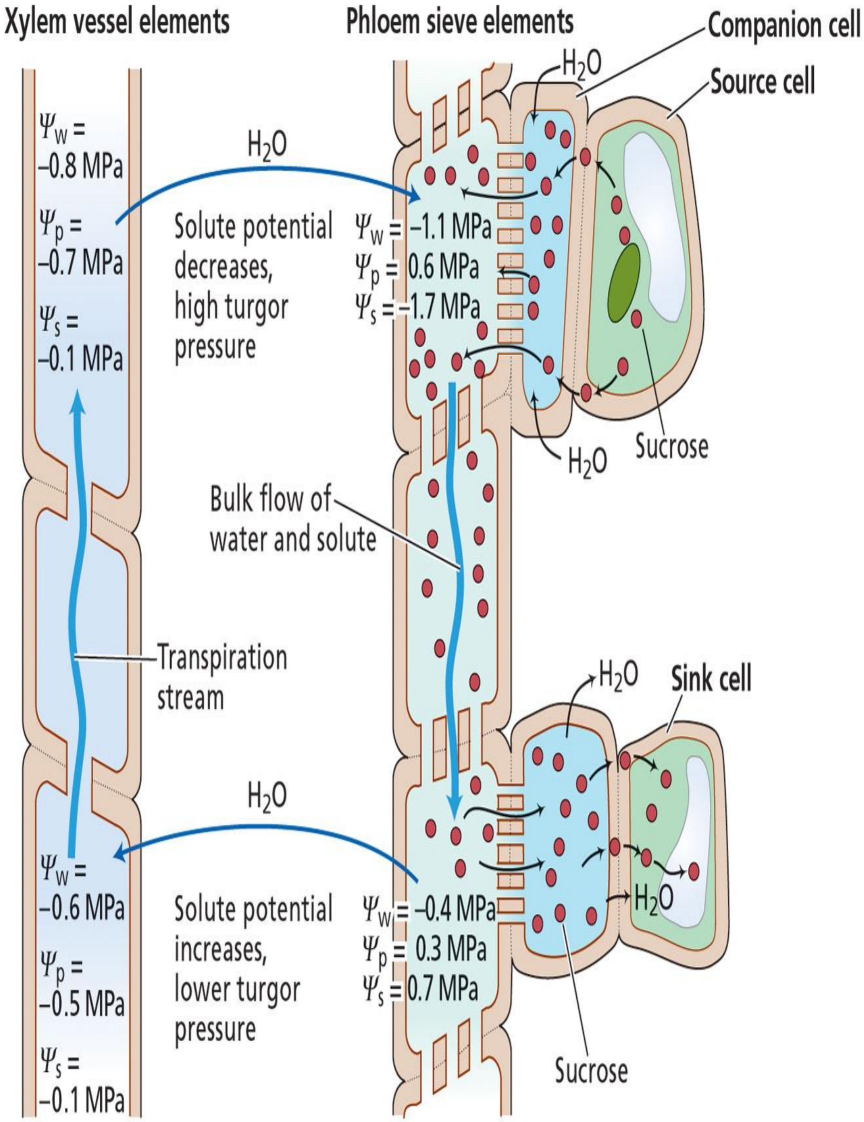
The Pressure -Flow Model

- $\psi w = \psi s + \psi p + \psi g$
- In ***source tissue***, energy driven phloem loading leads to a buildup of sugars
  - Makes **low (-ve)** solute potential
  - Causes a steep **drop** in water potential
  - In response to this new water potential gradient, water enters sieve elements from xylem
    - ***Thus phlem turgor pressure increases***
- In ***sink tissue***, phloem unloading leads to lower sugar conc.
  - Makes a **higher (+ve)** solute potential
  - Water potential **increases**
  - Water leaves phloem and enters sink sieve elements and xylem
    - ***Thus phloem turgor pressure decreases***



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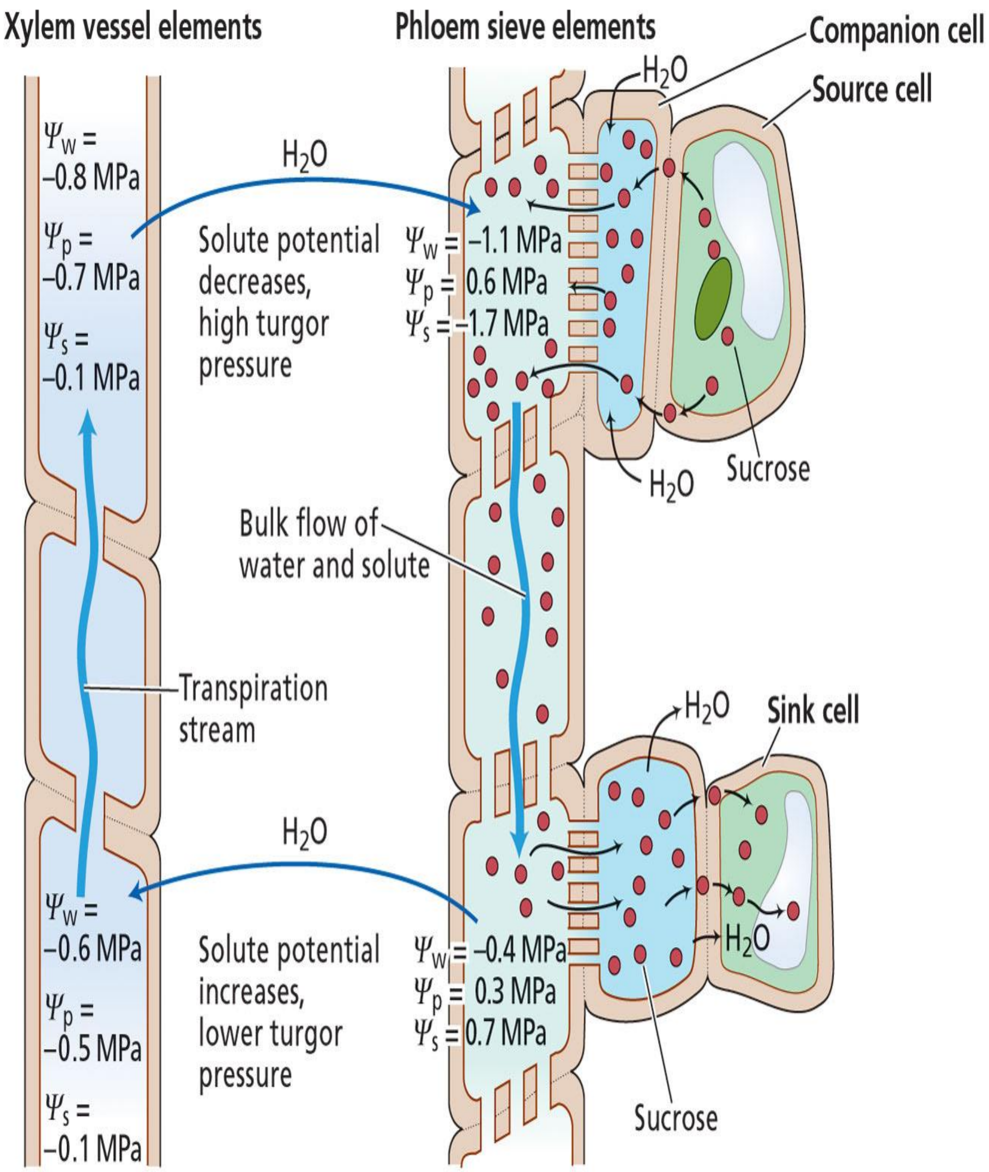
The Pressure-Flow Model

- So, the translocation pathway has cross walls
  - Allow water to move from xylem to phloem and back again
  - If absent- ***pressure difference from source to sink would quickly equilibrate***
- Water is moving in the phloem by ***Bulk Flow***
  - No membranes are crossed from one sieve tube to another
  - Solutes are moving at the same rate as the water
- Water movement is driven by ***pressure gradient*** and **NOT** ***water potential gradient***



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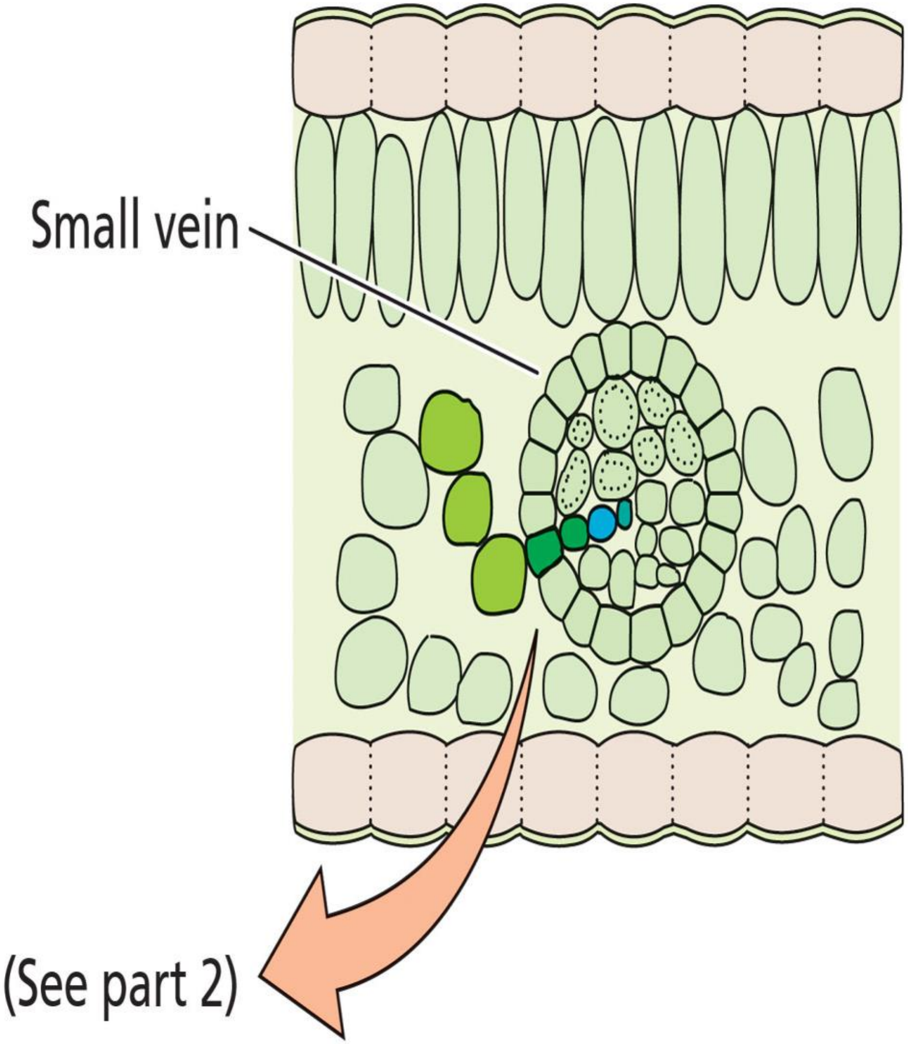
Phloem Loading:
Where do the solutes come from?

- Triose phosphate – formed from photosynthesis during the day is moved from chloroplast to cytosol
- At night, this compound, together with glucose from stored starch, is converted to sucrose
  - ***Both these steps occur in a mesophyll cell***
- Sucrose then moves from the mesophyll cell via the smallest veins in the leaf to near the sieve elements
  - Known as short distance pathway – ***only moves two or three cells***



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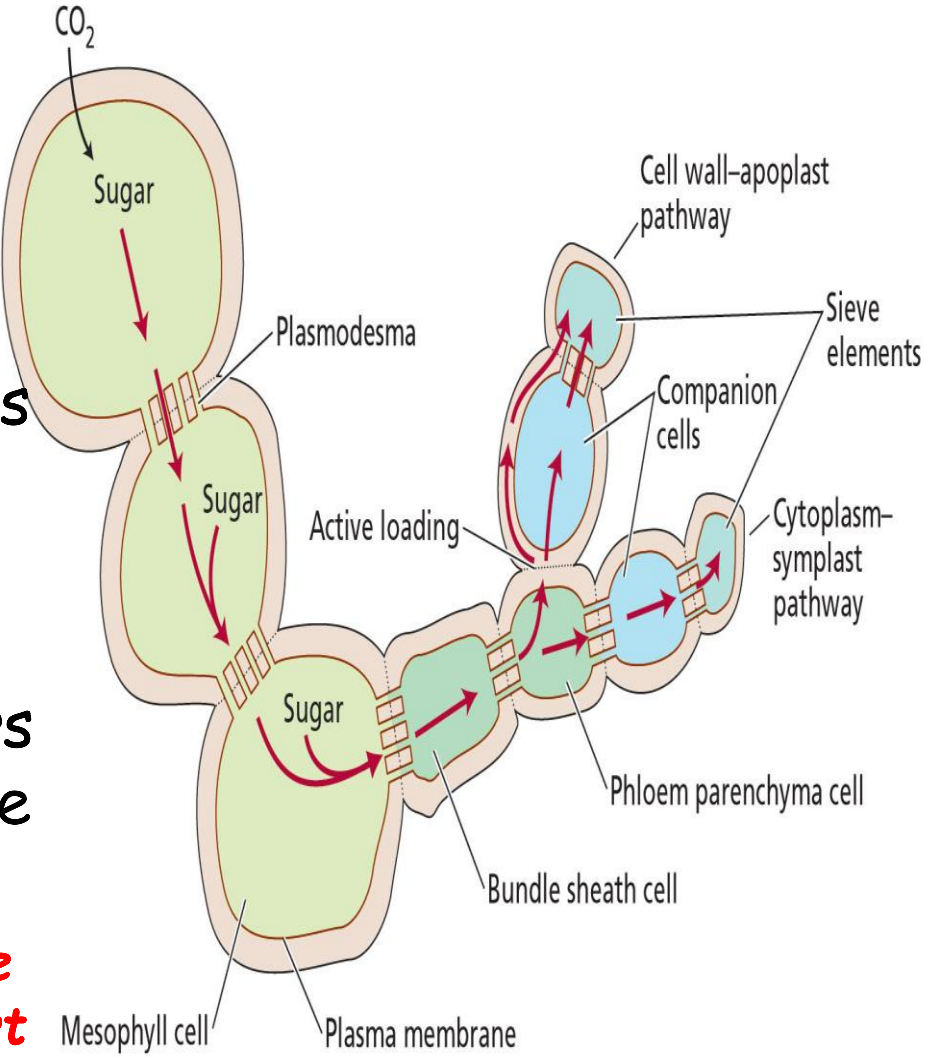
Phloem Loading:
Where do the solutes come from?

- In a process called ***sieve element loading***, sugars are transported into the sieve elements and companion cells
- Sugars become more concentrated in sieve elements and companion cells than in mesophyll cells
- Once in the sieve element /companion cell complex sugars are transported away from the source tissue – called ***export***
  - ***Translocation to the sink tissue is called long distance transport***



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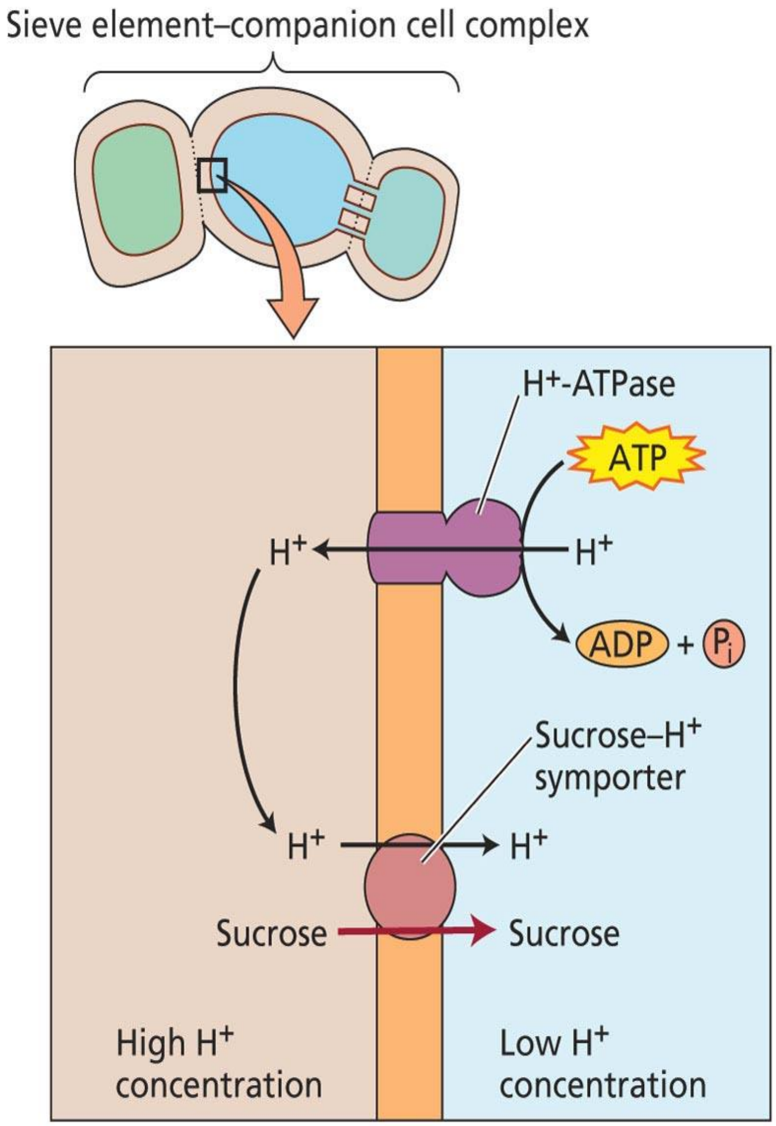
Phloem Loading:
Where do the solutes come from?

- Movement is via either apoplast or symplast
- Via ***apoplastic pathway*** requires

- ***Active transport against it's chemical potential gradient***

- ***Involves a sucrose-H+ symporter***
  - ***The energy dissipated by protons moving back into the cell is coupled to the uptake of sucrose***



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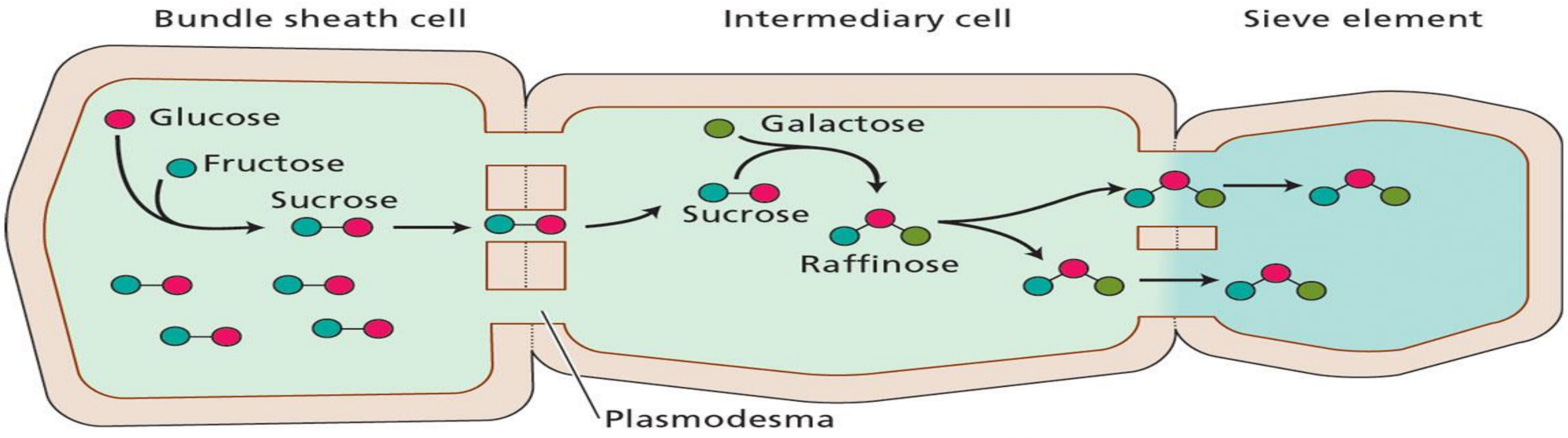
Symplastic phloem loading

- Depends on plant species
  - *Dependant on species that transport sugars other than sucrose*
- Requires the presence of open plasmodesmata between different cells in the pathway
- Dependant on plant species with intermediary companion cells



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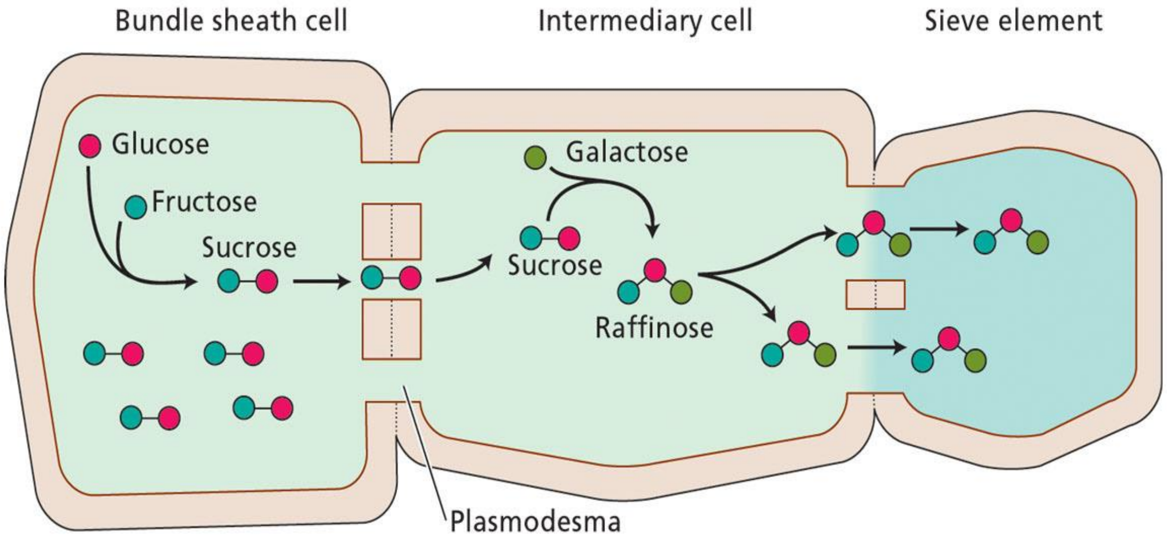
Symplastic phloem loading

- Sucrose, synthesized in mesophyll, diffuses into intermediary cells
- Here ***Raffinose*** is synthesized. Due to larger size, can **NOT** diffuse back into the mesophyll
- Raffinose and sucrose are able to diffuse into sieve element



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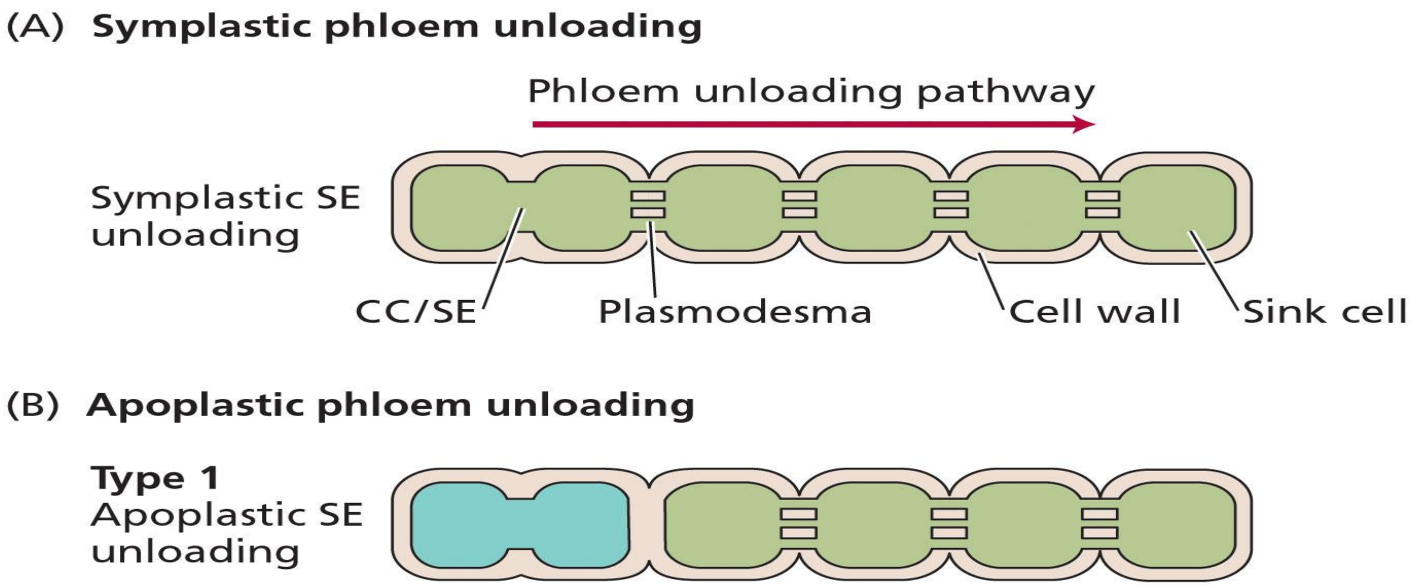
Phloem unloading

- Three steps
- (1) ***Sieve element unloading***:
  - Transported sugars leave the sieve elements of sink tissue
- (2) ***Short distance transport***:
  - After sieve element unloading, sugars transported to cells in the sink by means of a short distance pathway
- (3) ***storage and metabolism***:
  - Sugars are stored or metabolized in sink cells

Phloem unloading

- Also can occur by symplastic or apoplatic pathways
- *Varies greatly from growing vegetative organs (root tips and young leaves) to storage tissue (roots and stems) to reproductive organs*
- *Symplastic*:
- Appears to be a completely symplastic pathway in young dicot leaves
- Again, moves through open plasmodesmata



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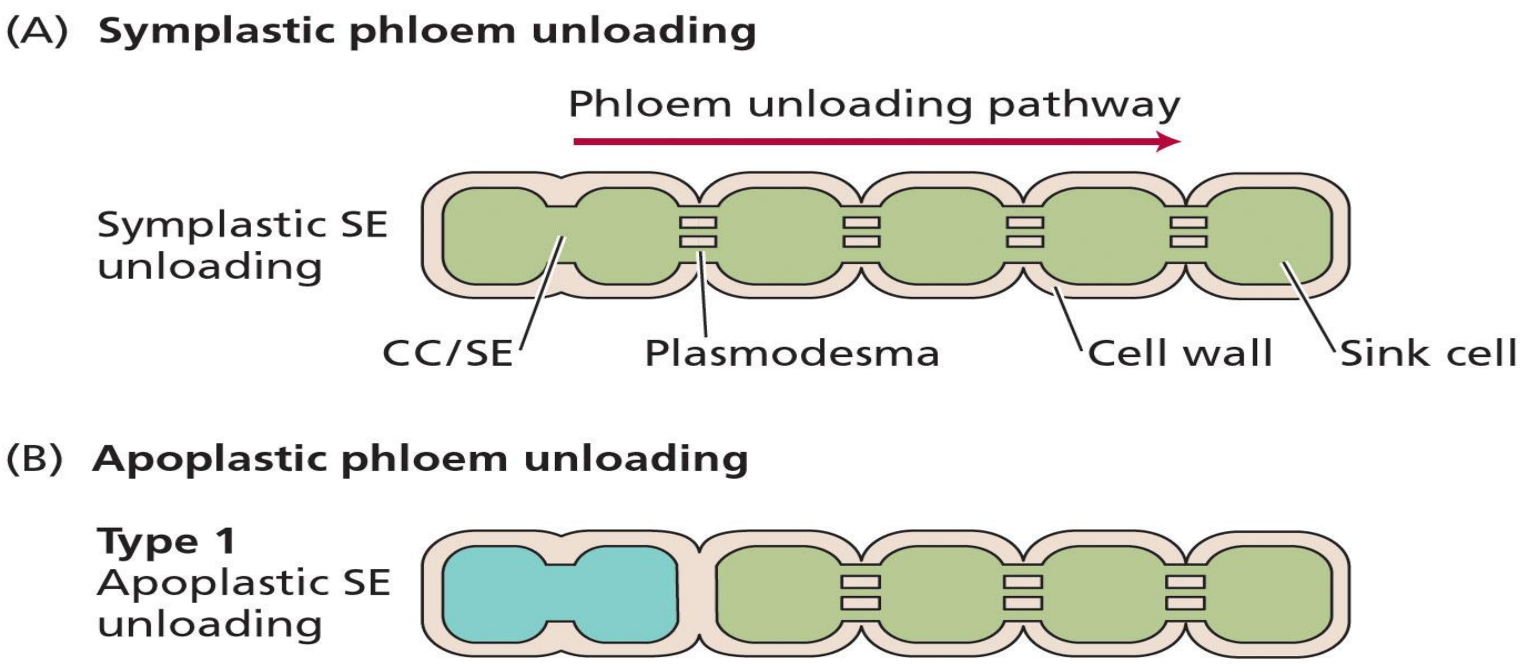
Phloem unloading

- *Apoplastic*: three types
- (1) [B] One step, transport from the sieve element-companion cell complex to successive sink cells, occurs in the apoplast.
- Once sugars are taken back into the symplast of adjoining cells transport is symplastic



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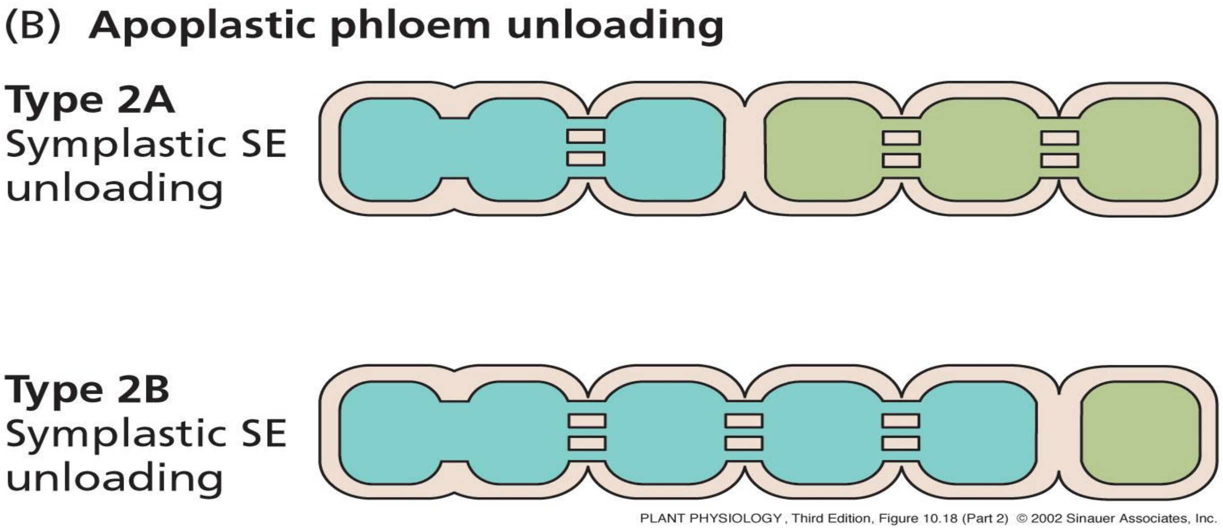
Phloem unloading

- *Apoplastic*: three types
- (2) [A] involves an apoplastic step close to the sieve element companion cell.
- (3) [B] involves an apoplastic step father from the sieve element companion cell
- ***Both involve movement through the plant cell wall***



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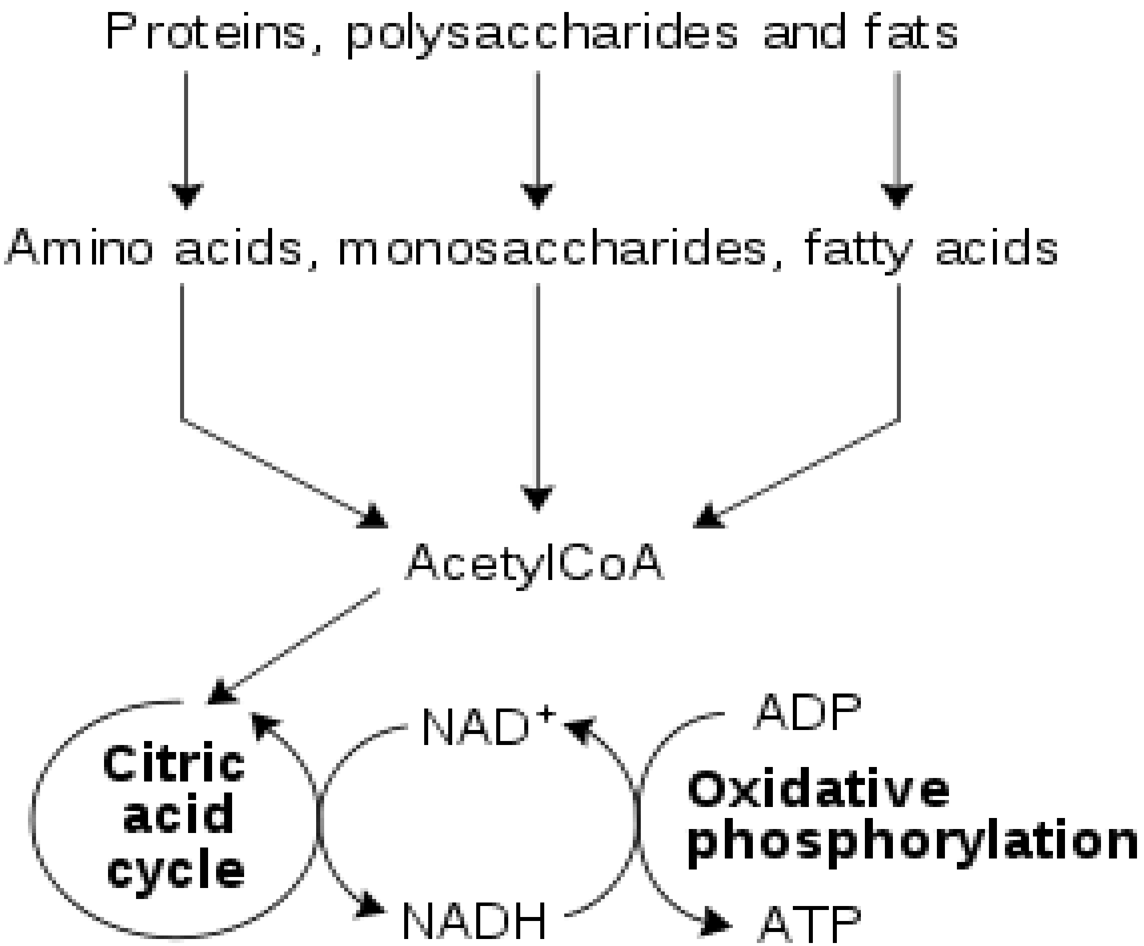
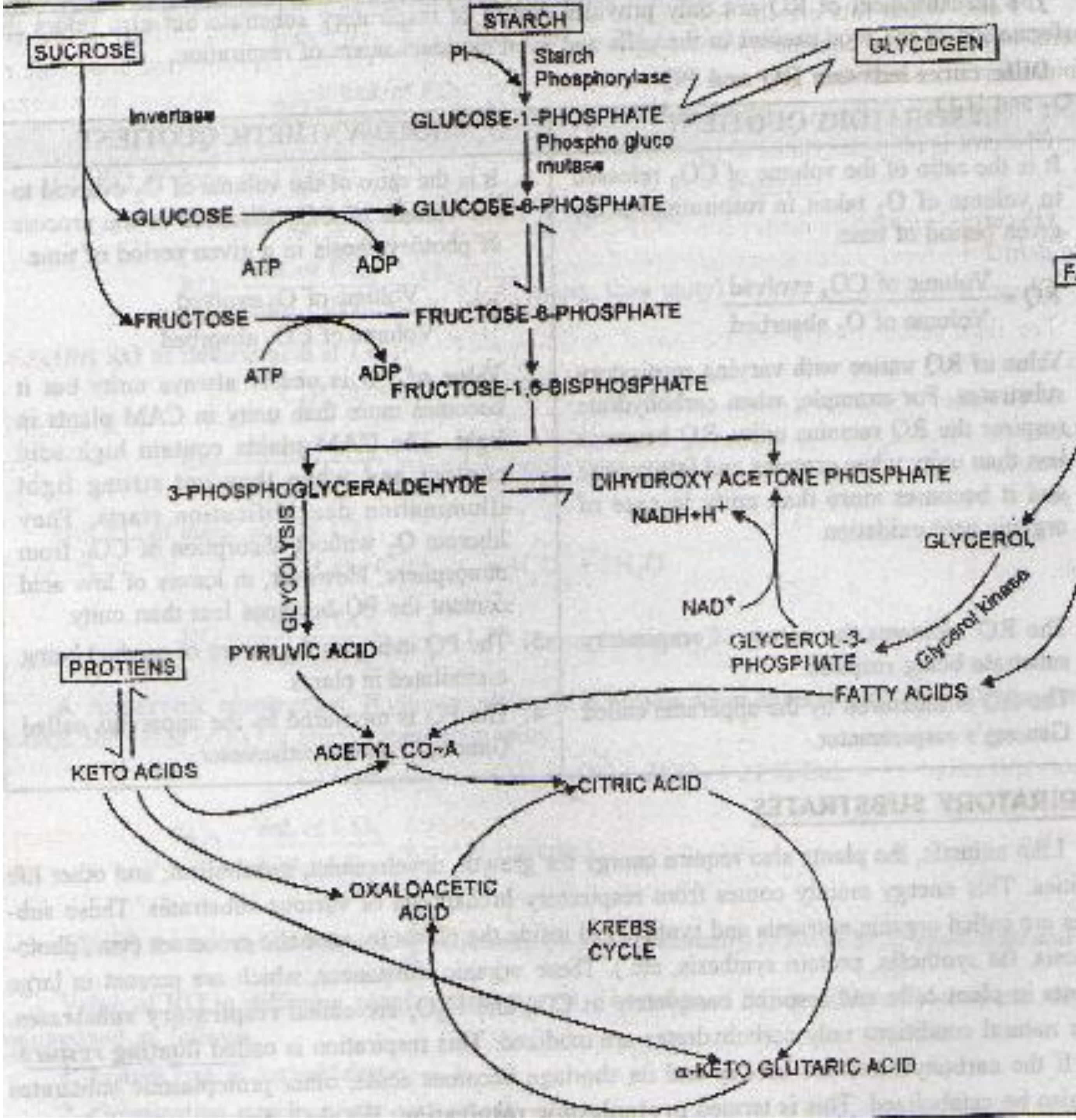
RESPIRATION

Outline of catabolism

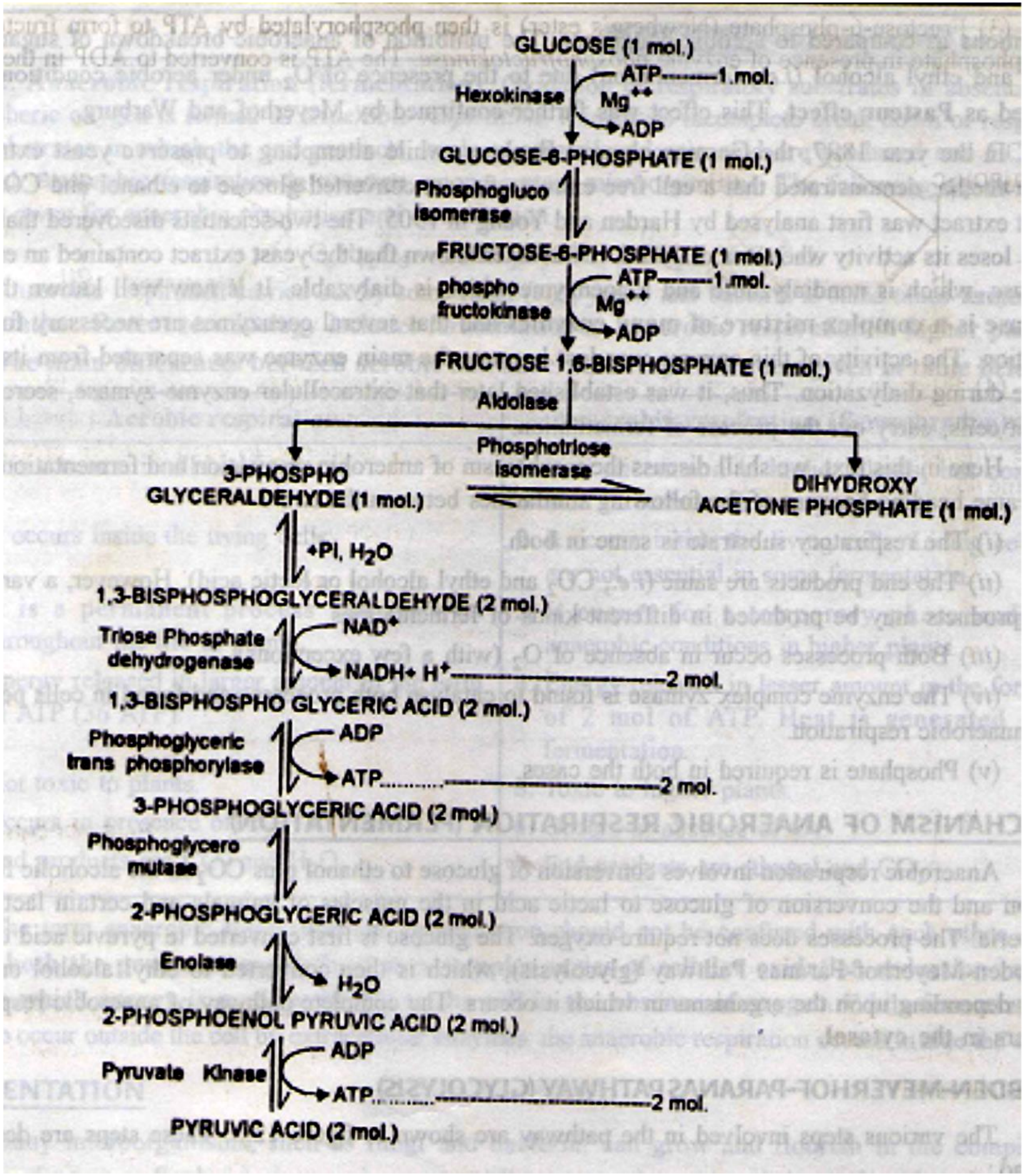



STARCH
SUCROSE
GLYCOGEN
Pi
Starch Phosphorylase
Invertase
GLUCOSE-1-PHOSPHATE
Phospho gluco mutase
GLUCOSE
GLUCOSE-6-PHOSPHATE
ATP
ADP
FAT
FRUCTOSE
FRUCTOSE-6-PHOSPHATE
ATP
ADP
FRUCTOSE-1,6-BISPHOSPHATE
3-PHOSPHOGLYCERALDEHYDE
DIHYDROXY ACETONE PHOSPHATE
NADH+H$^+$
GLYCEROL
GLYCOLYSIS
NAD$^+$
Glycerol Kinase
GLYCEROL-3-PHOSPHATE
PYRUVIC ACID
PROTIENS
FATTY ACIDS
ACETYL CO-A
KETO ACIDS
CITRIC ACID
OXALOACETIC ACID
KREBS CYCLE
α-KETO GLUTARIC ACID

Significance

- Release on 5.2% of the total energy
- Very few organisms depend only on glycolysis completely
- Only metabolic pathway common to all organisms, all cells
- Anaerobic pathway--- Can be depended when oxygen limitations occur
- Provides building blocks
- Most ancient pathway
- Evolutionary significance- most conserved pathway

Glycolysis


GLUCOSE (1 mol.)
Hexokinase
ATP---------1.mol.
Mg^{++}
ADP
GLUCOSE-6-PHOSPHATE (1 mol.)
Phosphogluco isomerase
FRUCTOSE-6-PHOSPHATE (1 mol.)
phospho fructokinase
ATP---------1.mol.
Mg^{++}
ADP
FRUCTOSE 1,6-BISPHOSPHATE (1 mol.)
Aldolase
Phosphotriose isomerase
3-PHOSPHO GLYCERALDEHYDE (1 mol.)
DIHYDROXY ACETONE PHOSPHATE (1 mol.)
+Pi, H_2O
1,3-BISPHOSPHOGLYCERALDEHYDE (2 mol.)
Triose Phosphate dehydrogenase
NAD^+
NADH+ H^+--------------------2 mol.
1,3-BISPHOSPHO GLYCERIC ACID (2 mol.)
Phosphoglyceric trans phosphorylase
ADP
ATP..........--------------------2 mol.
3-PHOSPHOGLYCERIC ACID (2 mol.)
Phosphoglycero mutase
2-PHOSPHOGLYCERIC ACID (2 mol.)
Enolase
H_2O
2-PHOSPHOENOL PYRUVIC ACID (2 mol.)
Pyruvate Kinase
ADP
ATP..........--------------------2 mol.
PYRUVIC ACID (2 mol.)

Role of NADH in sustaining glycolysis

- For every glucose, 2 NADH molecules are formed
- NAD depletion occurs during anaerobic pathway
- Pyruvic acid + NADH-----lactic acid + NAD

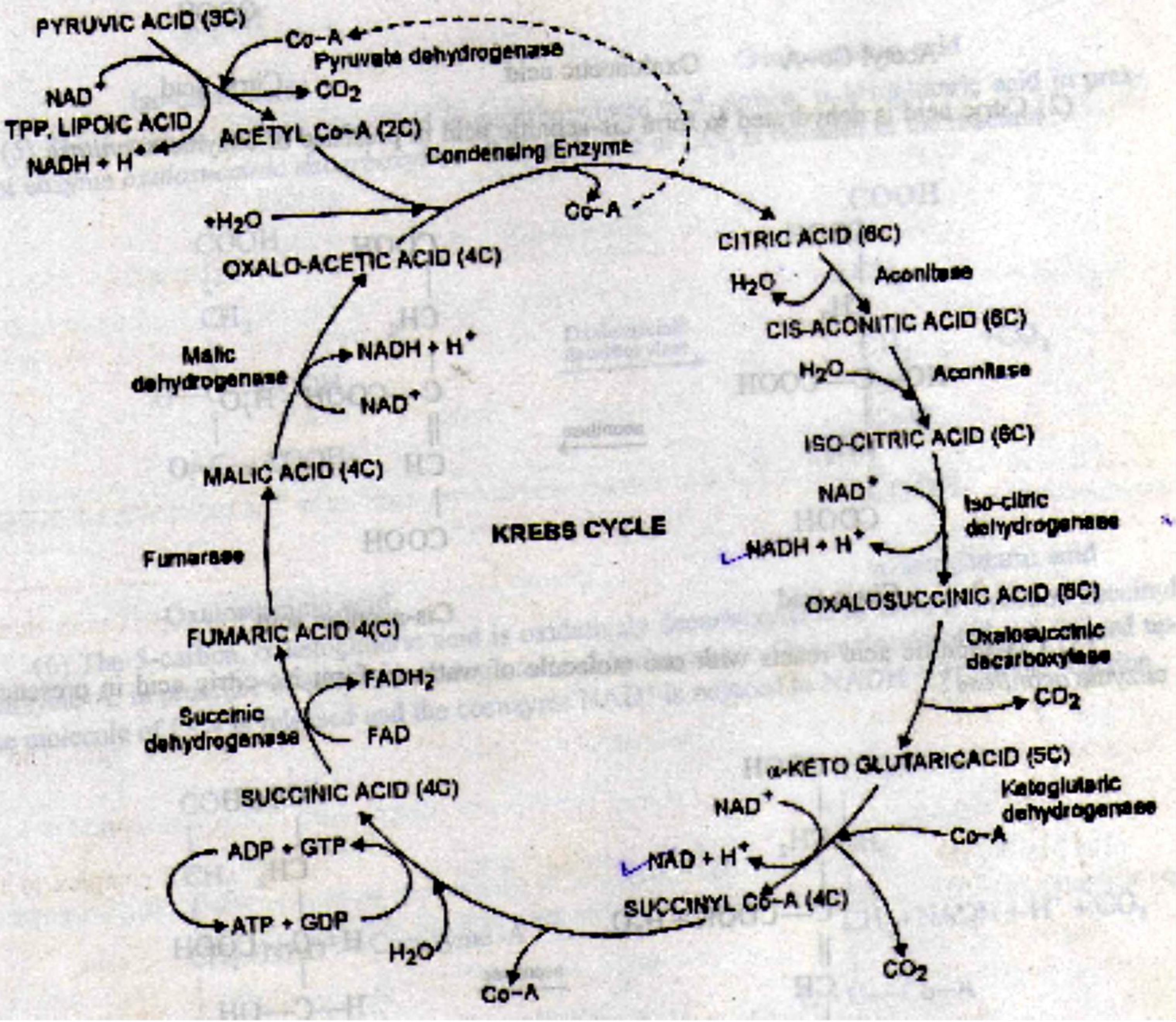
Energy Balance Sheet

- Glucose + 2Pi + 2 ADP +2NAD ------- 2 pyruvate +2ATP + 2NADH

- Energy required for synthesis of 2 ATP -----100 KJ
- Release ---- 195 KJ
- Efficiency 50%

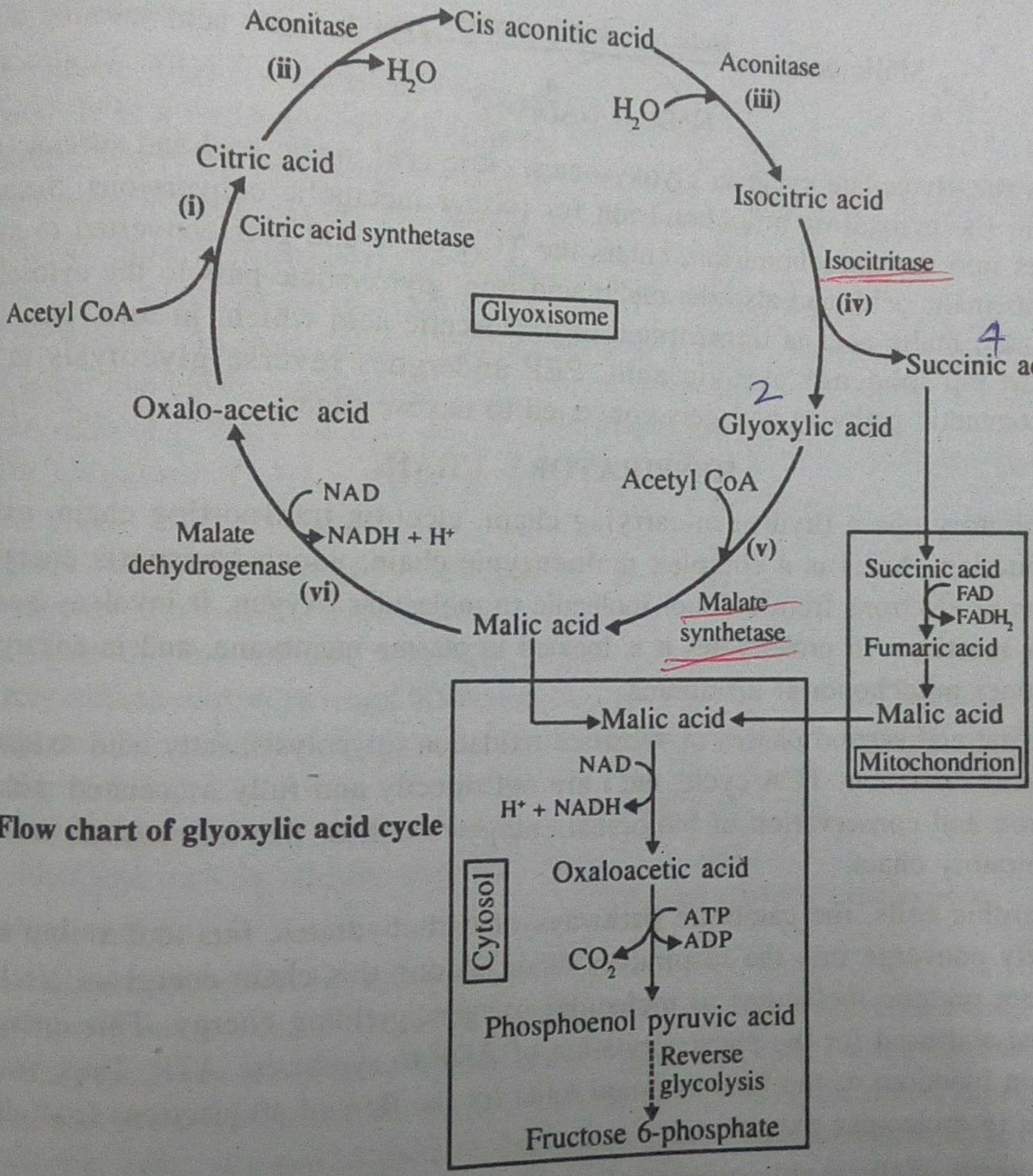
Fate of pyruvic acid

- Ethanol
- Lactic acid
- Acetyl CoA

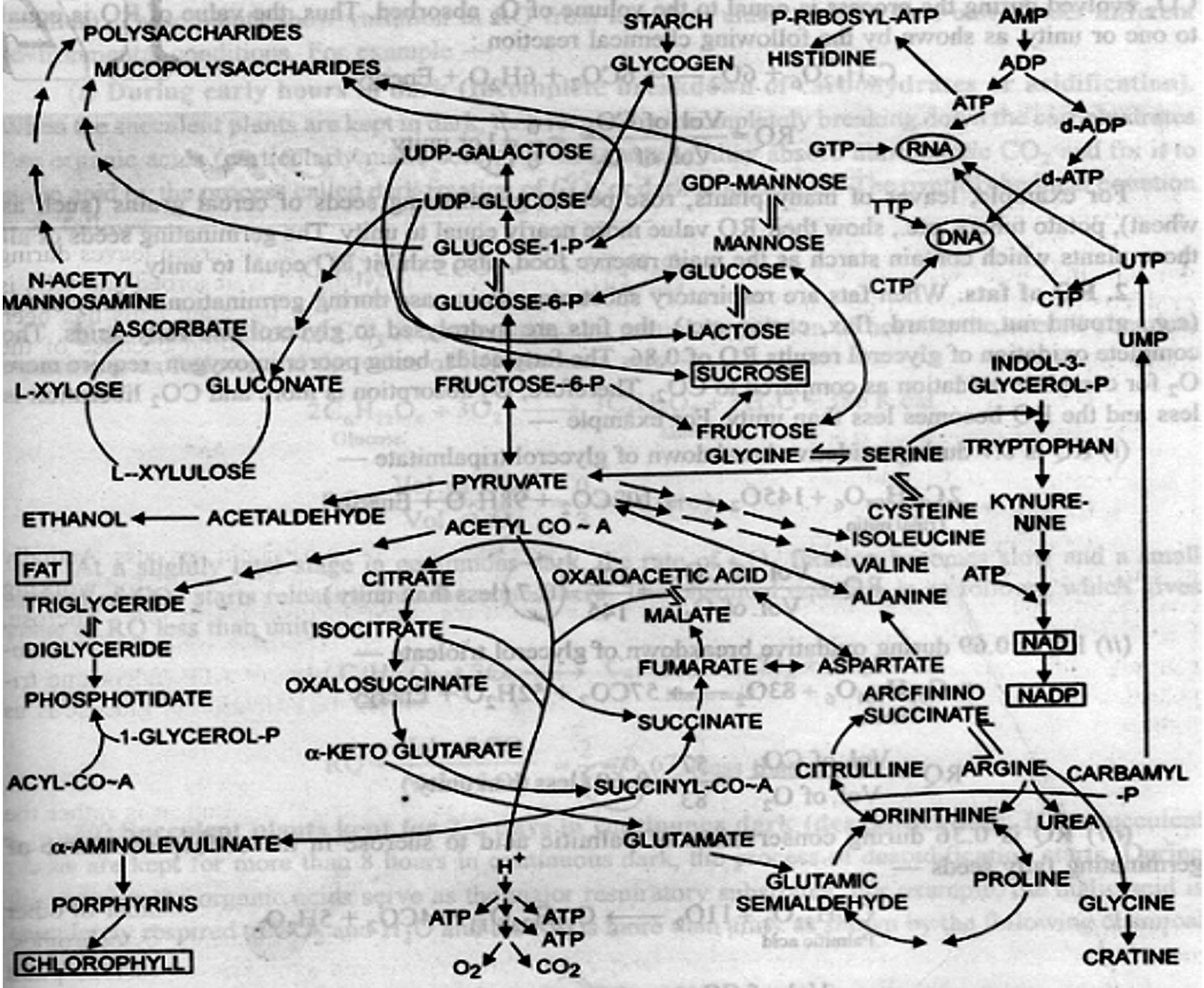

PYRUVIC ACID (3C)
Co–A
Pyruvate dehydrogenase
NAD$^+$
CO$_2$
TPP, LIPOIC ACID
ACETYL Co–A (2C)
NADH + H$^+$
Condensing Enzyme
+H$_2$O
Co–A
CITRIC ACID (6C)
OXALO-ACETIC ACID (4C)
H$_2$O
Aconitase
CIS-ACONITIC ACID (6C)
Malic dehydrogenase
NADH + H$^+$
NAD$^+$
H$_2$O
Aconitase
ISO-CITRIC ACID (6C)
MALIC ACID (4C)
NAD$^+$
Iso-citric dehydrogenase
KREBS CYCLE
Fumarase
NADH + H$^+$
OXALOSUCCINIC ACID (6C)
FUMARIC ACID 4(C)
Oxalosuccinic decarboxylase
FADH$_2$
CO$_2$
Succinic dehydrogenase
FAD
α-KETO GLUTARICACID (5C)
SUCCINIC ACID (4C)
NAD$^+$
Ketoglutaric dehydrogenase
Co–A
ADP + GTP
NAD + H$^+$
SUCCINYL Co–A (4C)
ATP + GDP
H$_2$O
CO$_2$
Co–A

Efficiency

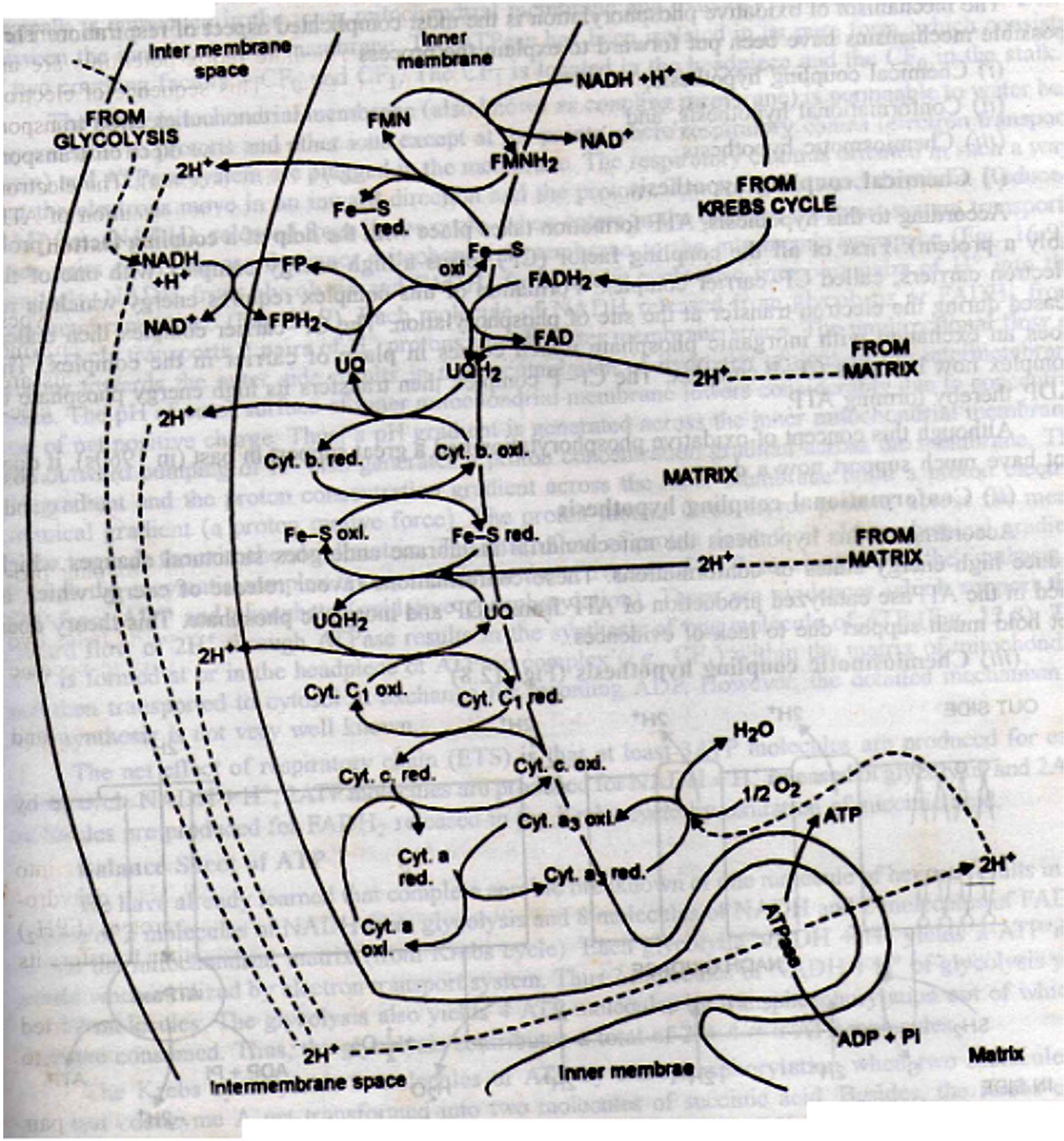
- Production ---- 209000 cal
- Net gain ----- 84000 cal
- Efficiency 40%

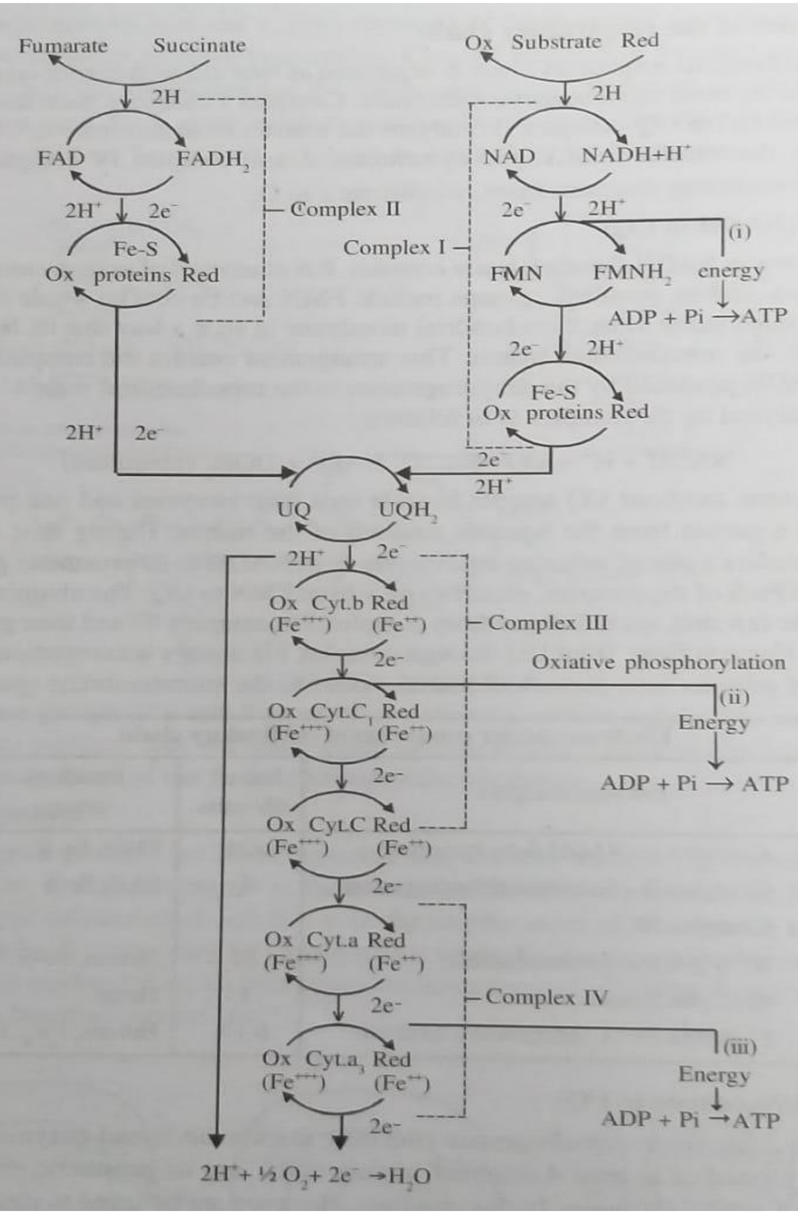


Flow chart of glyoxylic acid cycle


POLYSACCHARIDES
MUCOPOLYSACCHARIDES
STARCH
GLYCOGEN
P-RIBOSYL-ATP
HISTIDINE
AMP
ADP
ATP
d-ADP
GTP
RNA
d-ATP
UDP-GALACTOSE
UDP-GLUCOSE
GDP-MANNOSE
MANNOSE
TTP
DNA
CTP
UTP
CTP
N-ACETYL MANNOSAMINE
GLUCOSE-1-P
GLUCOSE
GLUCOSE-6-P
LACTOSE
ASCORBATE
SUCROSE
L-XYLOSE
GLUCONATE
FRUCTOSE--6-P
UMP
INDOL-3-GLYCEROL-P
FRUCTOSE
GLYCINE
SERINE
TRYPTOPHAN
L--XYLULOSE
PYRUVATE
CYSTEINE
KYNURE-NINE
ETHANOL
ACETALDEHYDE
ACETYL CO ~ A
ISOLEUCINE
FAT
VALINE
CITRATE
OXALOACETIC ACID
ATP
TRIGLYCERIDE
ALANINE
MALATE
DIGLYCERIDE
ISOCITRATE
NAD
FUMARATE
ASPARTATE
PHOSPHOTIDATE
OXALOSUCCINATE
NADP
ARCFININO SUCCINATE
SUCCINATE
1-GLYCEROL-P
α-KETO GLUTARATE
CITRULLINE
ARGINE
CARBAMYL -P
ACYL-CO~A
SUCCINYL-CO~A
ORINITHINE
UREA
α-AMINOLEVULINATE
GLUTAMATE
H⁺
GLUTAMIC SEMIALDEHYDE
PROLINE
PORPHYRINS
ATP
ATP
ATP
GLYCINE
CHLOROPHYLL
O₂
CO₂
CRATINE

ETS & Oxidative phosphorylation




Fumarate
Succinate
2H
FAD
FADH$_2$
2H$^+$
2e$^-$
Complex II
Fe-S
Ox proteins Red
Ox Substrate Red
2H
NAD
NADH+H$^+$
2e$^-$
2H$^+$
(i)
Complex I
FMN
FMNH$_2$
energy
ADP + Pi → ATP
2e$^-$
2H$^+$
Fe-S
Ox proteins Red
2H$^+$
2e$^-$
2e$^-$
2H$^+$
UQ
UQH$_2$
2H$^+$
2e$^-$
Ox Cyt.b Red
(Fe^{+++}) (Fe^{++})
Complex III
2e-
Oxiative phosphorylation
(ii)
Energy
ADP + Pi → ATP
Ox Cyt.C$_1$ Red
(Fe^{+++}) (Fe^{++})
2e-
Ox Cyt.C Red
(Fe^{+++}) (Fe^{++})
2e-
Ox Cyt.a Red
(Fe^{+++}) (Fe^{++})
Complex IV
2e-
(iii)
Energy
ADP + Pi → ATP
Ox Cyt.a$_3$ Red
(Fe^{+++}) (Fe^{++})
2e-
2H$^+$+ ½ O$_2$+ 2e$^-$ → H$_2$O

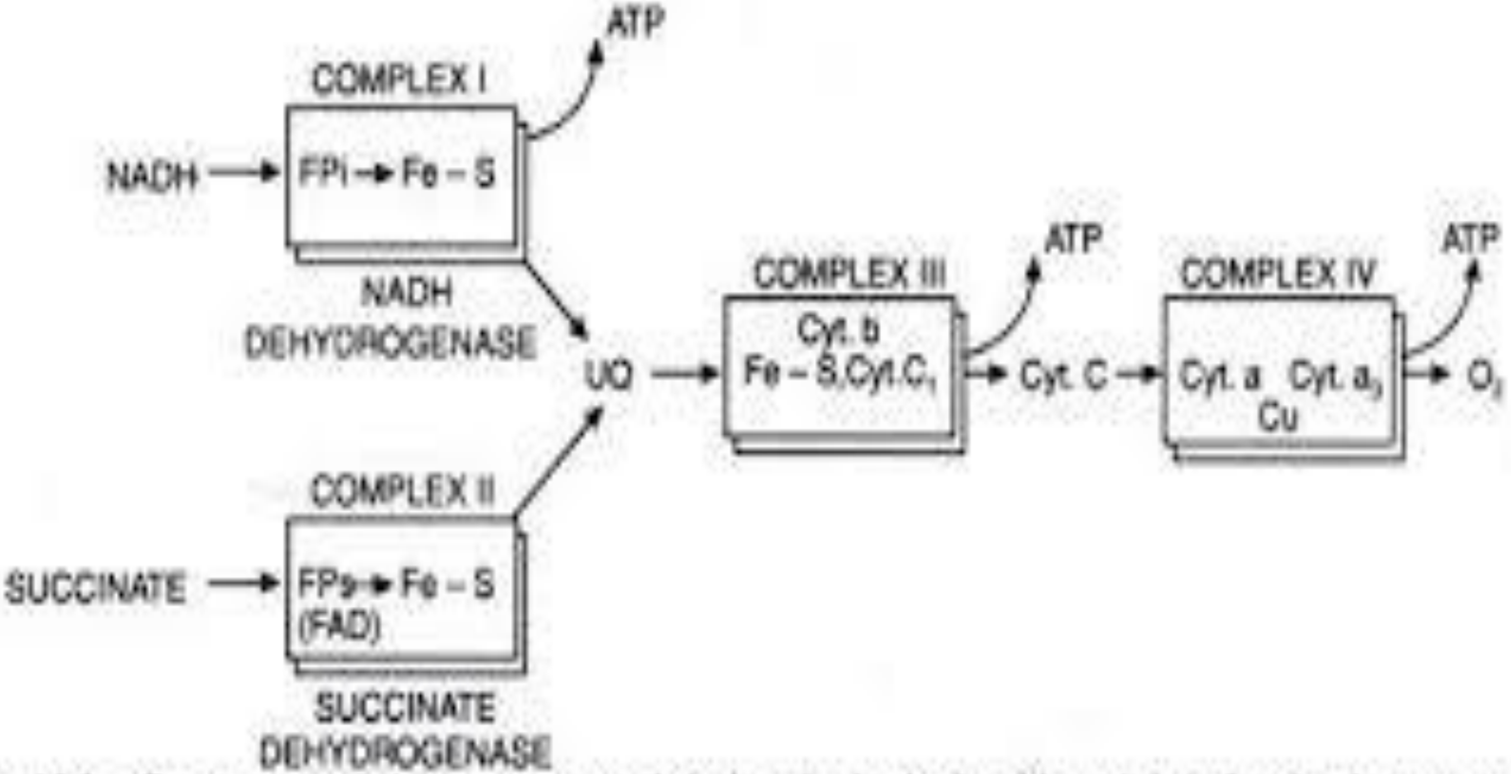
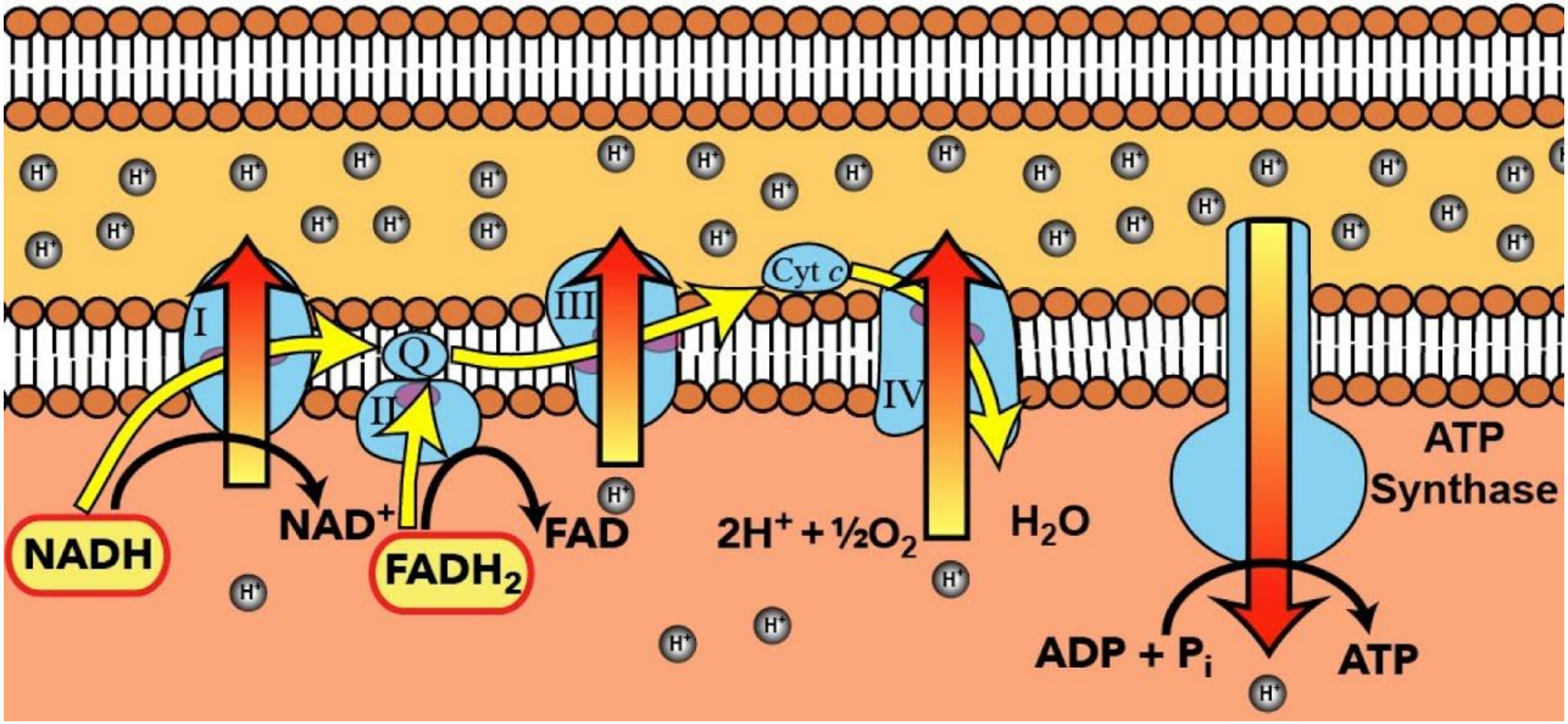
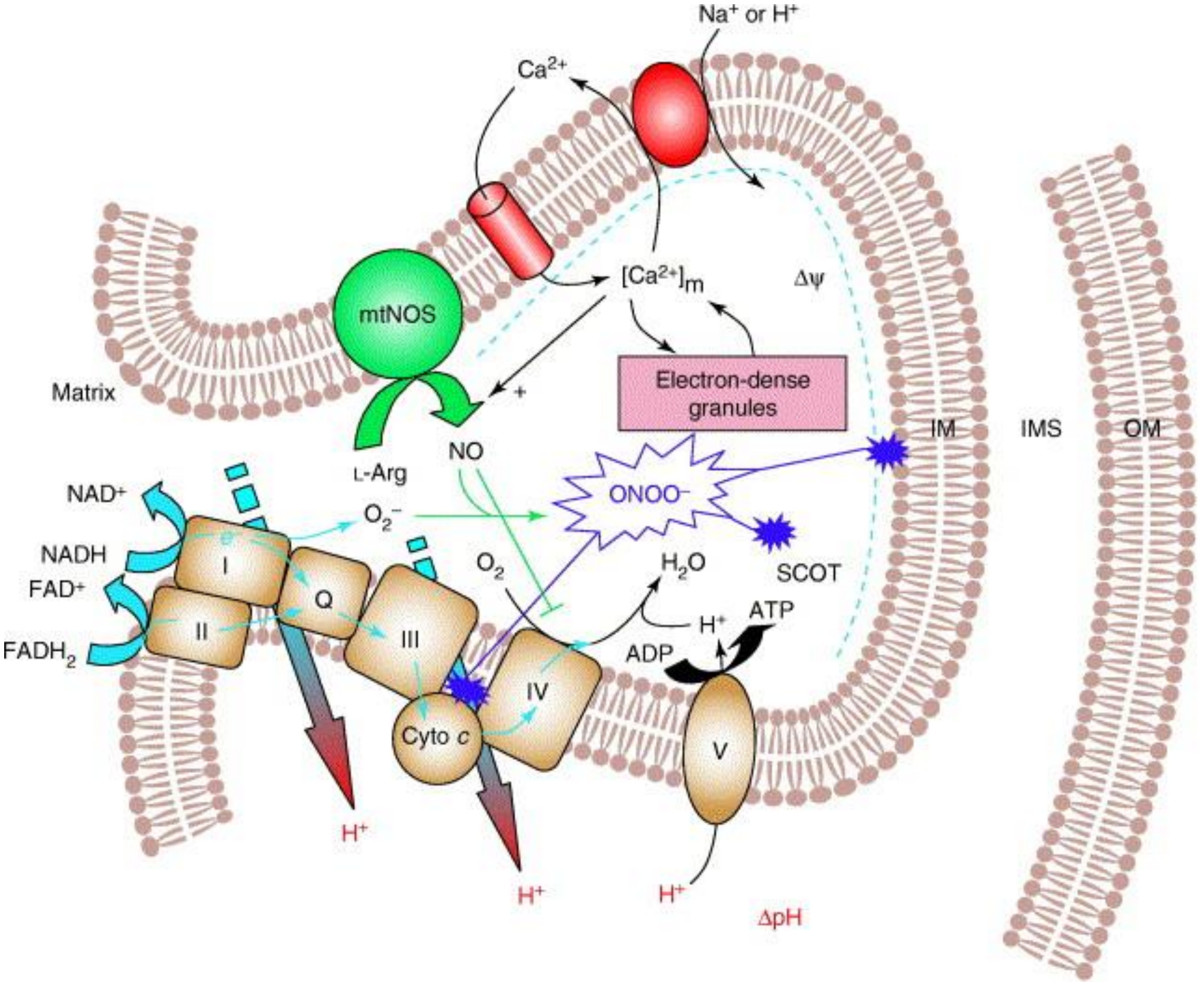


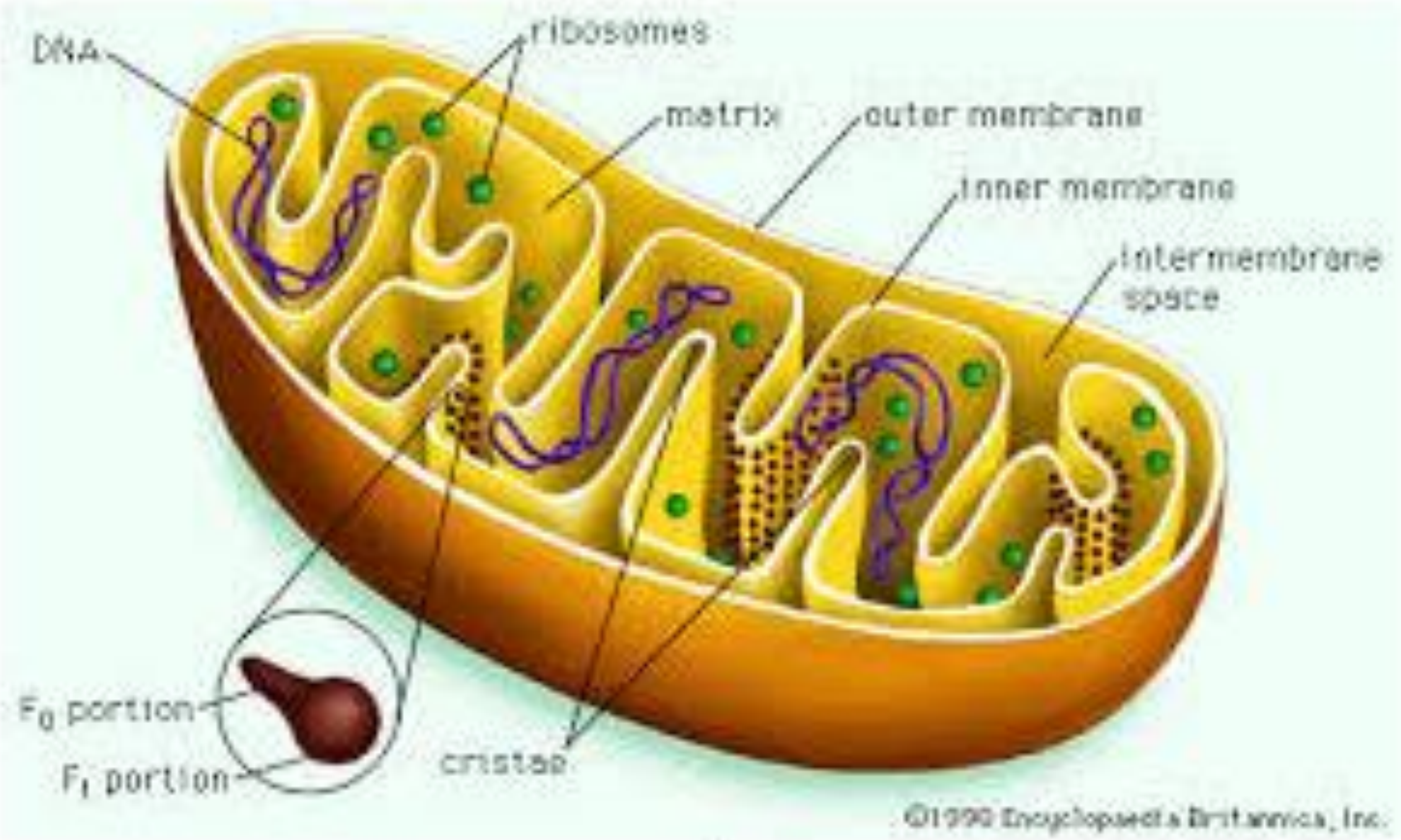
Fig. 16.6. Components of electron transport chain in animal mitochondria and their functional arrangement into the four complexes (see text for abbreviations).

Electron Transport Chain





TRENDS in Pharmacological Sciences



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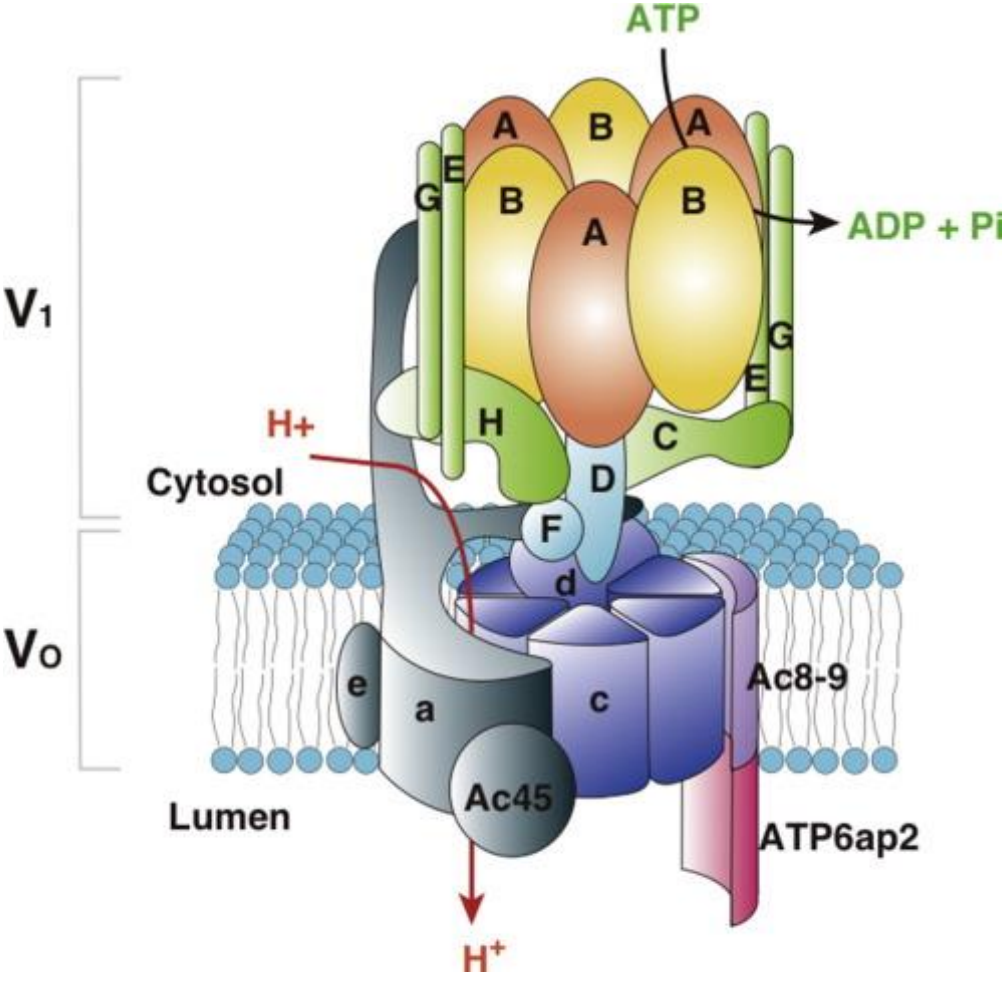
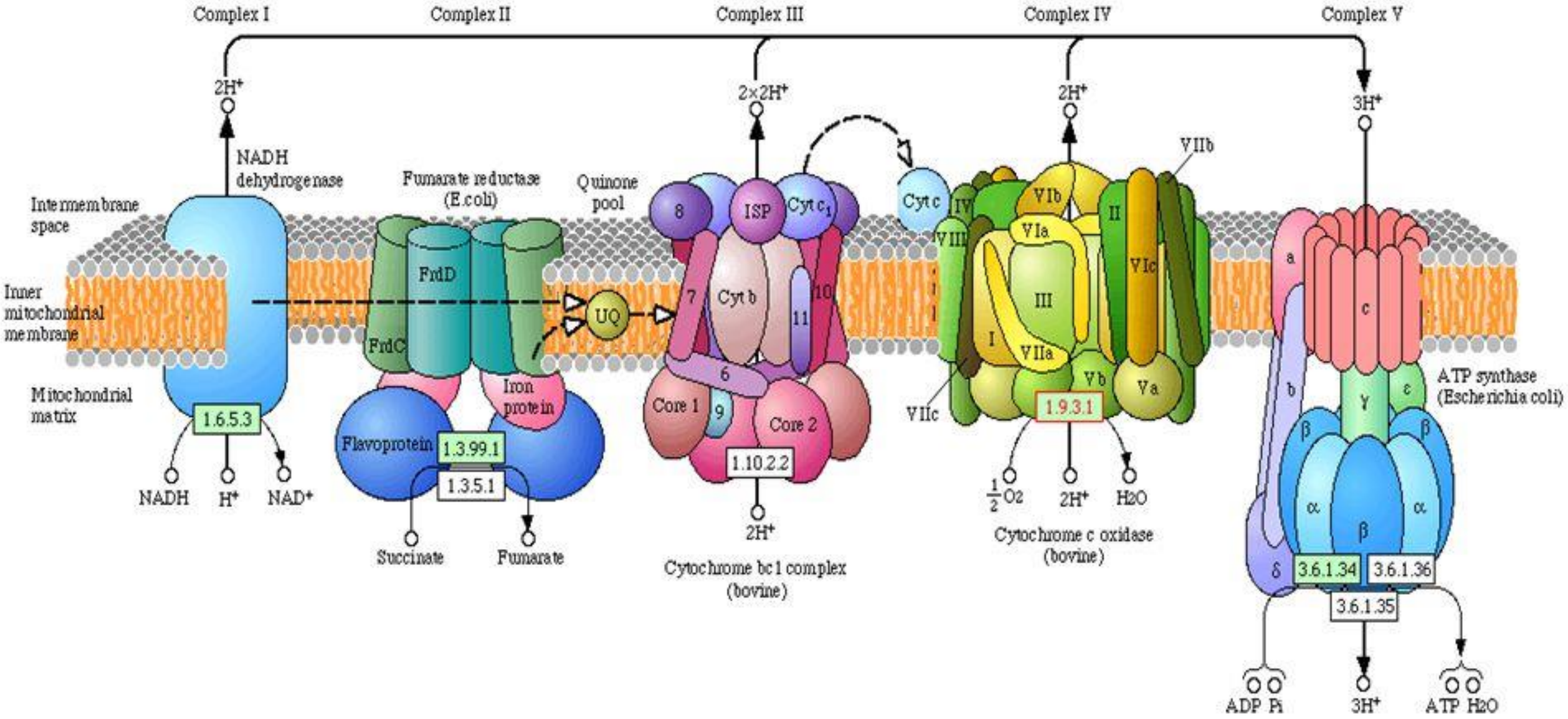
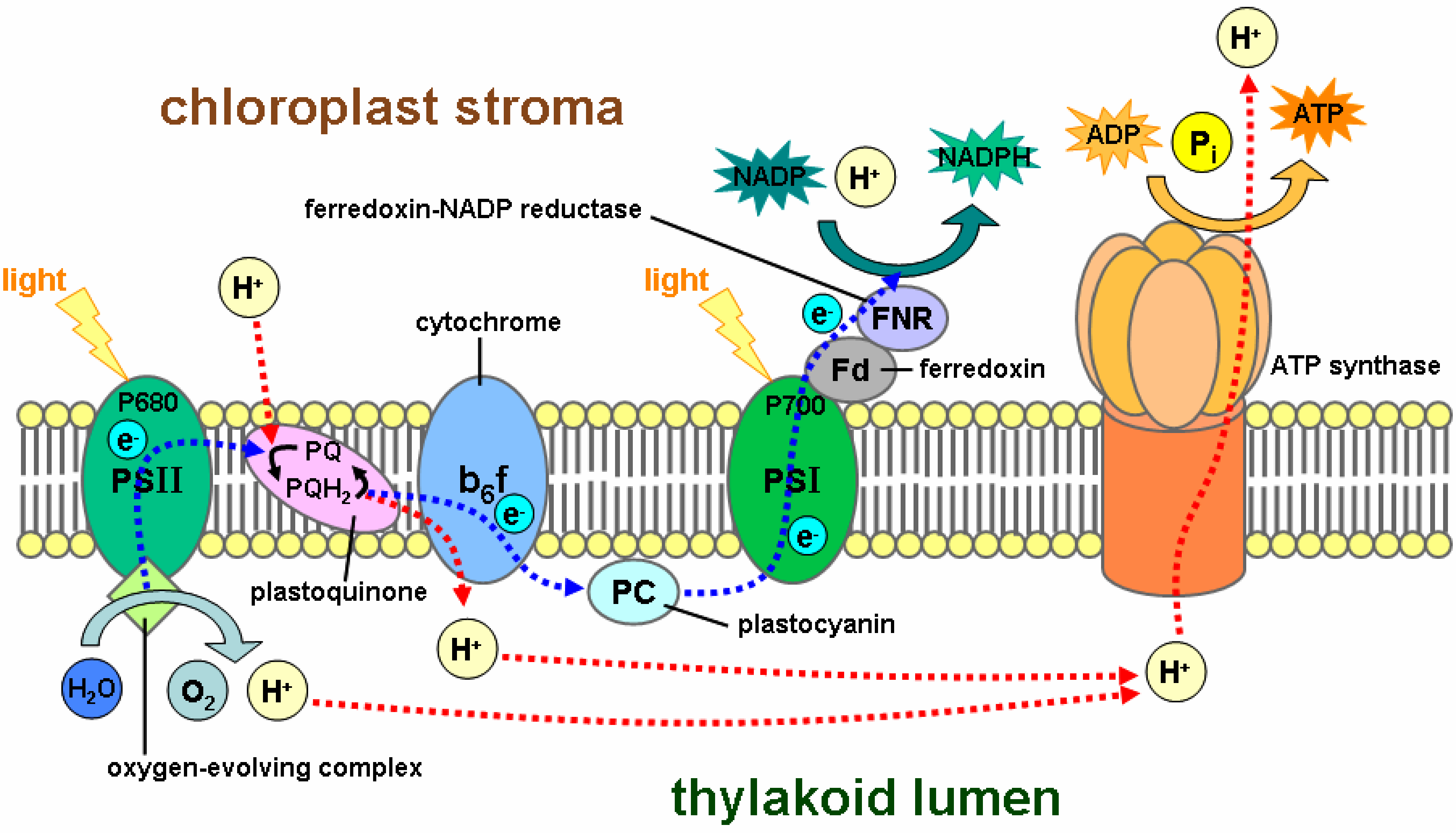

ATP
A
B
A
E
G
B
A
B
ADP + Pi
V1
G
E
H+
H
C
Cytosol
D
F
d
Vo
e
a
c
Ac8-9
Lumen
Ac45
ATP6ap2
H+

Respiratory chain subunits encoded by two genomes: Nuclear and Mitochondria



complex	I: NADH DH	II: SDH	III: cyt c red	IV: COX	V: ATPase
Mito/ nuclear	7/43	0/4	1/11	3/13	2/13

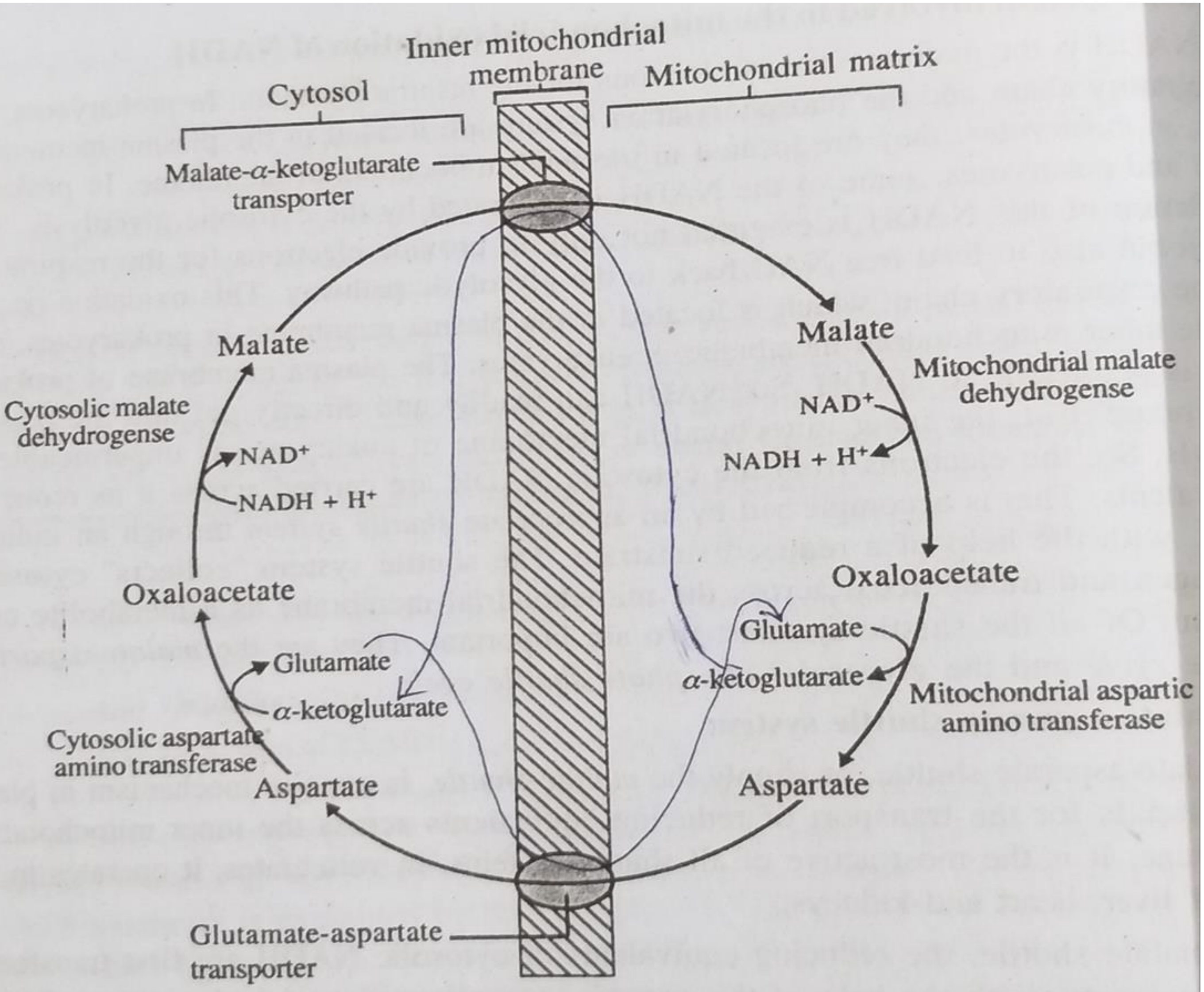
Non Cyclic Electron Transport & Photophosphorylation



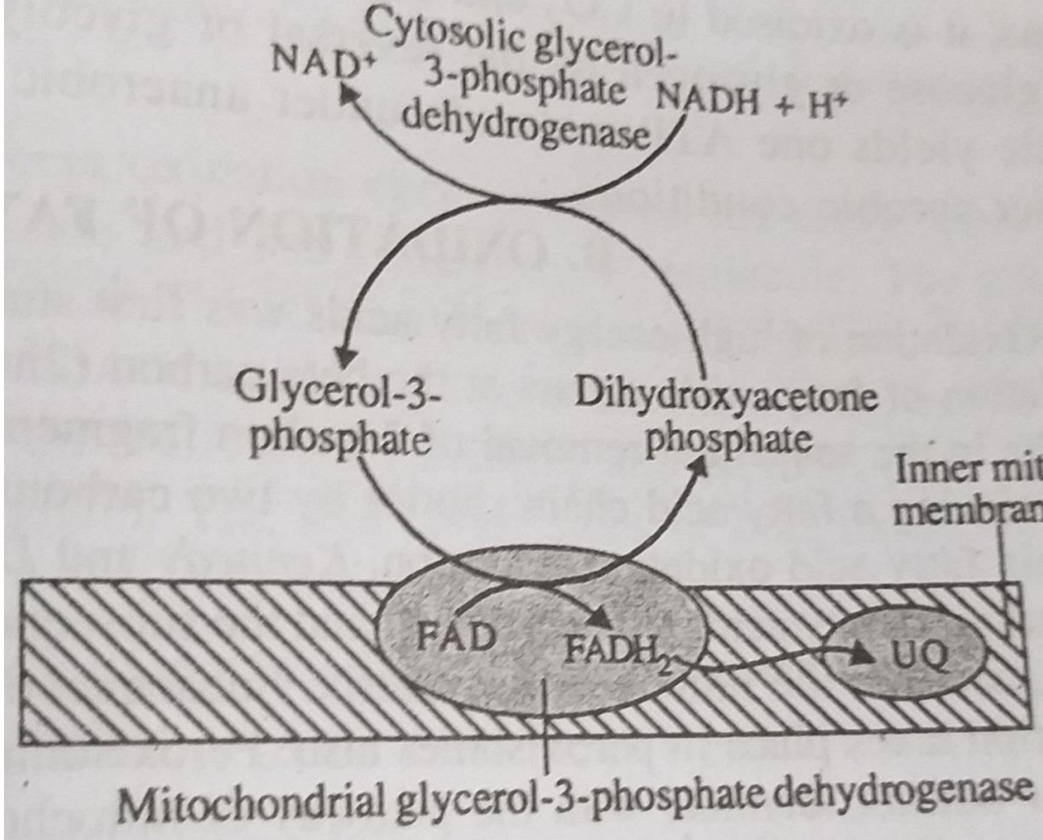
Mechanism of Oxidative Phosphorylation

- 1) **Chemical coupling hypothesis**
- with the help of a coupling factor (probably a protein).
- coupling factor (CF) forms a high energy complex with one of the electron carriers, called CF-carrier complex.
- Formation of this complex requires energy which is released during the electron transfer at the site of phosphorylation.
- The CF-carrier complex then undergoes an exchange with inorganic phosphate which comes in place of carrier in the complex.
- The complex now becomes CF-P complex. The CF-P complex then transfers its high energy phosphate to ADP, thereby forming ATP.
- 2) **Conformational coupling hypothesis**
- mitochondrial membrane undergoes structural changes which induce high energy states or conformations.
- These conformations favour release of energy which is used in the ATPase catalyzed production of ATP from ADP and inorganic phosphate.
- 3) **Chemiosmotic coupling hypothesis**

Malate aspartate shuttle



Malate-asparate shuttle (diagrammatic)



Glycerol-3-phosphate shuttle

NITROGEN METABOLISM

Nitrogen is cycled between organisms and inanimate environment

- The principal inorganic forms of N are in an oxidized state
  - As N_2 in the atmosphere
  - As nitrate (NO_3^-) in the soils and ocean
- All biological compounds contain N in a reduced form (NH_4^+)

The Reduction of Nitrogen

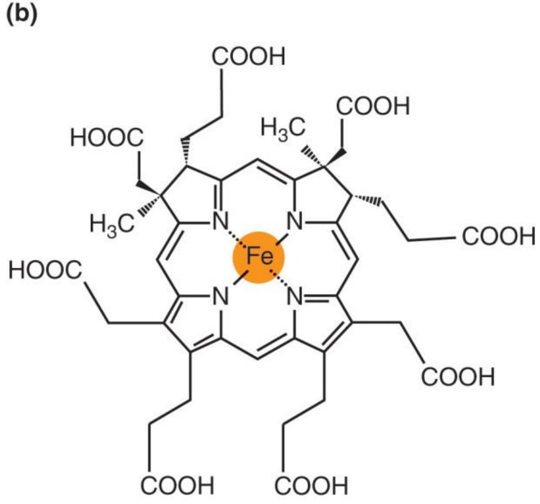
Nitrogen assimilation and nitrogen fixation

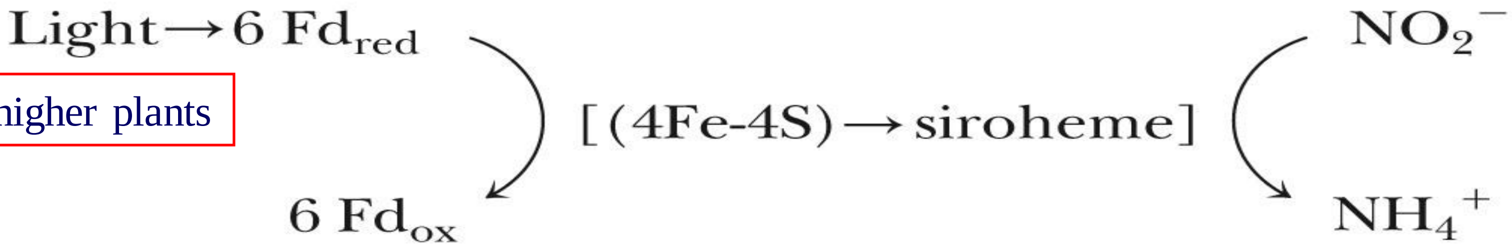
1. Nitrate assimilation occurs in two steps:
   - 2e^- reduction of nitrate to nitrite
   - 6e^- reduction of nitrite to ammonium
   - Nitrate assimilation accounts for 99% of N acquisition by the biosphere
2. Nitrogen fixation involves reduction of N_2 in prokaryotes by nitrogenase

Nitrite Reductase

- In higher plants, nitrite reductase is in chloroplasts, but nitrate reductase is cytosolic

siroheme





In higher plants

Nitrate Assimilation

- **Nitrate assimilation**
  - the reduction of nitrate to NH_4^+ in plants, various fungi, and certain bacteria
  - Two steps:

1. Nitrate reductase

$$NO_3^- + 2\,H^+ + 2\,e^- \rightarrow NO_2^- + H_2O$$

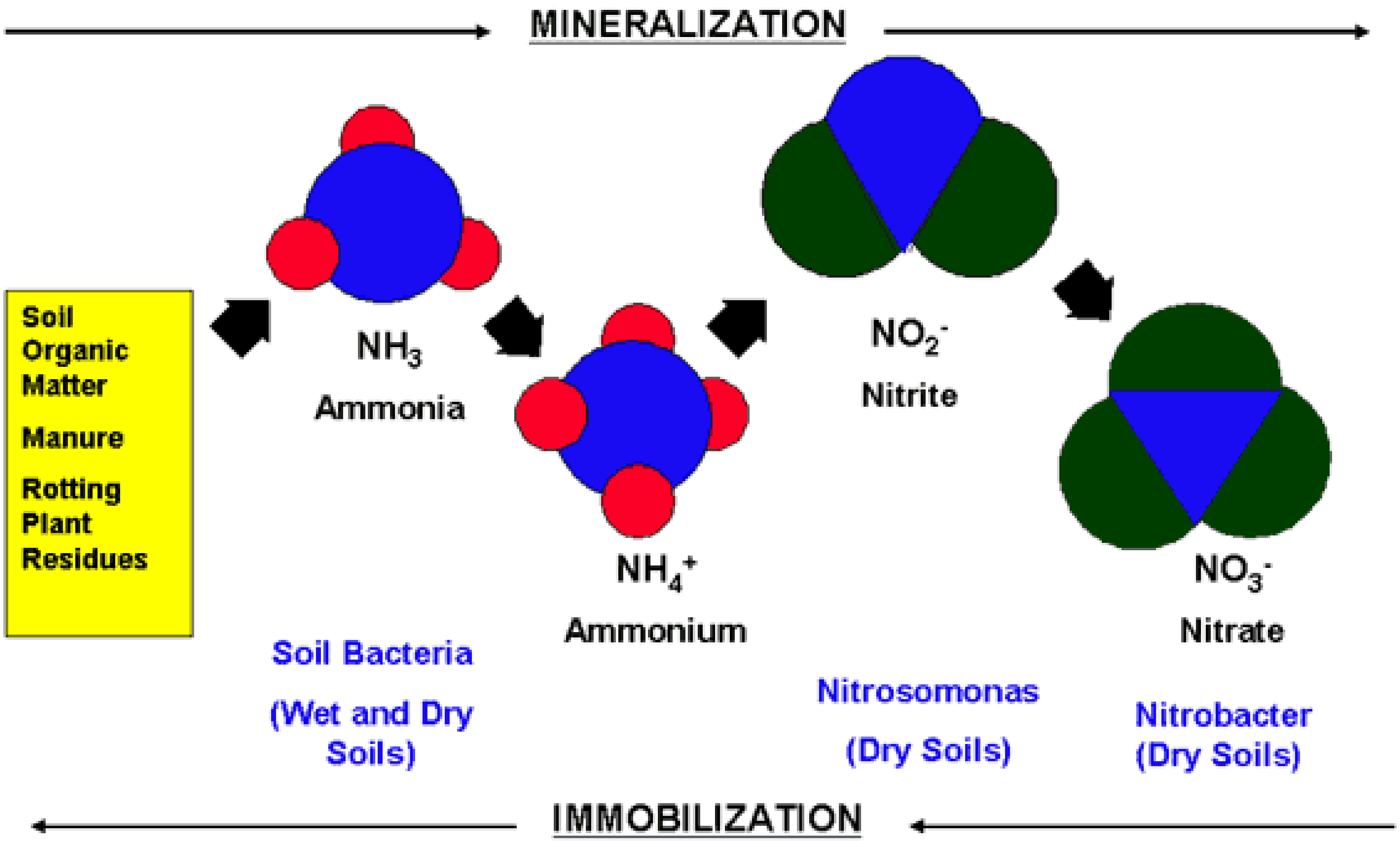
2. Nitrite reductase

$$NO_2^- + 8\,H^+ + 6\,e^- \rightarrow NH_4^+ + 2\,H_2O$$

- Electrons are transferred from NADH to nitrate

Mineralization and Immobilization

Created by J. Strock
University of Minnesota



MINERALIZATION

Soil
Organic
Matter

Manure

Rotting
Plant
Residues

NH_3
Ammonia

NH_4^+
Ammonium

NO_2^-
Nitrite

NO_3^-
Nitrate

Soil Bacteria

(Wet and Dry Soils)

Nitrosomonas

(Dry Soils)

Nitrobacter
(Dry Soils)

IMMOBILIZATION

Symbiotic Nitrogen Fixation

The *Rhizobium*-legume association

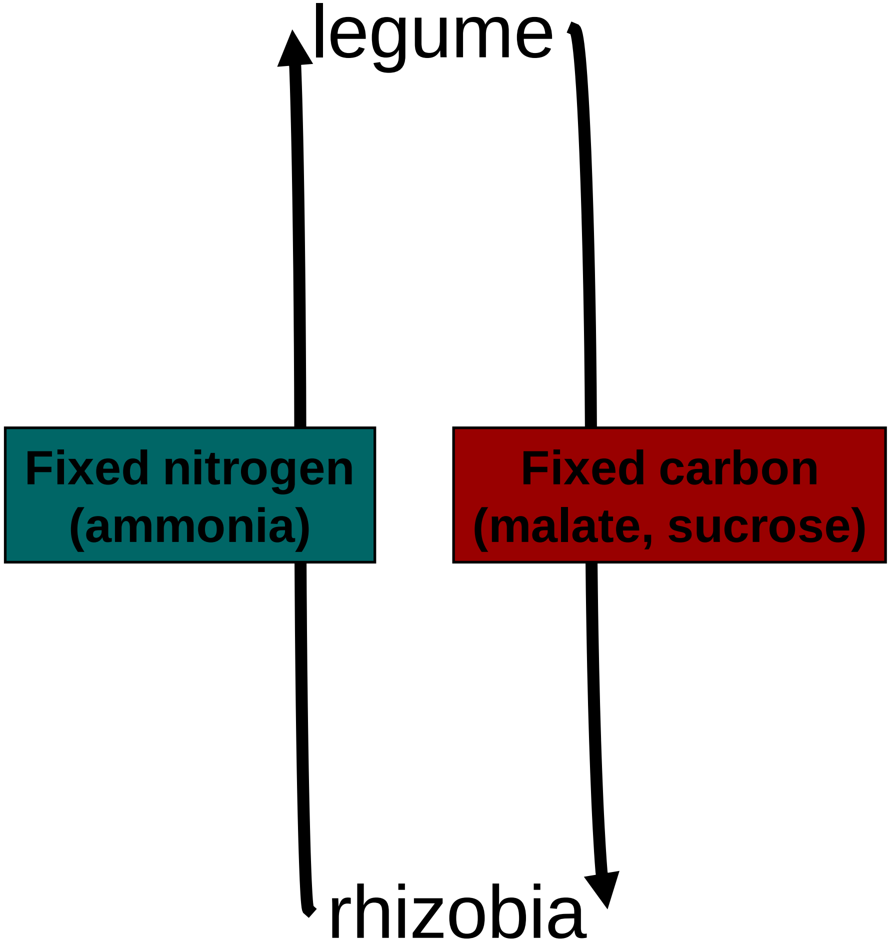
Bacterial associations with certain plant families, primarily **legume** species, make the largest single contribution to biological nitrogen fixation in the biosphere

Nitrogen fixation

$$\mathbf{N_2 + 10\,H^+ + 8\,\mathit{e}^- \rightarrow 2\,NH_4^+ + H_2}$$

- *Only occurs in certain prokaryotes*
  - *Rhizobia* fix nitrogen in symbiotic association with leguminous plants
  - *Rhizobia* fix N for the plant and plant provides *Rhizobia* with carbon substrates
- Fundamental requirements:

1. Nitrogenase
2. A strong reductant (reduced ferredoxin)
3. ATP
4. O-free conditions



legume

Fixed nitrogen (ammonia)

Fixed carbon (malate, sucrose)

rhizobia

Nod D (the sensor)

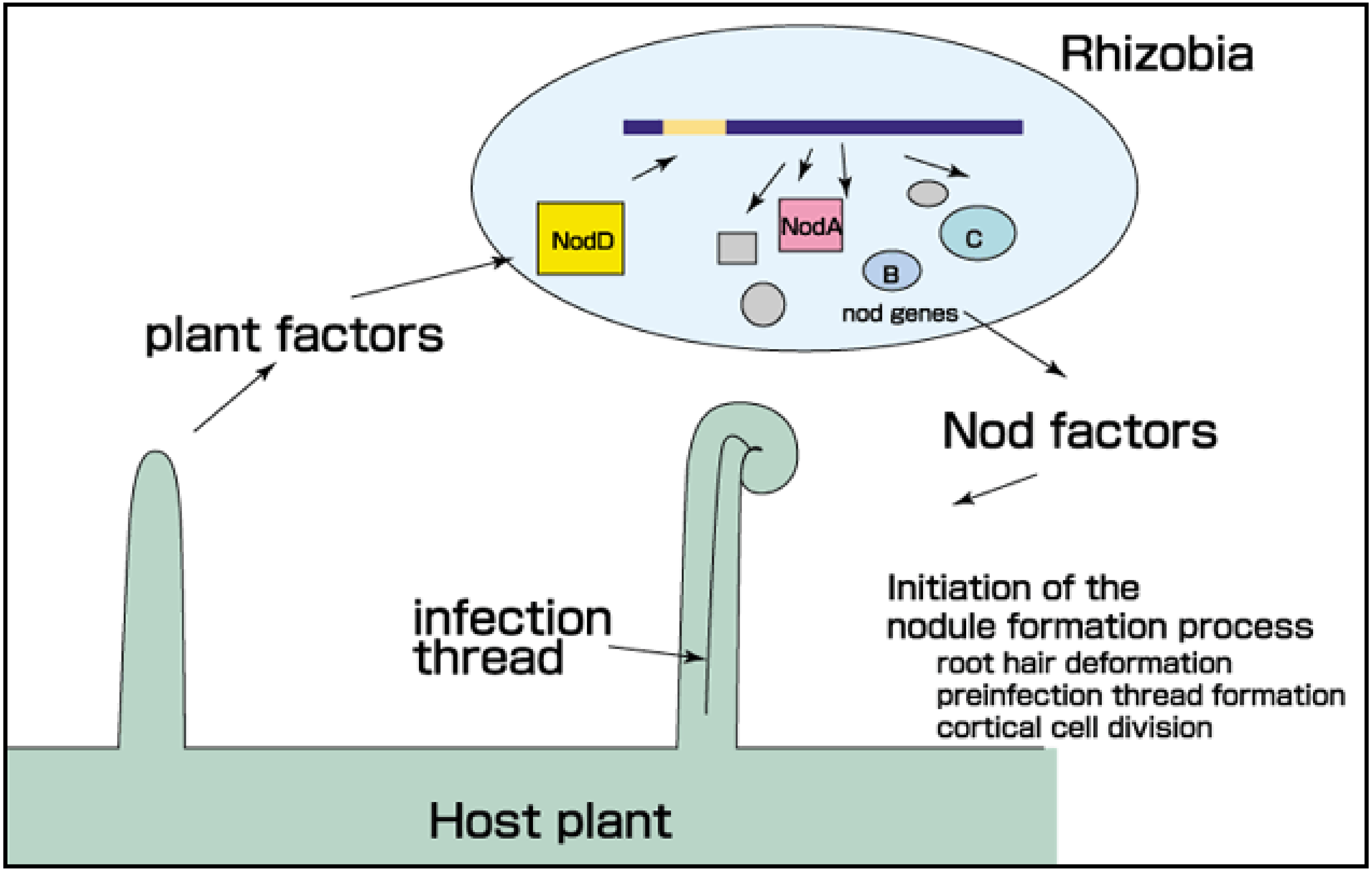
the **nod D** gene product recognizes molecules
(phenylpropanoid-derived **flavonoids**)
produced by plant roots and becomes
activated as a result
of that binding

activated nodD protein positively
controls the expression of the
other genes in the nod gene
"regulon" (signal transduction)

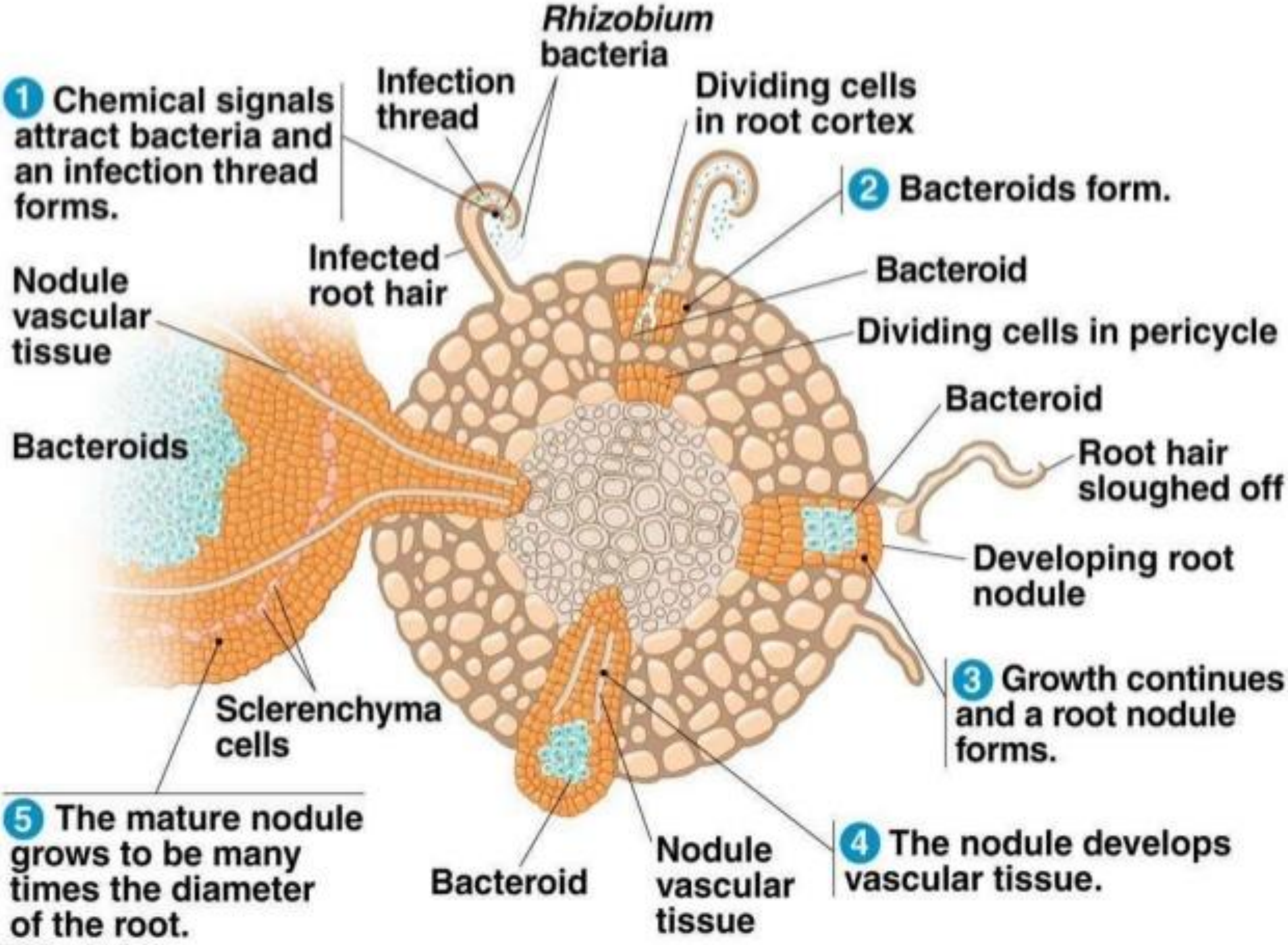
different nodD alleles recognize **various flavonoid**
structures with different affinities, and respond with
differential patterns of nod gene activation

Biological nitrogen fixation is the reduction of atmospheric nitrogen gas (N_2) to ammonium ions (NH_4^+) by the oxygen-sensitive enzyme, nitrogenase.

Plant genomes lack any genes encoding this enzyme, which occurs only in prokaryotes (bacteria).



Initiation of the
nodule formation process
  root hair deformation
  preinfection thread formation
  cortical cell division



① Chemical signals attract bacteria and an infection thread forms.

② Bacteroids form.

③ Growth continues and a root nodule forms.

④ The nodule develops vascular tissue.

⑤ The mature nodule grows to be many times the diameter of the root.

Nitrogen fixing genes

- **Bacterial genes**
  - 17 nif genes
    - Structural genes coding for nitrogenase
      - nif D & K –2 subunits of MoFe protein
      - F & H feredoxin & Fe protein)
    - Regulating genes
  - Nod genes on sym plasmid
  - Fix genes

- **Host genes**
  - NOD genes

Genetic Clusters

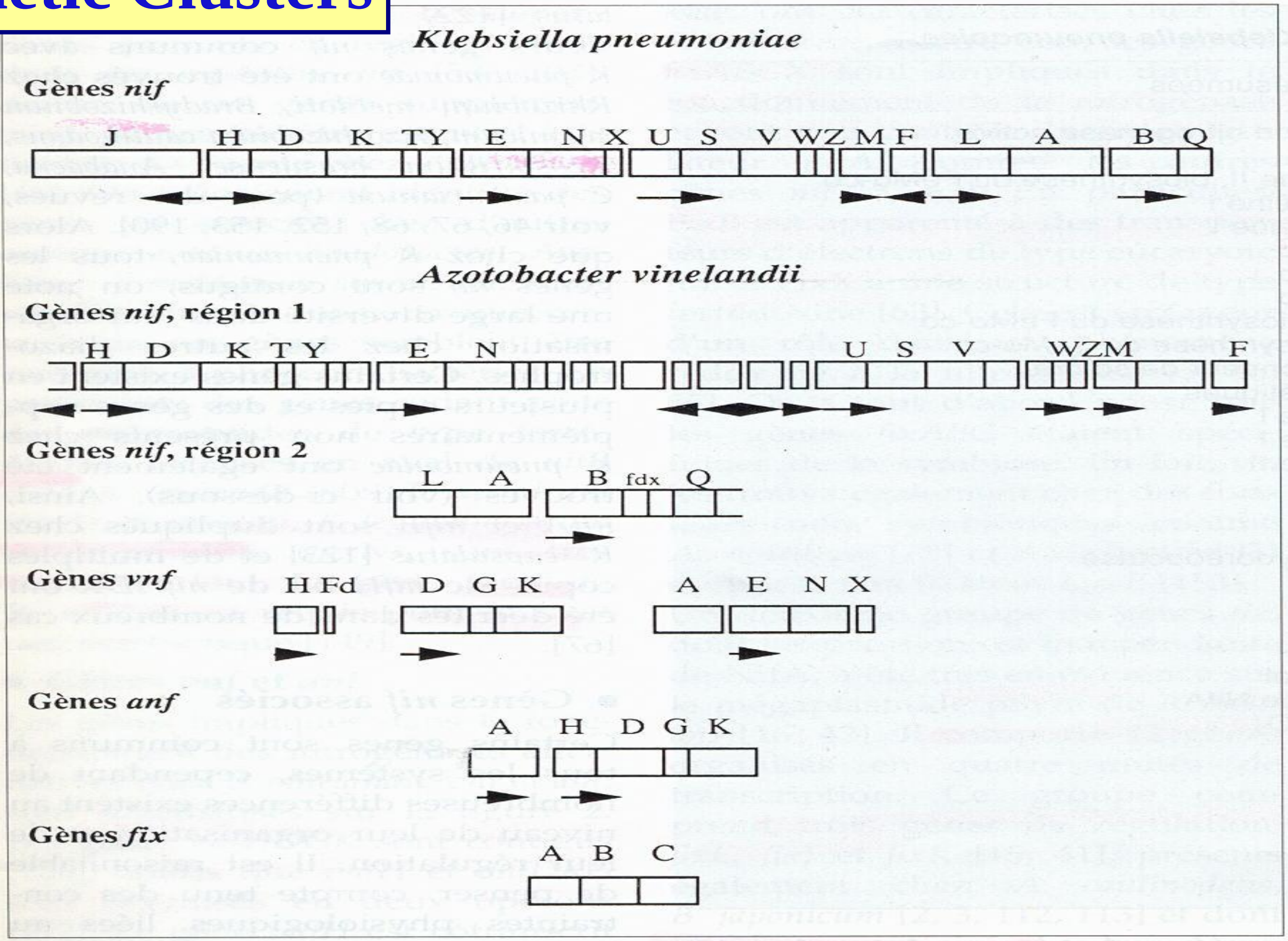


Fig 2. Organisation des gènes de la fixation de l'azote de Klebsiella pneumoniae *et d'*Azotobacter vinelandii. *Les gènes contigus correspondent à des opérons polycistroniques. Les flèches indiquent le sens de transcription à partir de promoteurs dépendant du facteur* σ^{54}.

The enzyme **nitrogenase** catalyses the conversion of atmospheric, gaseous dinitrogen (N_2) and dihydrogen (H_2) to ammonia (NH_3), as shown in the chemical equation below:

$$N_2 + 3\ H_2 \Rightarrow\ 2\ NH_3$$

The incredibly strong (triple) bond in N_2 makes this reaction very difficult to carry out efficiently.
In fact, nitrogenase consumes ~16 moles of ATP for every molecule of N_2 it reduces to NH_3, which makes it
one of the most energy-expensive processes known
in Nature.

Stages of Nitrogen fixation

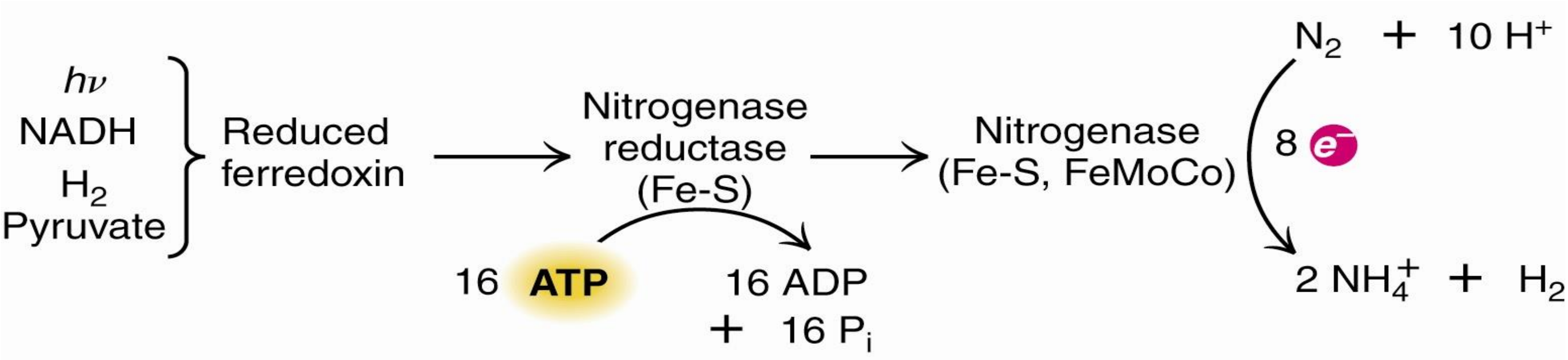
- Activation of dinitrogen N_2 --- N + N
- Activation of hydrogen H_2----$2H^+$ + $2e^-$
- Reduction of dinitrogen to ammonia
- 2N + $6H^+$ + $6e^-$ -------$2NH_3$

- Catalysed by NITROGENASE

Nitrogenase Complex

Two metalloprotein components:

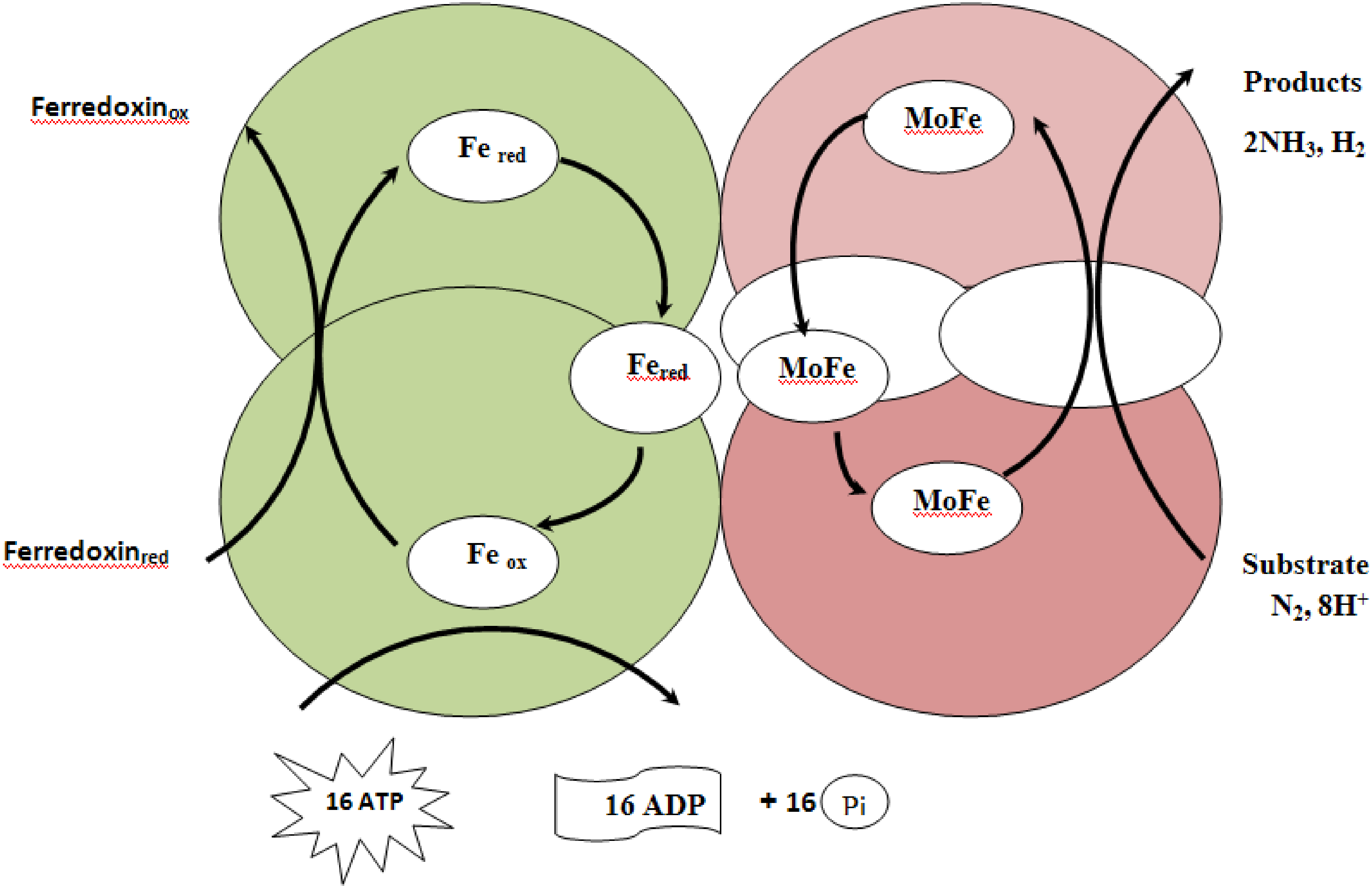
1. *Nitrogenase reductase*
2. *Nitrogenase*



Nitrogenase Complex

Two protein components: nitrogenase reductase and nitrogenase

- Nitrogenase reductase is a 60 kD homodimer with a single 4Fe-4S cluster
- Very oxygen-sensitive
- Binds MgATP
- 4ATP required per pair of electrons transferred
- Reduction of N_2 to $2NH_3 + H_2$ requires 4 pairs of electrons, so **16 ATP are consumed per N_2**


Ferredoxin$_{ox}$
Fe $_{red}$
Fe$_{red}$
Fe $_{ox}$
Ferredoxin$_{red}$
MoFe
MoFe
MoFe
Products
$2NH_3$, H_2
Substrate
N_2, $8H^+$
16 ATP
16 ADP
+ 16 Pi

Nitrogenase reductase

- Nitrogenase reductase
  - Fe-protein
  - A 60 kD homodimer with a single 4Fe-4S cluster
- Extremely O_2-sensitive
- Binds MgATP and hydrolyzes 2 ATPs per electron transferred
- Because reduction of N_2 to $2NH_4^+ + H_2$ requires 8 electrons, 16 ATP are consumed per N_2 reduced

Nitrogenase

- MoFe-protein—a 220 kD $\alpha_2\beta_2$ heterotetramer
- An $\alpha\beta$–dimer serve as the functional unit
  - Contains two types of metal centers

1. P-cluster (figure 25.5a)

   8Fe-7S center

2. FeMo-cofactor (figure 25.5b)

   7Fe-1-Mo-9S cluster

- Oxygen labile
- Nitrogenase is a rather slow enzyme
  - 12 e^- pairs per second, i.e., only three molecules of N_2 per second
  - As much as 5% of cellular protein may be nitrogenase

The Metabolic Fate of Ammonium

NH_4^+ enters organic linkage via three major reactions in all cells

1. Glutamate dehydrogenase (GDH)
2. Glutamine synthetase (GS)
3. Carbamoyl-phosphate synthetase I (CPS-I)

- Asparagine synthetase (some microorganisms)

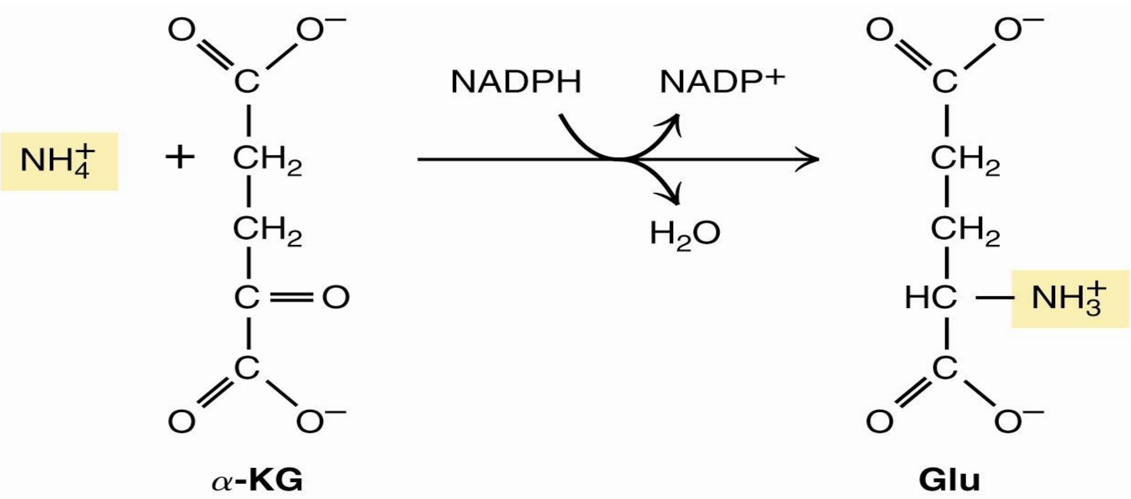
*1. **Glutamate dehydrogenase (GDH)***

- Reductive amination of α-ketoglutarate to form glutamate

NH_4^+ + α-ketoglutarate + NADPH + 2 H^+ →

glutamate + $NADP^+$ + H_2O

- Mammalian GDH plays a prominent role in amino acid catabolism (oxidative amination)



2. Glutamine synthetase (GS)

- ATP-dependent amidation of γ-carboxyl of glutamate to glutamine

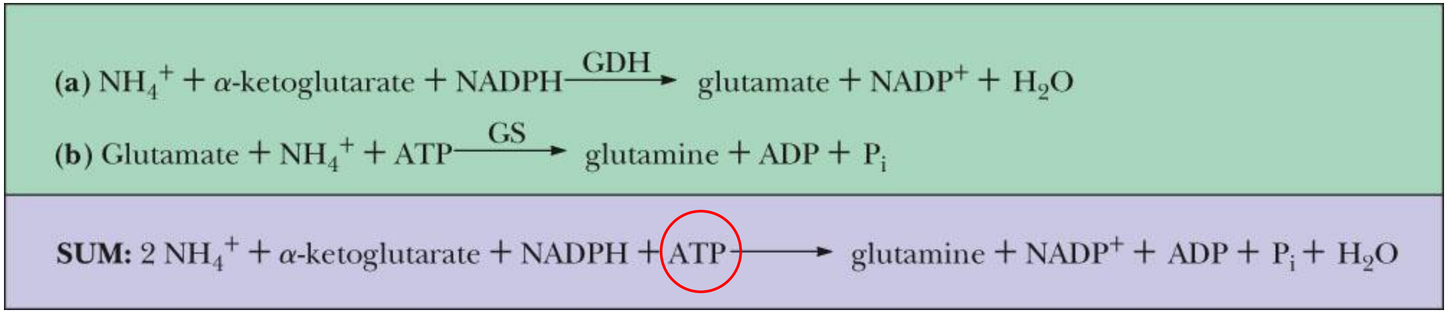
$$NH_4^+ + \text{glutamate} + ATP \rightarrow \text{glutamine} + ADP + P_i$$

- Glutamine is a major N donor in the biosynthesis of many organic N compounds, therefore GS activity is tightly regulated
- Glutamine is the most abundant amino acid in human

The major pathways of Ammonium Assimilation lead to glutamin synthesis

Two principal pathways :

1. Principal route: GDH/GS in organisms rich in N



(a) $NH_4^+ + \alpha\text{-ketoglutarate} + NADPH \xrightarrow{GDH} \text{glutamate} + NADP^+ + H_2O$

(b) $\text{Glutamate} + NH_4^+ + ATP \xrightarrow{GS} \text{glutamine} + ADP + P_i$

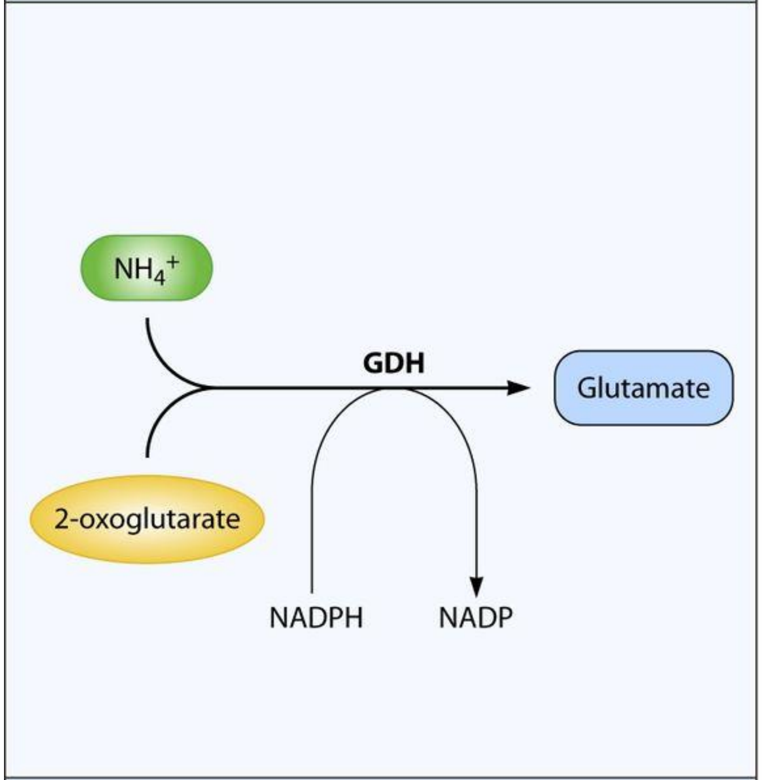
SUM: $2\ NH_4^+ + \alpha\text{-ketoglutarate} + NADPH + \boxed{ATP} \longrightarrow \text{glutamine} + NADP^+ + ADP + P_i + H_2O$

2. Secondary route: GS/GOGAT in organisms confronting N limitation
   - GOGAT is glutamate synthase or glutamate:oxo-glutarate amino transferase
   - GDH has a higher *Km* for NH_4^+ than does GS

GS GOGAT

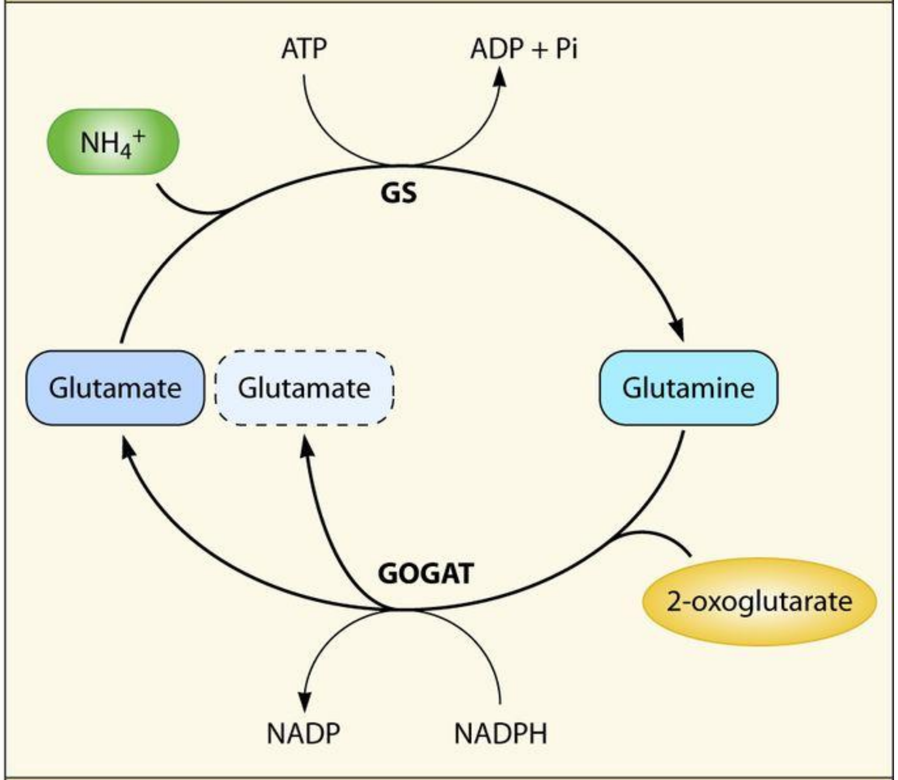
- **GS**
- NH4 + glutamate + ATP ----Glutamine
- **GOGAT**
- Glutamine + alpha keto glutaric acid + NADH ----2 glutamate

GDH pathway
glutamate dehydrogenase



One net glutamate
No ATP consumed
Low affinity for NH$_4^+$ ($K_M = 1.0$ mM)

GS-GOGAT pathway
glutamine synthetase-glutamate synthase

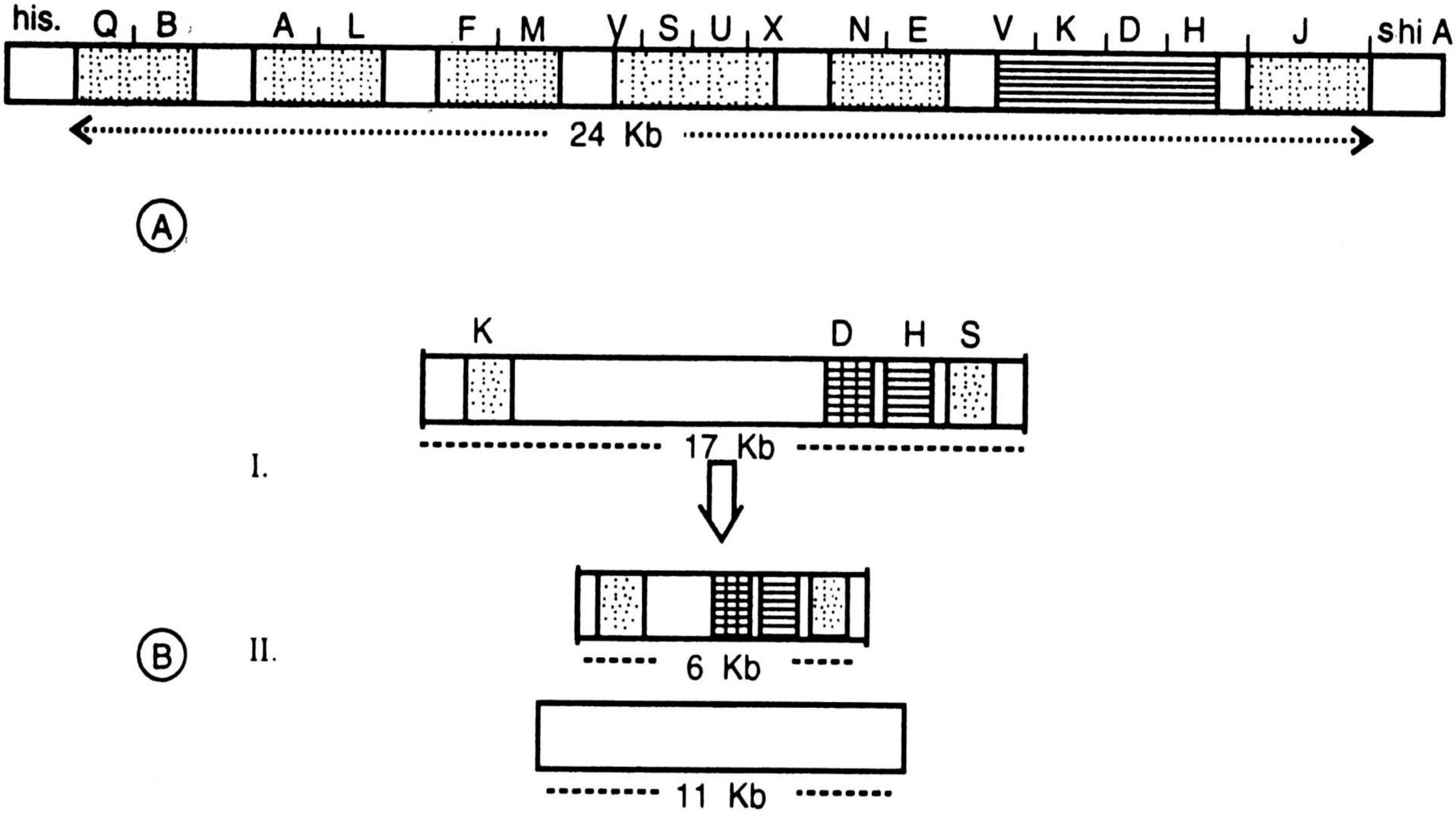


One net glutamate
One ATP consumed per NH$_4^+$
High affinity for NH$_4^+$ ($K_M = 0.1$ mM)

Export of fixed nitrogen from nodule

- Through xylem transport
- Main product glutamine (but exported as such rarely)
- Predominant export product asparagine (temperate legumes), ureides (tropical legumes)
- Glutamine + aspartate + ATP----glutanate +asparagine

Nif gene cluster



NOD GENES

- Nod genes are present on sym-plasmid.
- These genes are host specific
- Regulation of nod genes is controlled by Nod D genes.
- The common Nod A,B,C genes are conserved among *rhizobium* and inactivation of these genes completely depends on root hair infection and nodule formation.

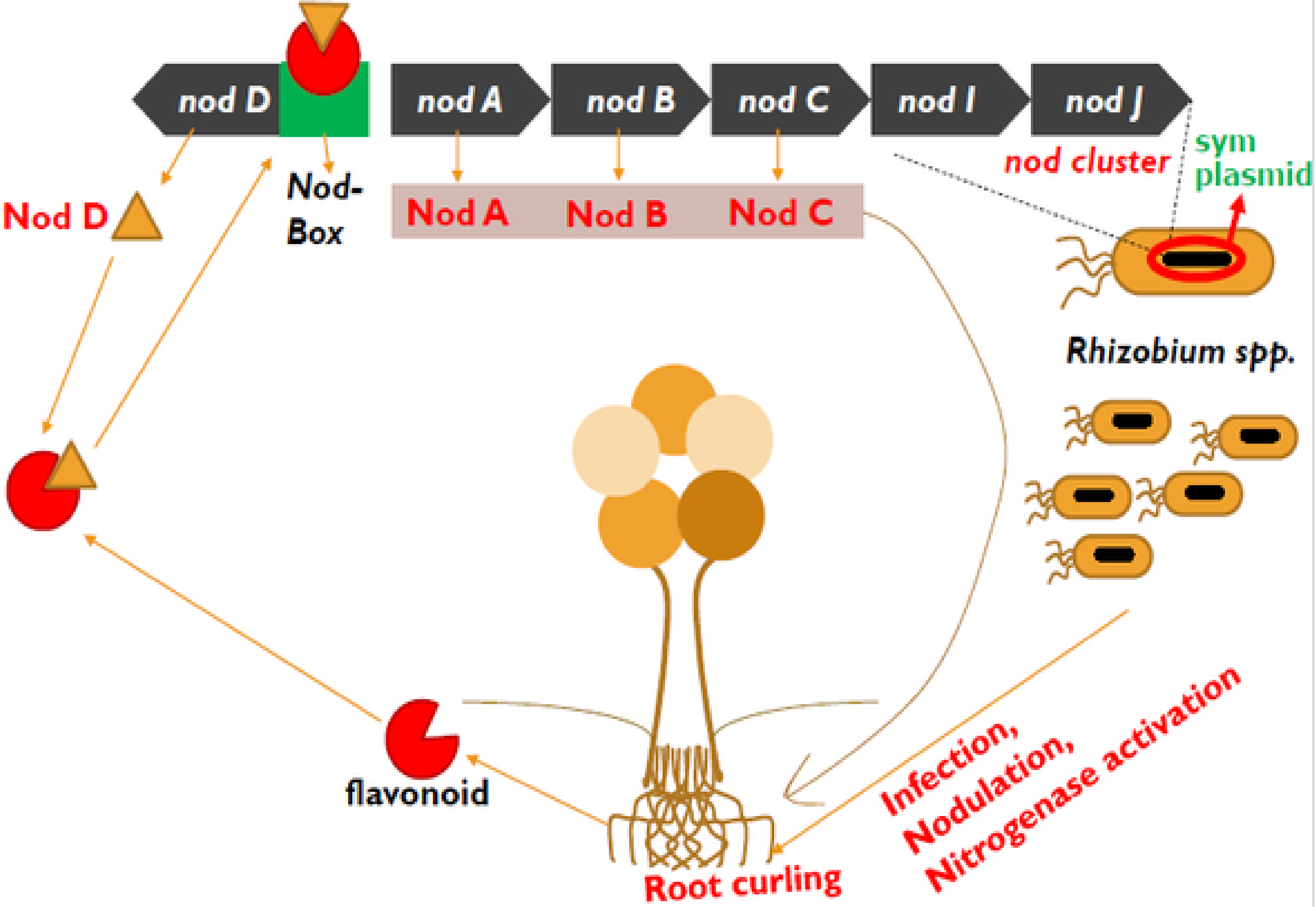
Nod D (the sensor)

- The nod D gene product recognizes molecules (phenylpropanoid-derived flavonoids) produced by plant roots and becomes activated as a result of that binding.

- activated nodD protein positively controls the expression of the other genes in the nod gene“regulon” (signal transduction)

- different nodD alleles recognize various flavonoid structures with different affinities, and respond with differential patterns of nod gene activation

NOD GENE CLUSTER FUNCTION



nod D

Nod-Box

nod A

nod B

nod C

nod I

nod J

nod cluster

sym plasmid

Nod D

Nod A

Nod B

Nod C

Rhizobium spp.

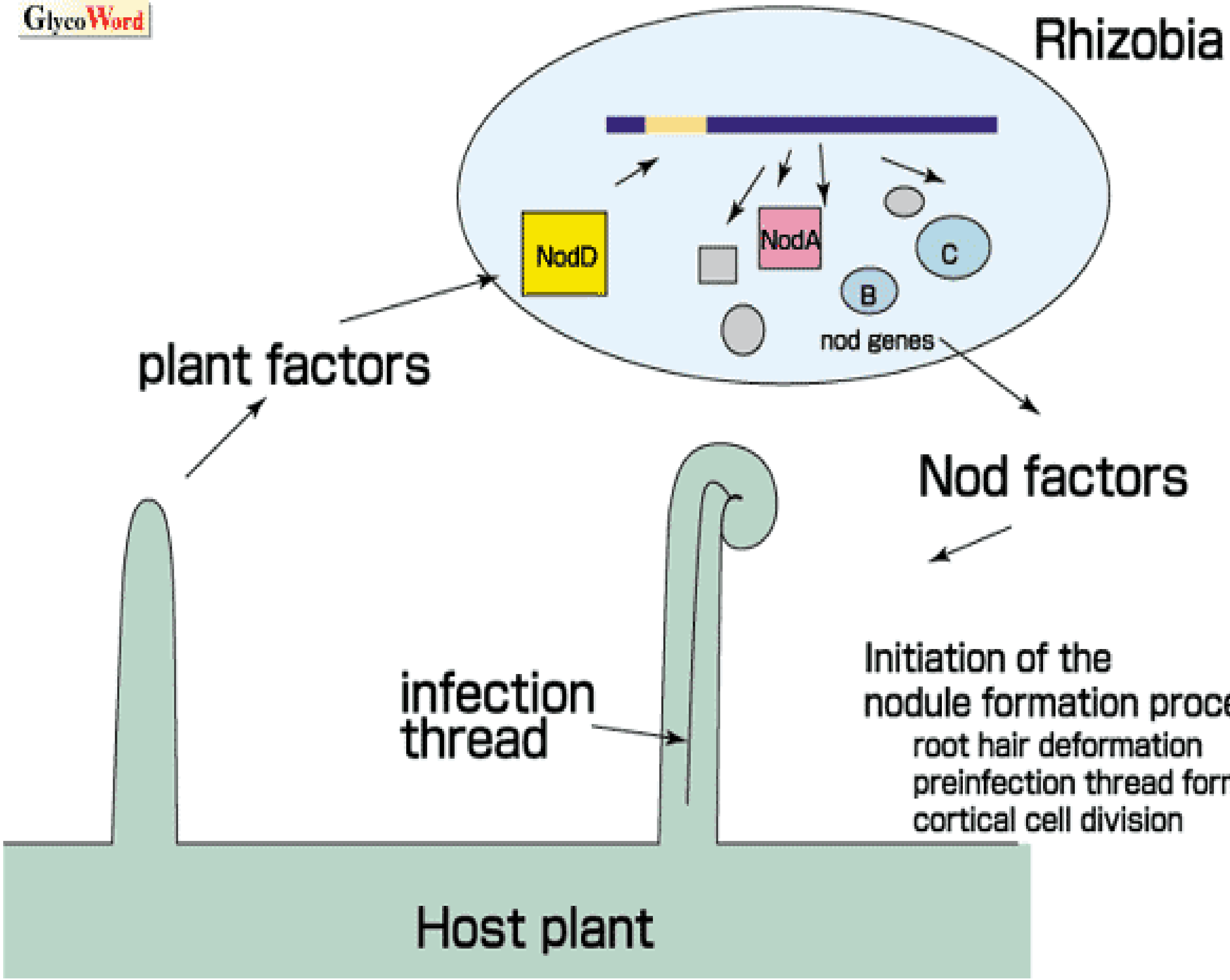
flavonoid

Root curling

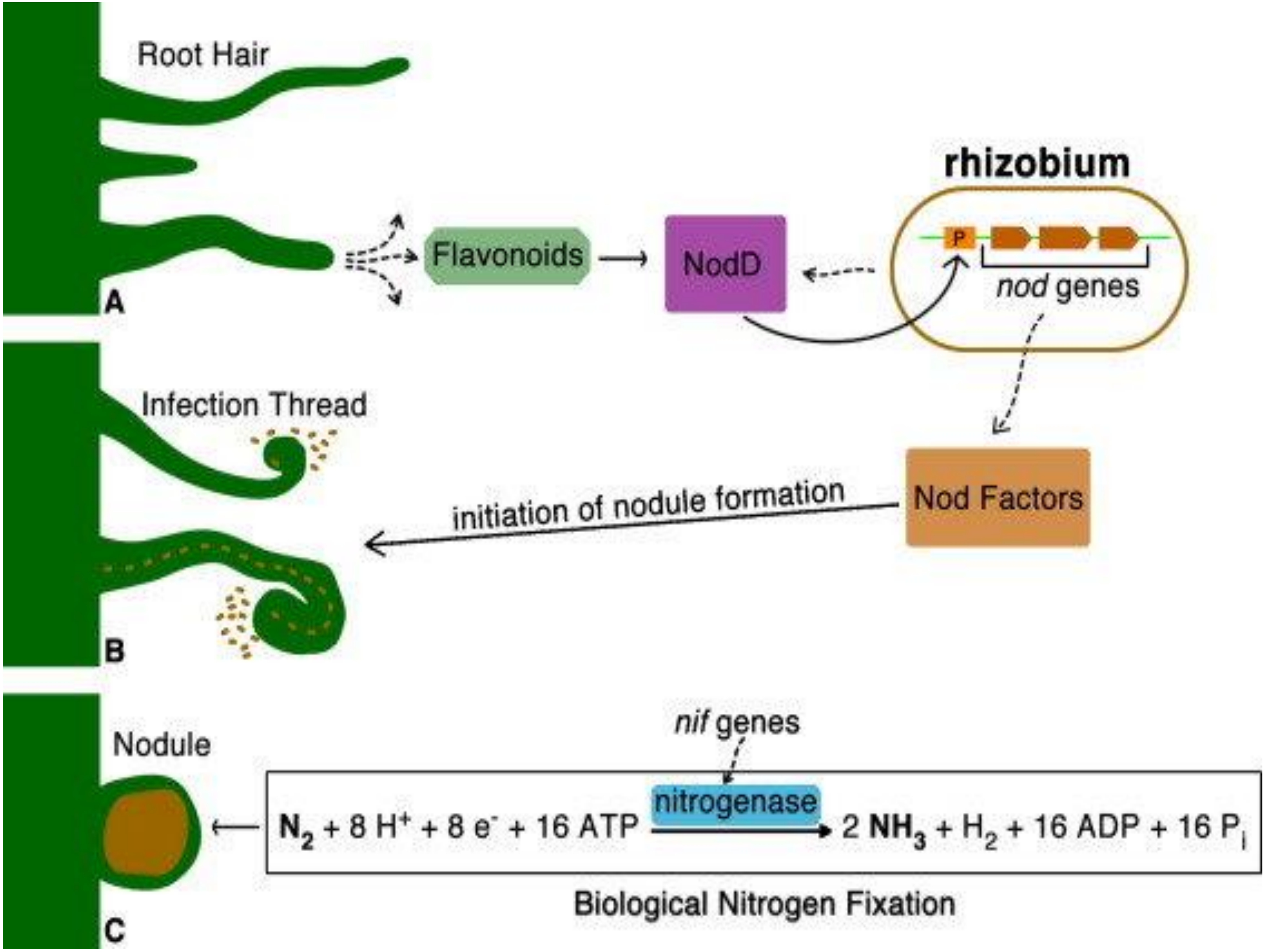
Infection,

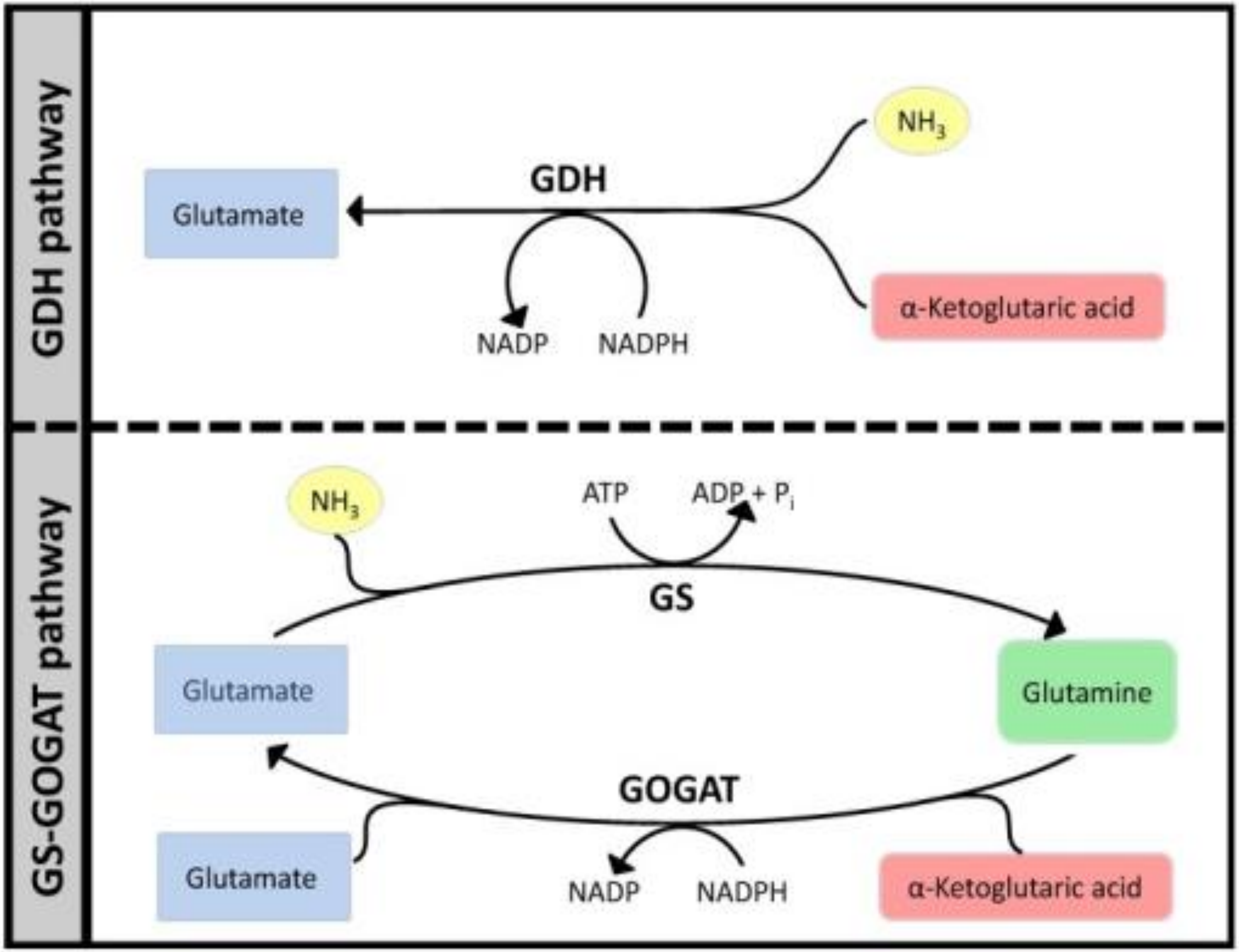
Nodulation,

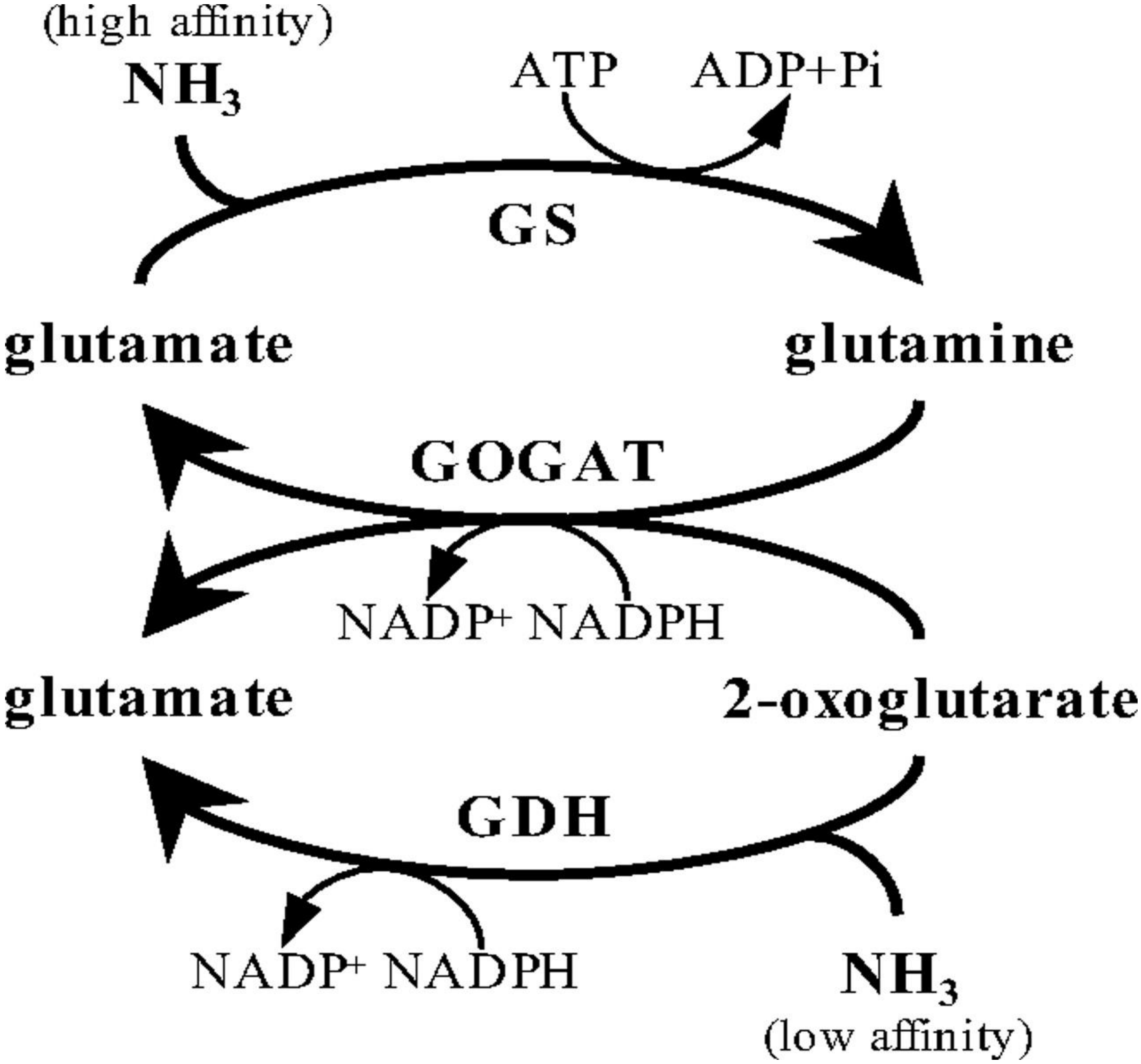
Nitrogenase activation



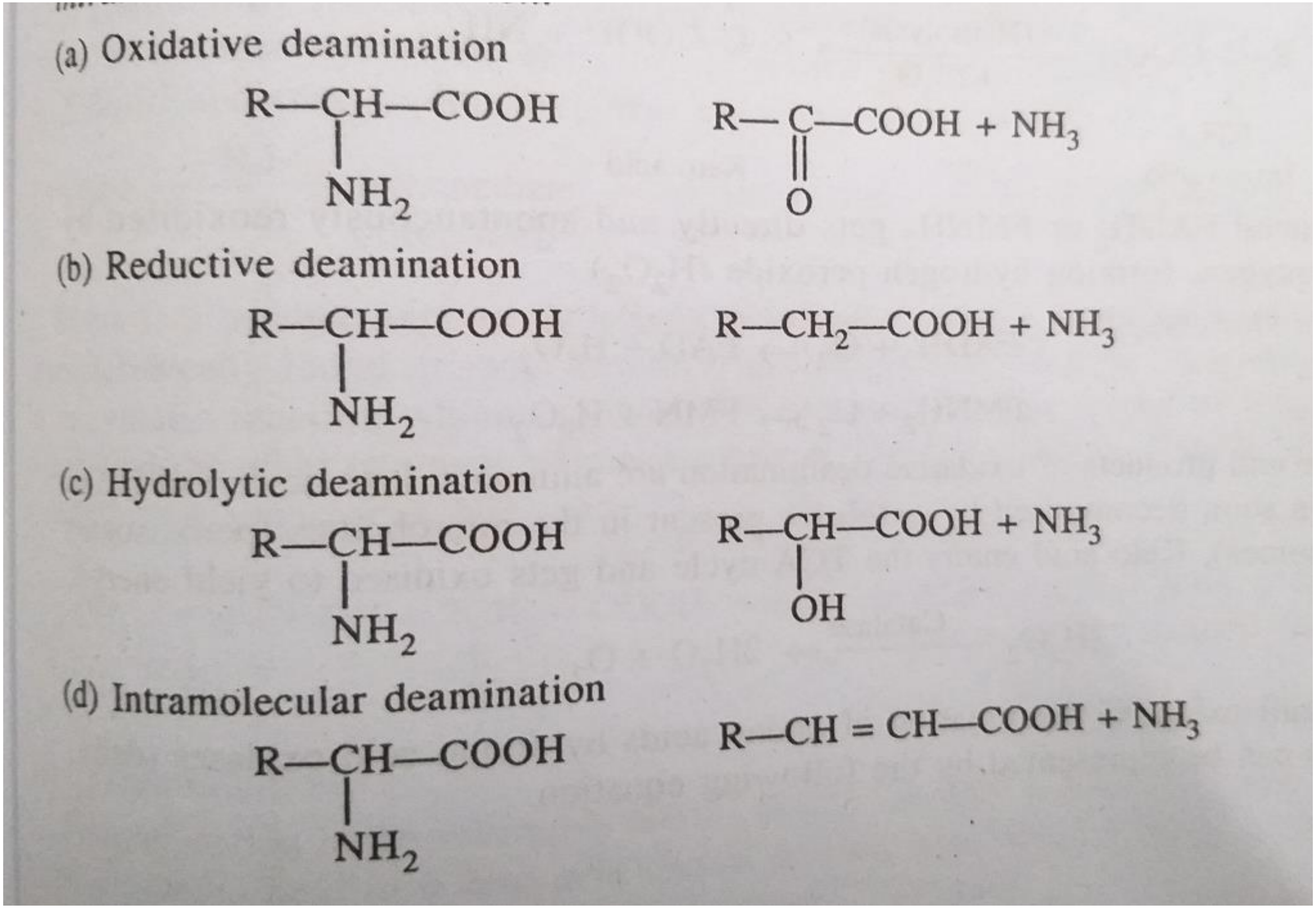
Initiation of the nodule formation process
- root hair deformation
- preinfection thread formation
- cortical cell division


Root Hair
A
Flavonoids
NodD
rhizobium
P
nod genes
Infection Thread
initiation of nodule formation
Nod Factors
B
Nodule
nif genes
nitrogenase
$\mathbf{N_2} + 8\ H^+ + 8\ e^- + 16\ ATP \longrightarrow 2\ \mathbf{NH_3} + H_2 + 16\ ADP + 16\ P_i$
Biological Nitrogen Fixation
C


GDH pathway
GDH
Glutamate
NH3
α-Ketoglutaric acid
NADP
NADPH
GS-GOGAT pathway
NH3
ATP
ADP + Pi
GS
Glutamate
Glutamine
GOGAT
Glutamate
NADP
NADPH
α-Ketoglutaric acid


(high affinity)
NH_3
ATP
ADP+Pi
GS
glutamate
glutamine
GOGAT
NADP+ NADPH
glutamate
2-oxoglutarate
GDH
NADP+ NADPH
NH_3
(low affinity)

Deamination



(a) Oxidative deamination

$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \qquad R-\underset{\displaystyle O}{\underset{\|}{C}}-COOH + NH_3$$

(b) Reductive deamination

$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \qquad R-CH_2-COOH + NH_3$$

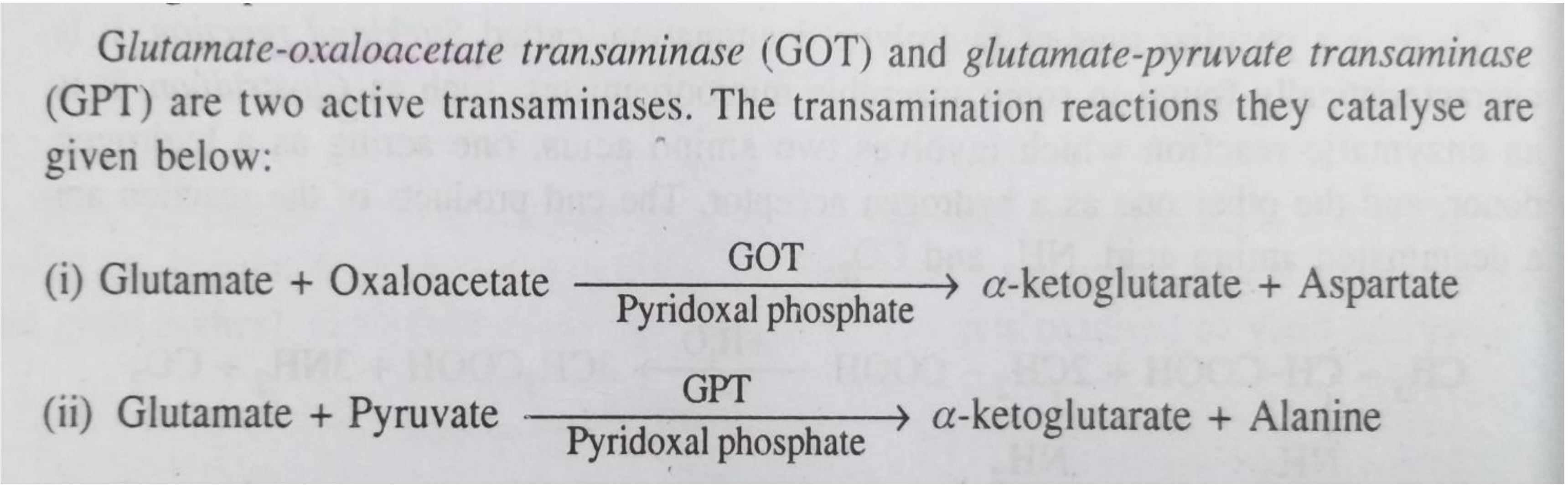
(c) Hydrolytic deamination

$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \qquad R-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH + NH_3$$

(d) Intramolecular deamination

$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \qquad R-CH=CH-COOH + NH_3$$

Transamination

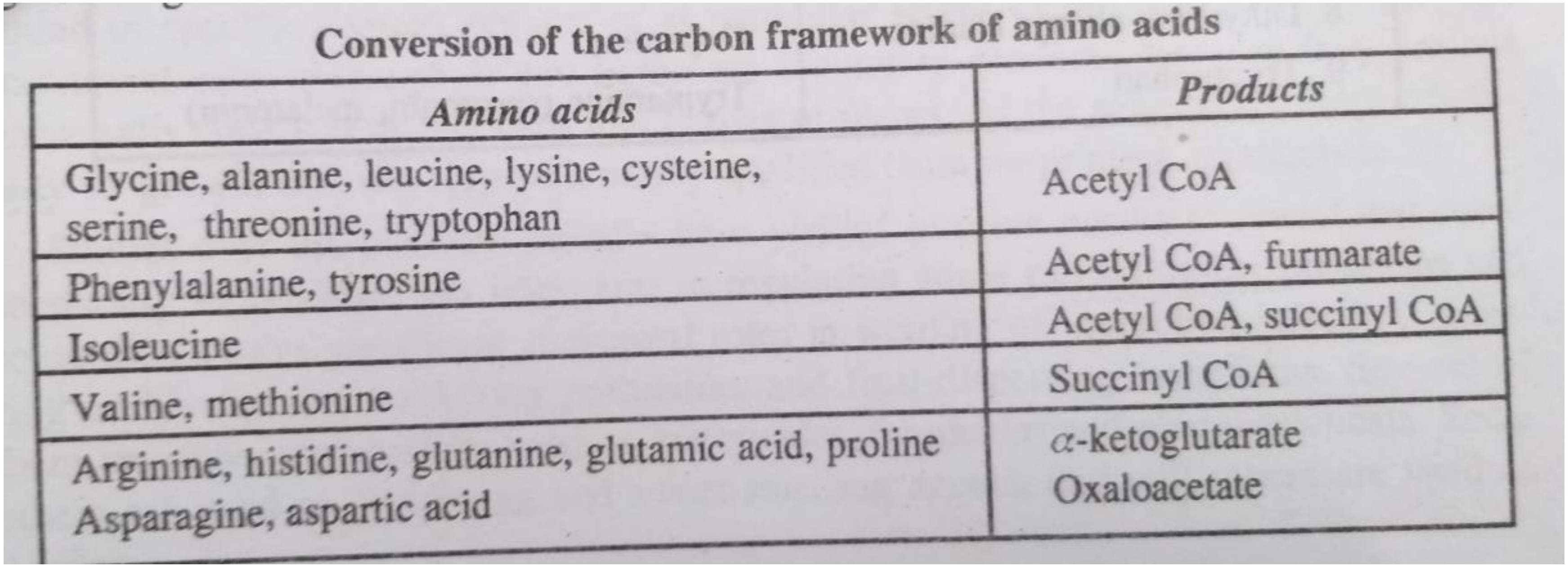


Glutamate-oxaloacetate transaminase (GOT) and *glutamate-pyruvate transaminase* (GPT) are two active transaminases. The transamination reactions they catalyse are given below:

(i) $$\text{Glutamate} + \text{Oxaloacetate} \xrightarrow[\text{Pyridoxal phosphate}]{\text{GOT}} \alpha\text{-ketoglutarate} + \text{Aspartate}$$

(ii) $$\text{Glutamate} + \text{Pyruvate} \xrightarrow[\text{Pyridoxal phosphate}]{\text{GPT}} \alpha\text{-ketoglutarate} + \text{Alanine}$$

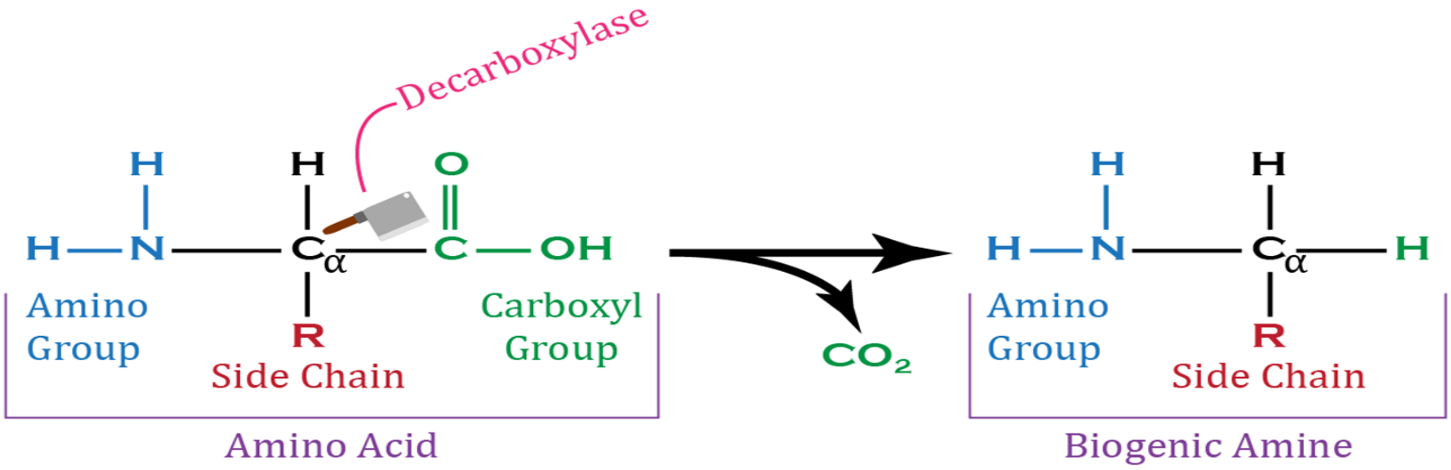
Conversion of carbon skeleton

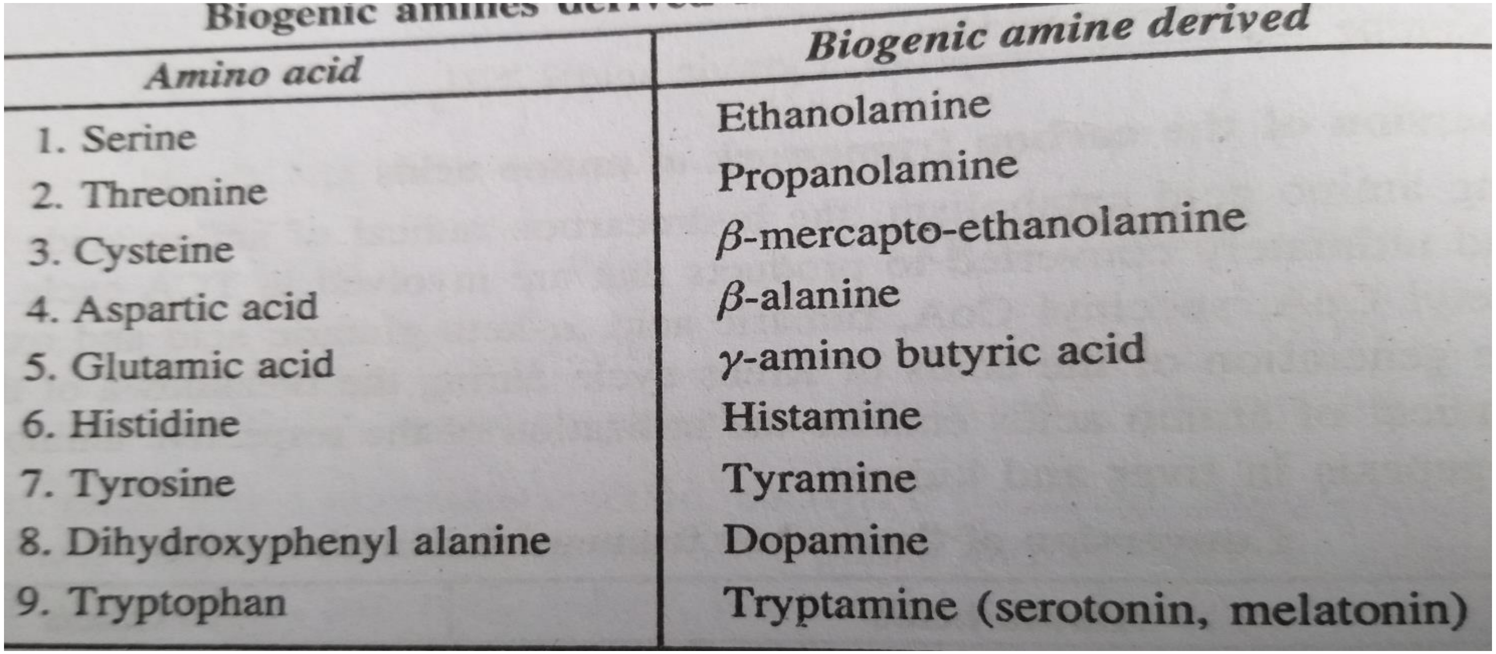


Conversion of the carbon framework of amino acids

Amino acids	*Products*
Glycine, alanine, leucine, lysine, cysteine, serine, threonine, tryptophan	Acetyl CoA
Phenylalanine, tyrosine	Acetyl CoA, furmarate
Isoleucine	Acetyl CoA, succinyl CoA
Valine, methionine	Succinyl CoA
Arginine, histidine, glutanine, glutamic acid, proline	α-ketoglutarate
Asparagine, aspartic acid	Oxaloacetate

Biogenic amines

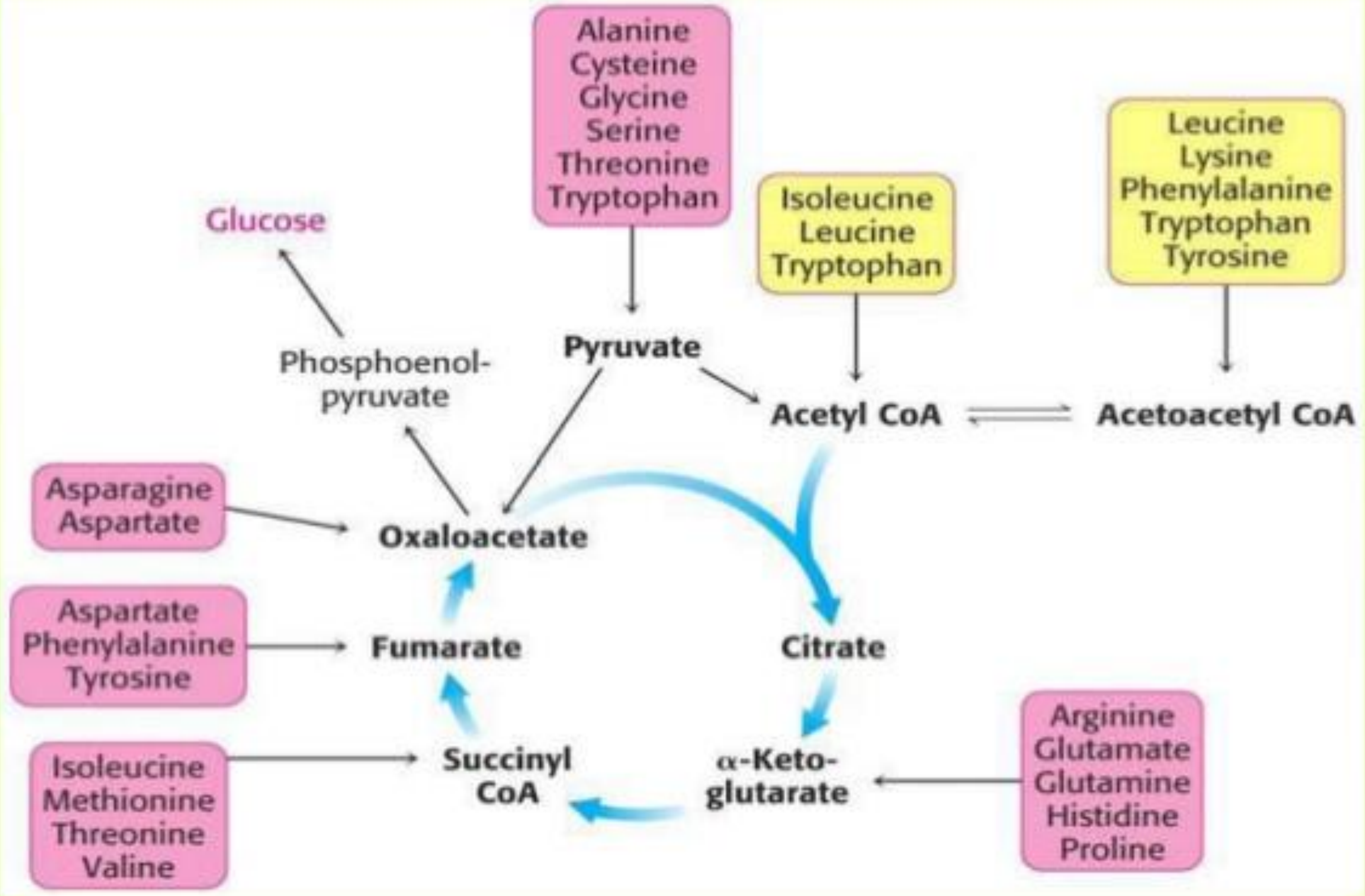




Biogenic amines

Amino acid	*Biogenic amine derived*
1. Serine	Ethanolamine
2. Threonine	Propanolamine
3. Cysteine	β-mercapto-ethanolamine
4. Aspartic acid	β-alanine
5. Glutamic acid	γ-amino butyric acid
6. Histidine	Histamine
7. Tyrosine	Tyramine
8. Dihydroxyphenyl alanine	Dopamine
9. Tryptophan	Tryptamine (serotonin, melatonin)

Amino Acid Degradation



Alanine
Cysteine
Glycine
Serine
Threonine
Tryptophan

Glucose

Isoleucine
Leucine
Tryptophan

Leucine
Lysine
Phenylalanine
Tryptophan
Tyrosine

Phosphoenol-pyruvate

Pyruvate

Acetyl CoA

Acetoacetyl CoA

Asparagine
Aspartate

Oxaloacetate

Aspartate
Phenylalanine
Tyrosine

Fumarate

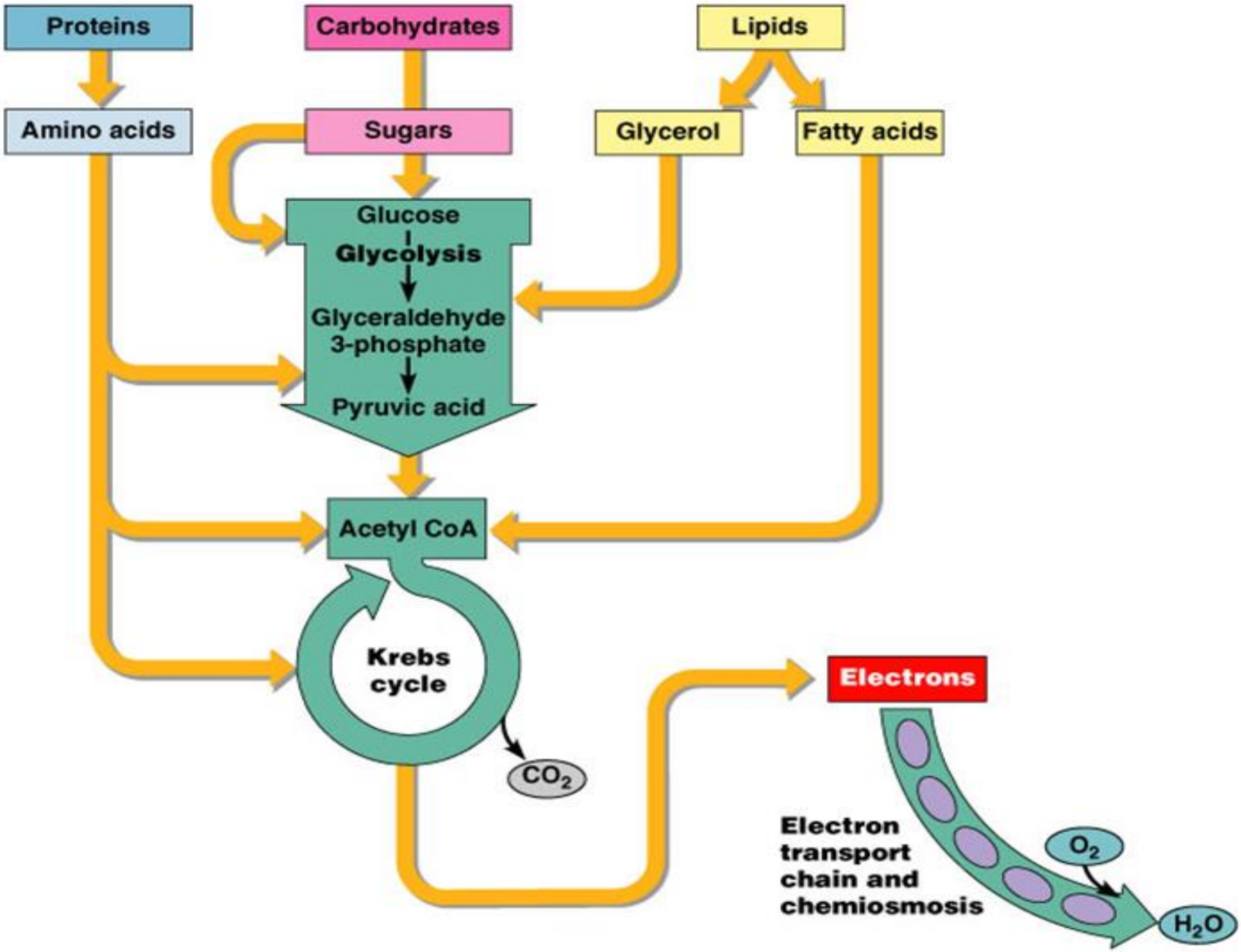
Citrate

Isoleucine
Methionine
Threonine
Valine

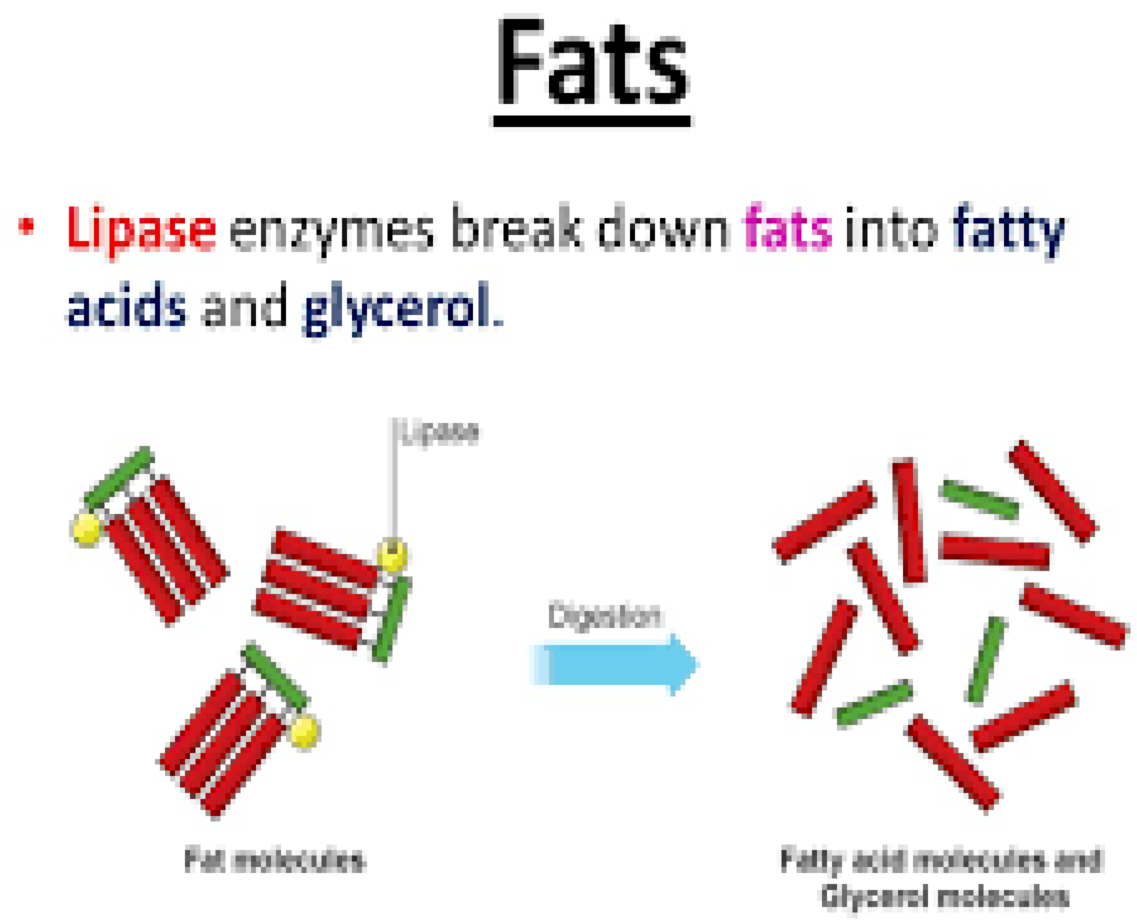
Succinyl CoA

α-Keto-glutarate

Arginine
Glutamate
Glutamine
Histidine
Proline


Proteins
Carbohydrates
Lipids
Amino acids
Sugars
Glycerol
Fatty acids
Glucose
Glycolysis
Glyceraldehyde 3-phosphate
Pyruvic acid
Acetyl CoA
Krebs cycle
CO_2
Electrons
Electron transport chain and chemiosmosis
O_2
H_2O

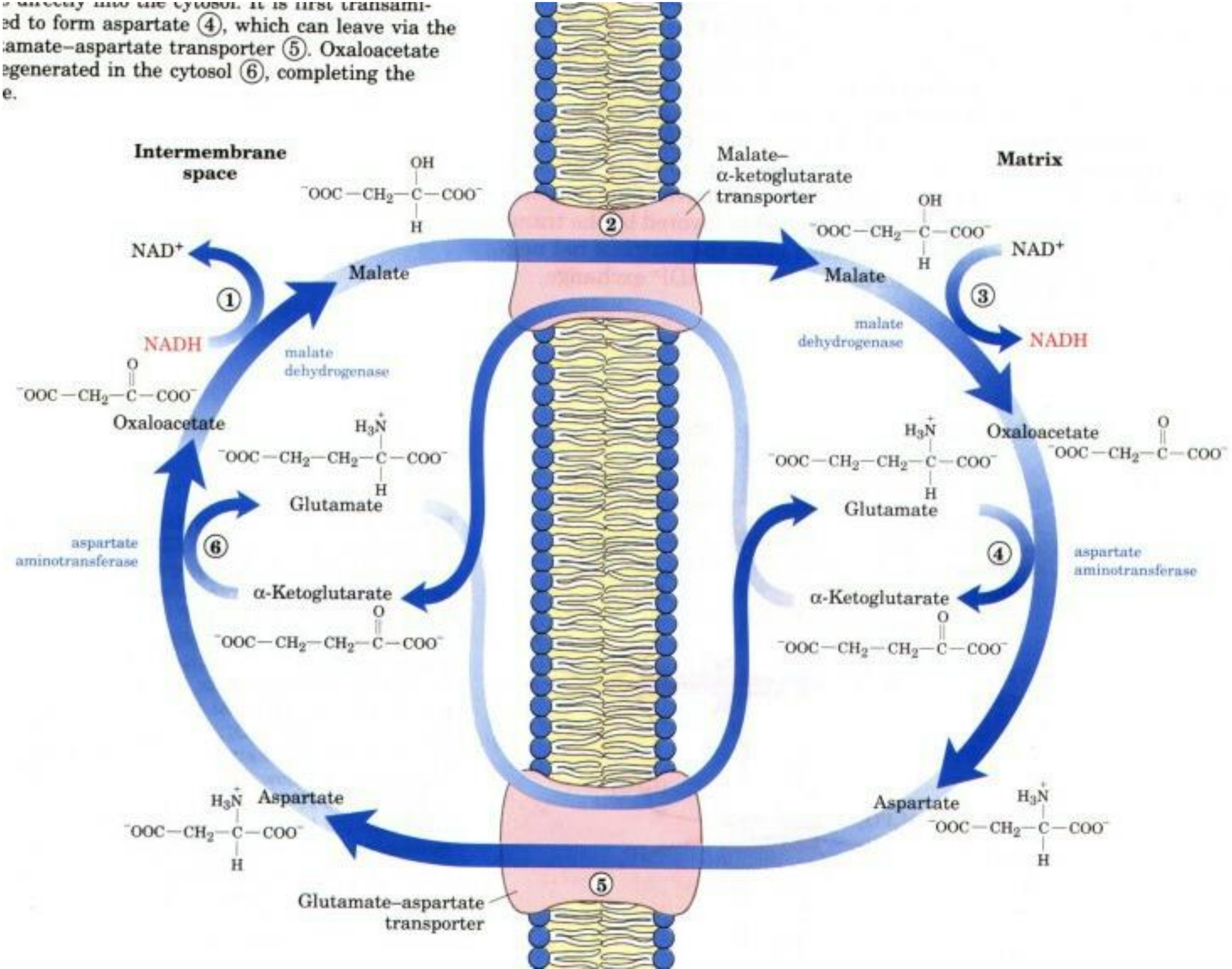
FAT METABOLISM

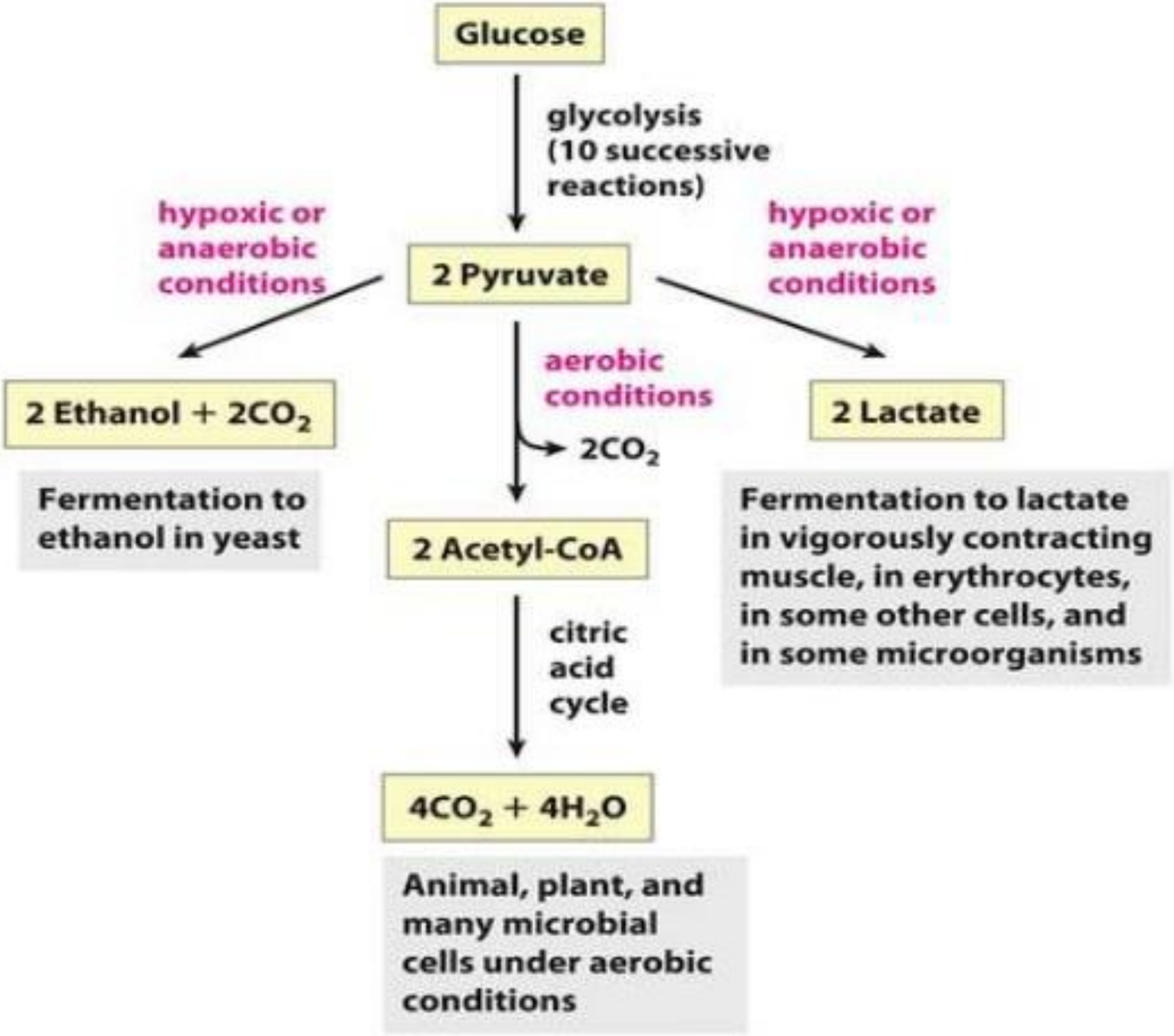


Fats

- **Lipase** enzymes break down **fats** into **fatty acids** and **glycerol**.

directly into the cytosol. It is first transami-
ed to form aspartate ④, which can leave via the
amate–aspartate transporter ⑤. Oxaloacetate
egenerated in the cytosol ⑥, completing the
e.





Glucose

glycolysis (10 successive reactions)

2 Pyruvate

hypoxic or anaerobic conditions

2 Ethanol + $2CO_2$

Fermentation to ethanol in yeast

aerobic conditions

$2CO_2$

2 Acetyl-CoA

citric acid cycle

$4CO_2 + 4H_2O$

Animal, plant, and many microbial cells under aerobic conditions

hypoxic or anaerobic conditions

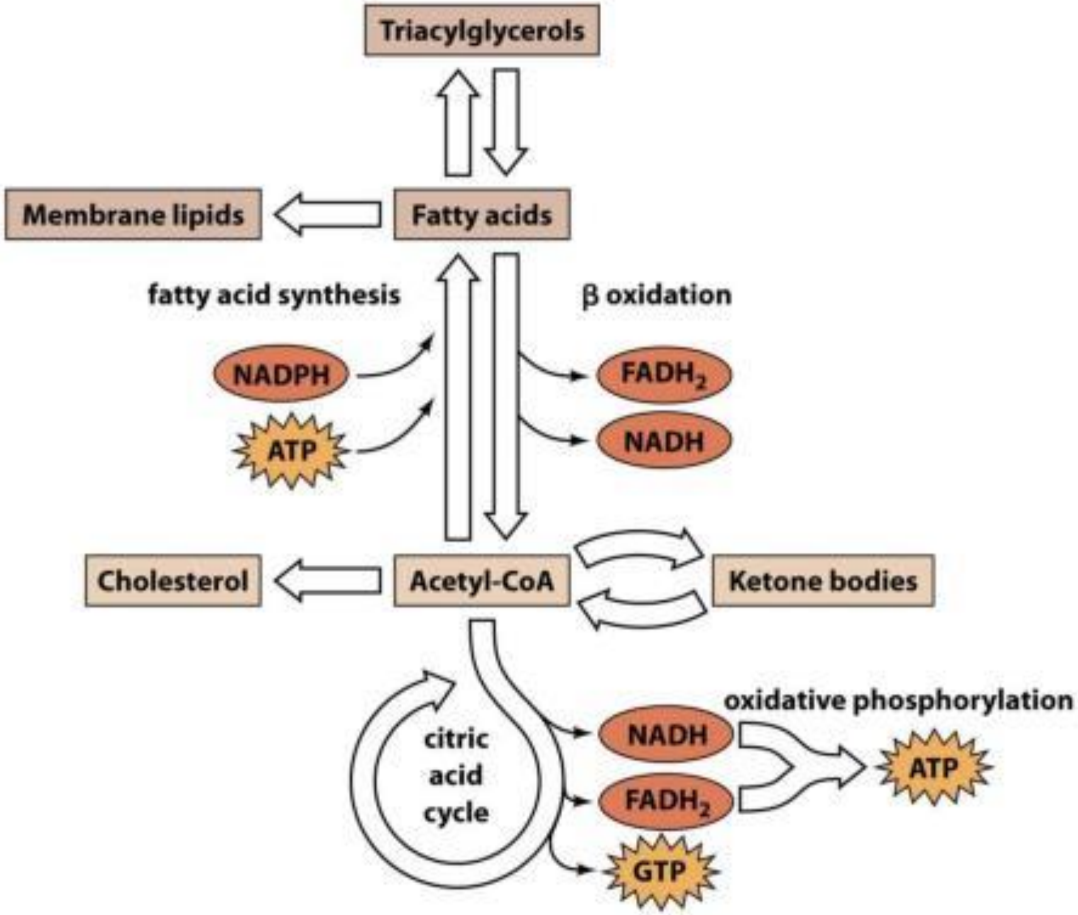
2 Lactate

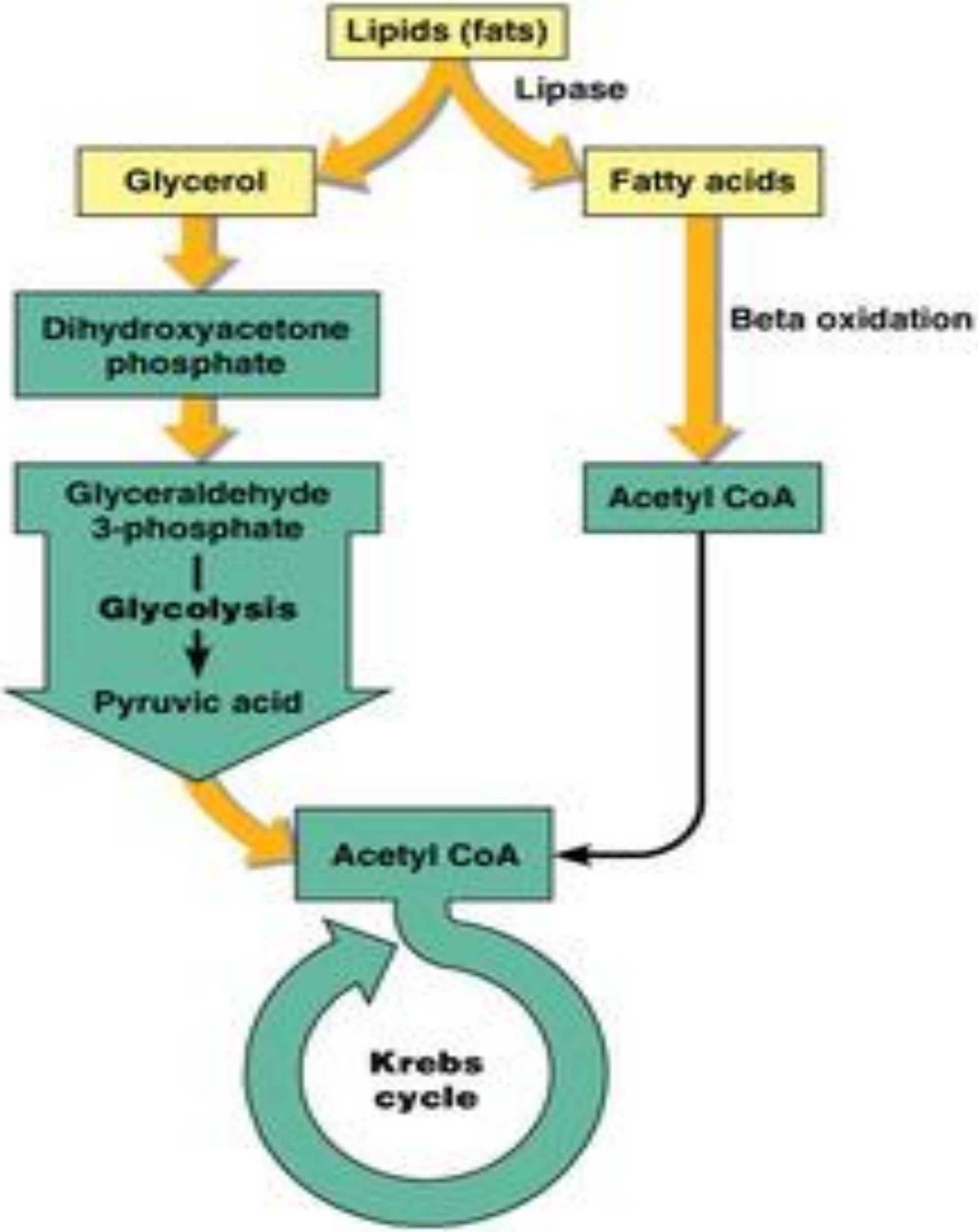
Fermentation to lactate in vigorously contracting muscle, in erythrocytes, in some other cells, and in some microorganisms

Diverse Fates of Pyruvate

Lipids are tied to metabolism through the TCA cycle

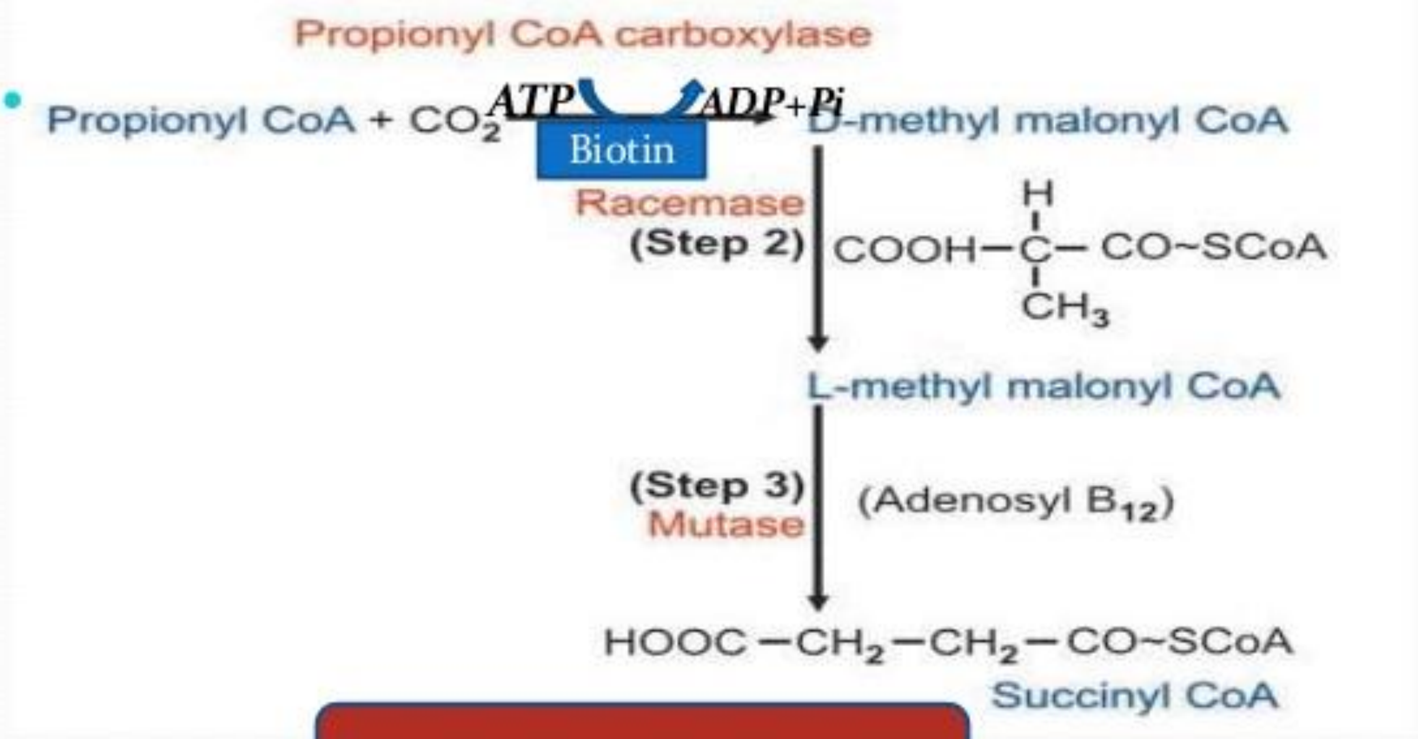
The dihydroxyacetone phosphate (DHAP) made by glycolysis or made from oxaloacetate by glyceroneogenesis; thus this system responds to the same hormones involved in regulation of carbohydrate metabolism.




Lipids (fats)
Lipase
Glycerol
Fatty acids
Dihydroxyacetone phosphate
Beta oxidation
Glyceraldehyde 3-phosphate
Glycolysis
Pyruvic acid
Acetyl CoA
Acetyl CoA
Krebs cycle

β- Oxidation for odd chain fatty acid

- Beta oxidation for odd chain fatty acid occurs in the same way as for even chain fatty acid except the cleavage step yields ***propionyl CoA*** and ***Acetyl CoA***



Propionyl CoA carboxylase

- $\text{Propionyl CoA} + CO_2 \xrightarrow[\text{Biotin}]{\text{ATP} \quad \text{ADP+Pi}} \text{D-methyl malonyl CoA}$

Racemase

(Step 2)

$COOH-\overset{H}{\underset{CH_3}{C}}-CO\sim SCoA$

L-methyl malonyl CoA

(Step 3)

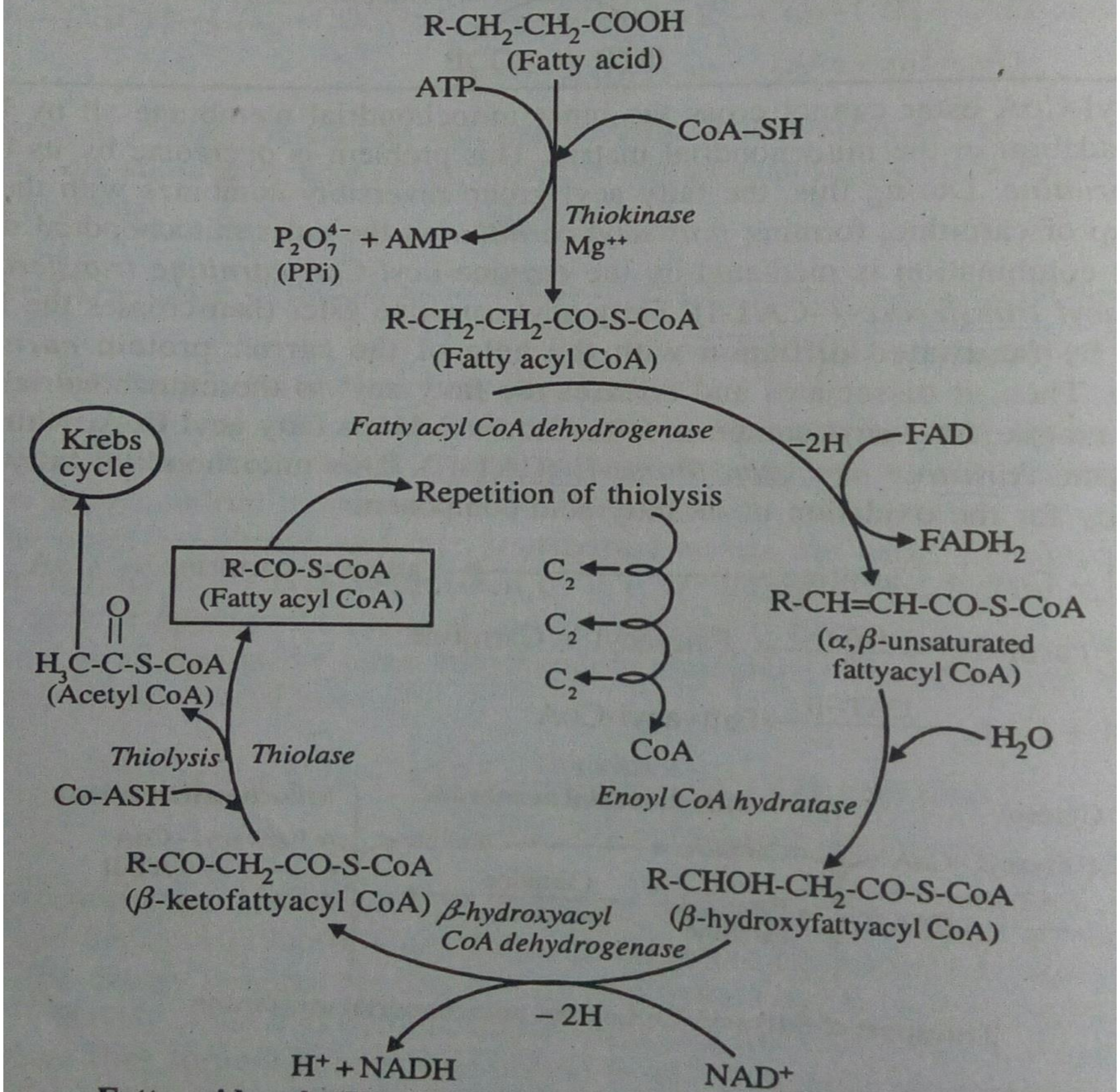
Mutase

(Adenosyl B_{12})

$HOOC-CH_2-CH_2-CO\sim SCoA$

Succinyl CoA

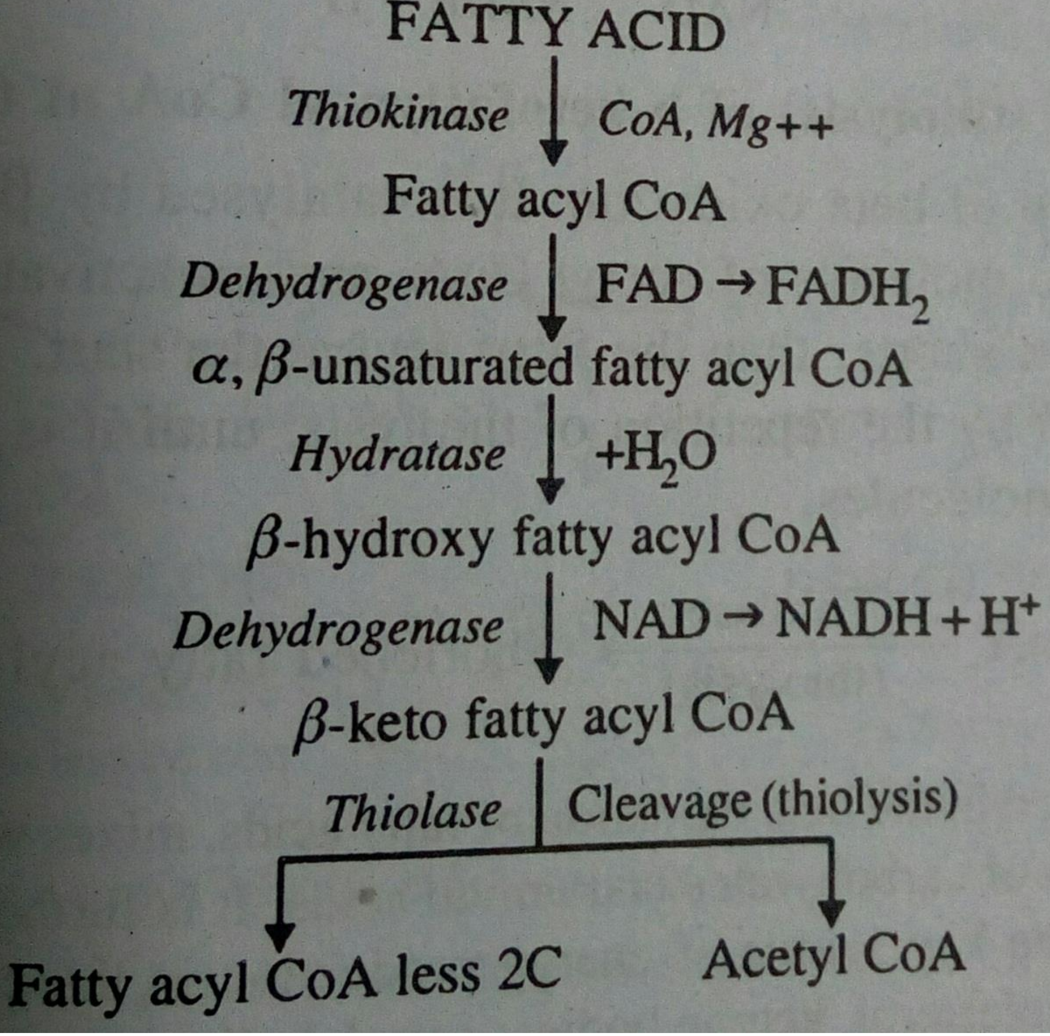
Fig: -Fate of Propionyl CoA

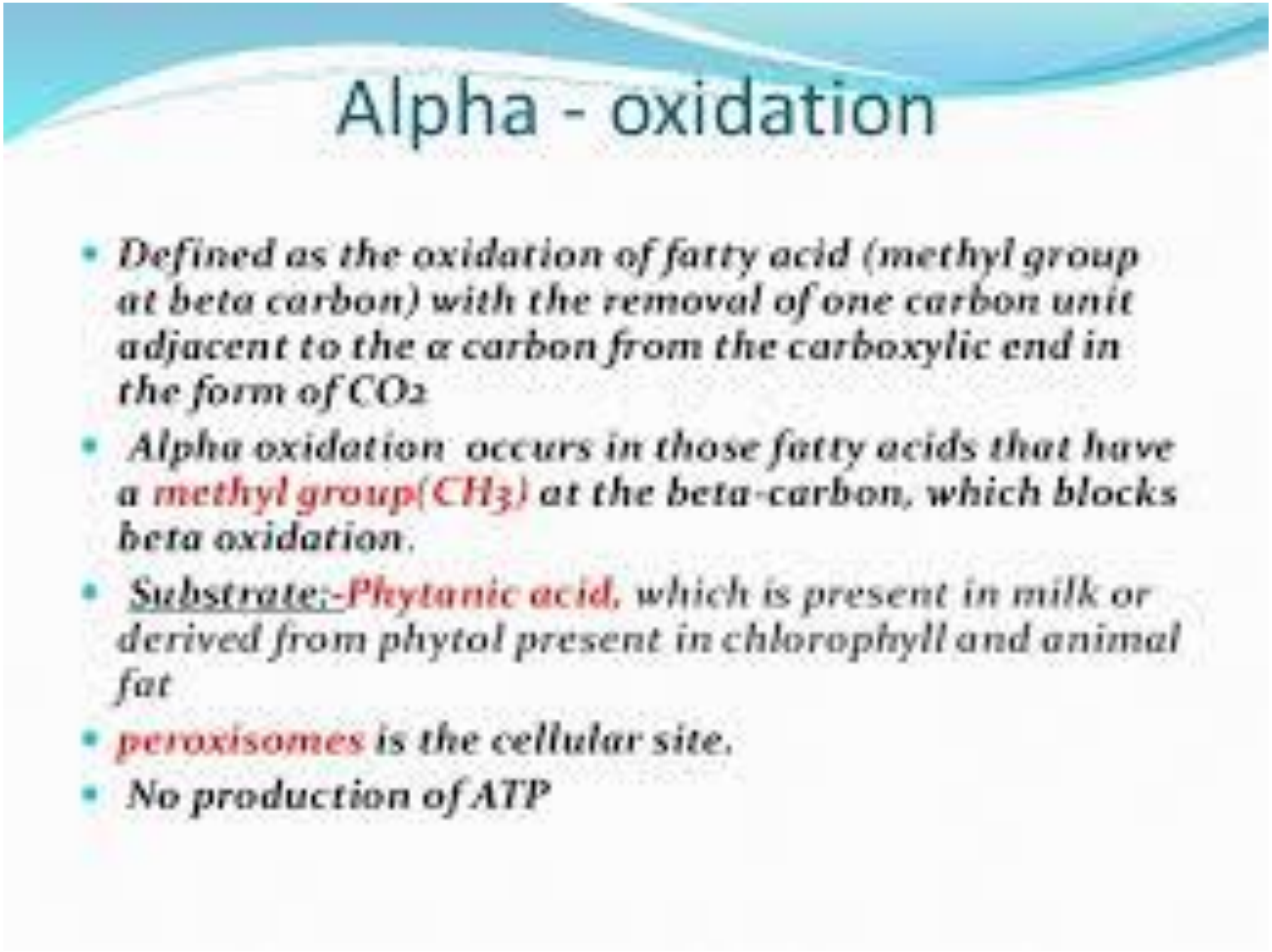


Fatty acid cycle (Knoop-Lynen cycle or Beta oxidation spiral)

NADH + H$^+$

Fatty acid cycle - removal of acetyl CoA unit
(Circular flow chart)

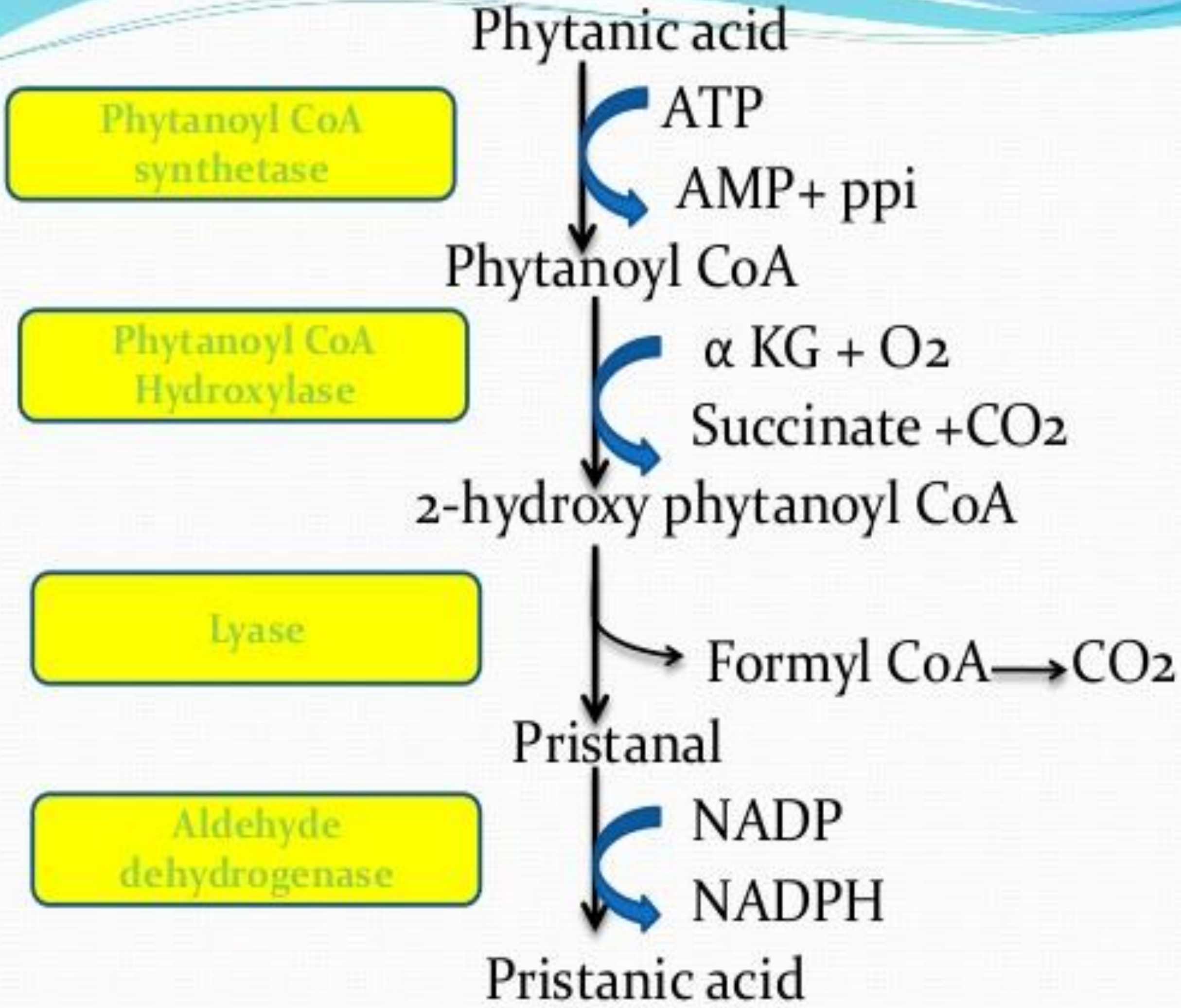




Alpha - oxidation

- *Defined as the oxidation of fatty acid (methyl group at beta carbon) with the removal of one carbon unit adjacent to the α carbon from the carboxylic end in the form of CO_2*
- *Alpha oxidation occurs in those fatty acids that have a methyl group(CH_3) at the beta-carbon, which blocks beta oxidation.*
- *Substrate:-Phytanic acid, which is present in milk or derived from phytol present in chlorophyll and animal fat*
- *peroxisomes is the cellular site.*
- *No production of ATP*

Alpha Oxidation



Phytanic acid

Phytanoyl CoA synthetase

ATP → AMP+ ppi

Phytanoyl CoA

Phytanoyl CoA Hydroxylase

α KG + O_2 → Succinate +CO_2

2-hydroxy phytanoyl CoA

Lyase

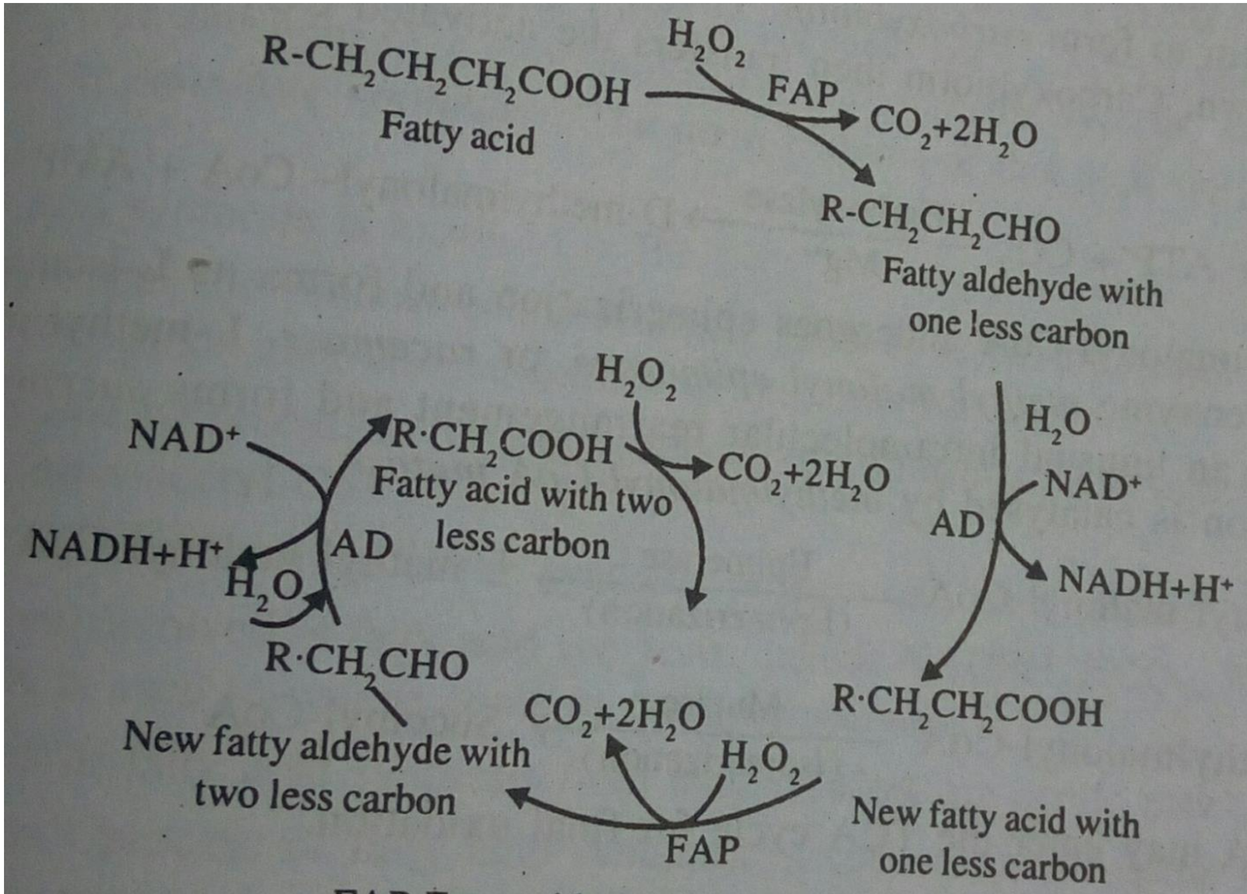
Formyl CoA → CO_2

Pristanal

Aldehyde dehydrogenase

NADP → NADPH

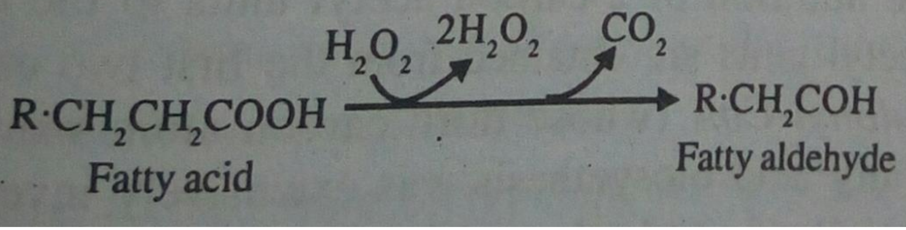
Pristanic acid



FAP-Fatty acid peroxidase

AD-Aldehyde dehydrogenase

α -Oxidation of fatty acids



Fatty Acid Synthesis

- **Intramitochondrail**

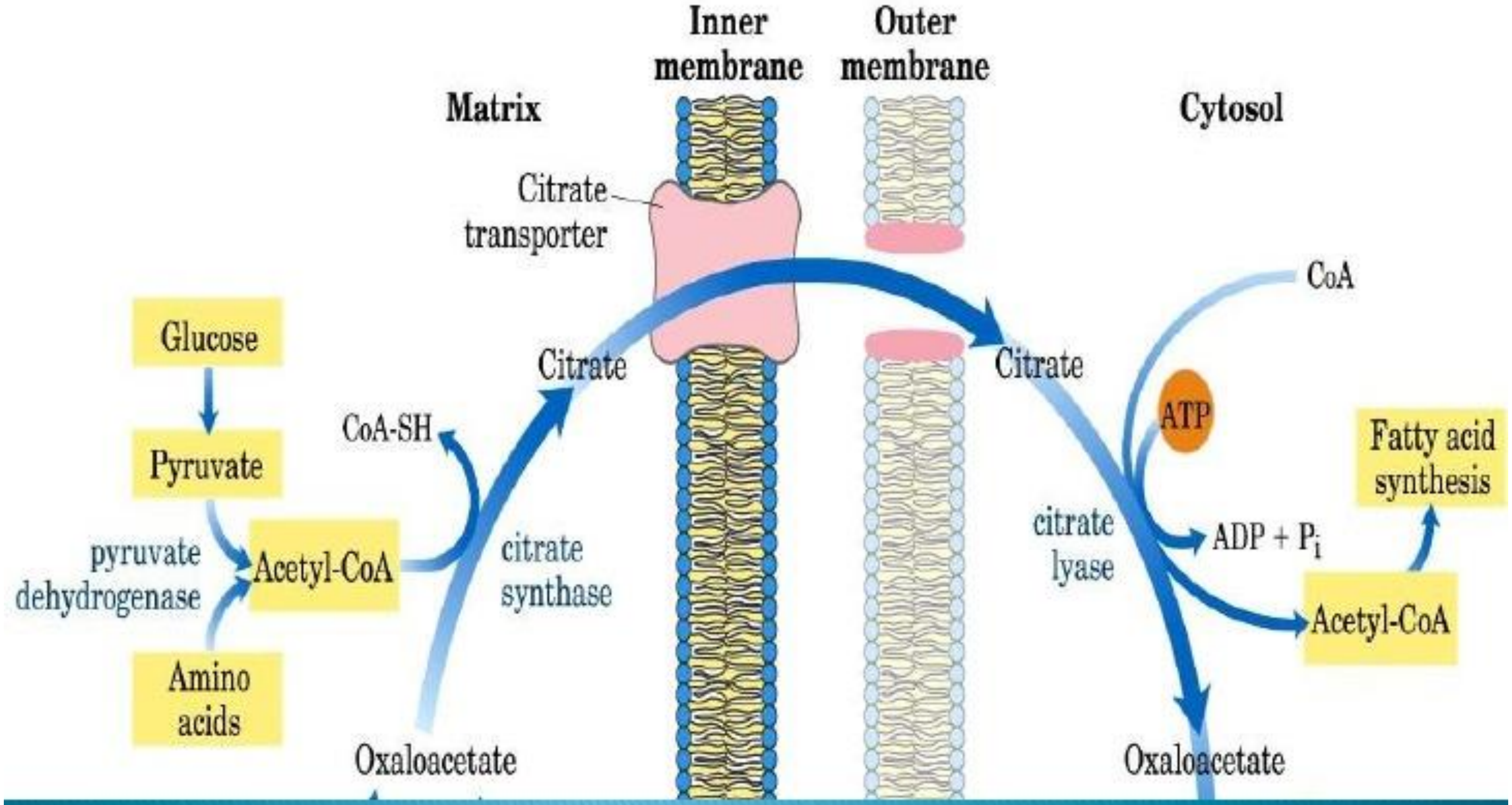
  (for long chain fatty acids & elongation of existing fatty acids)
  - Reversal of β oxidation
  - All steps reversible (except α β unsaturated fatty acyl CoA → β hydroxy fatty acyl CoA)
  - To bypass this, a new enzyme enol CoA reductase operates with NADPH as coenzyme.
- **Extramitochondrial**

  (exclusively for synthesis of palmitic acid – 16C)
- Located in ER
- Enzyme- fatty acid synthetase (palmitate synthetsae)
- Precursor is Malonyl CoA synthesised from Acetyl CoA.
- NADPH, ATP etc. required
- Successive assemblage of 7 Malonyl CoA with 1 Acetyl CoA

Acetyl CoA

- Inside mitochondria
  - From pyruvic acid
  - From Fatty acids
  - From Amino acids
- Can not diffuse to cytoplasm
- Need shuttle mechanisms
  - Transport protein Carnitine
  - Acetate thiokinase reaction
  - Citrate cleavage

Transportation of Acetyl co A



Transport of Aetyl-CoA from Mitochondria to Cytoplasm

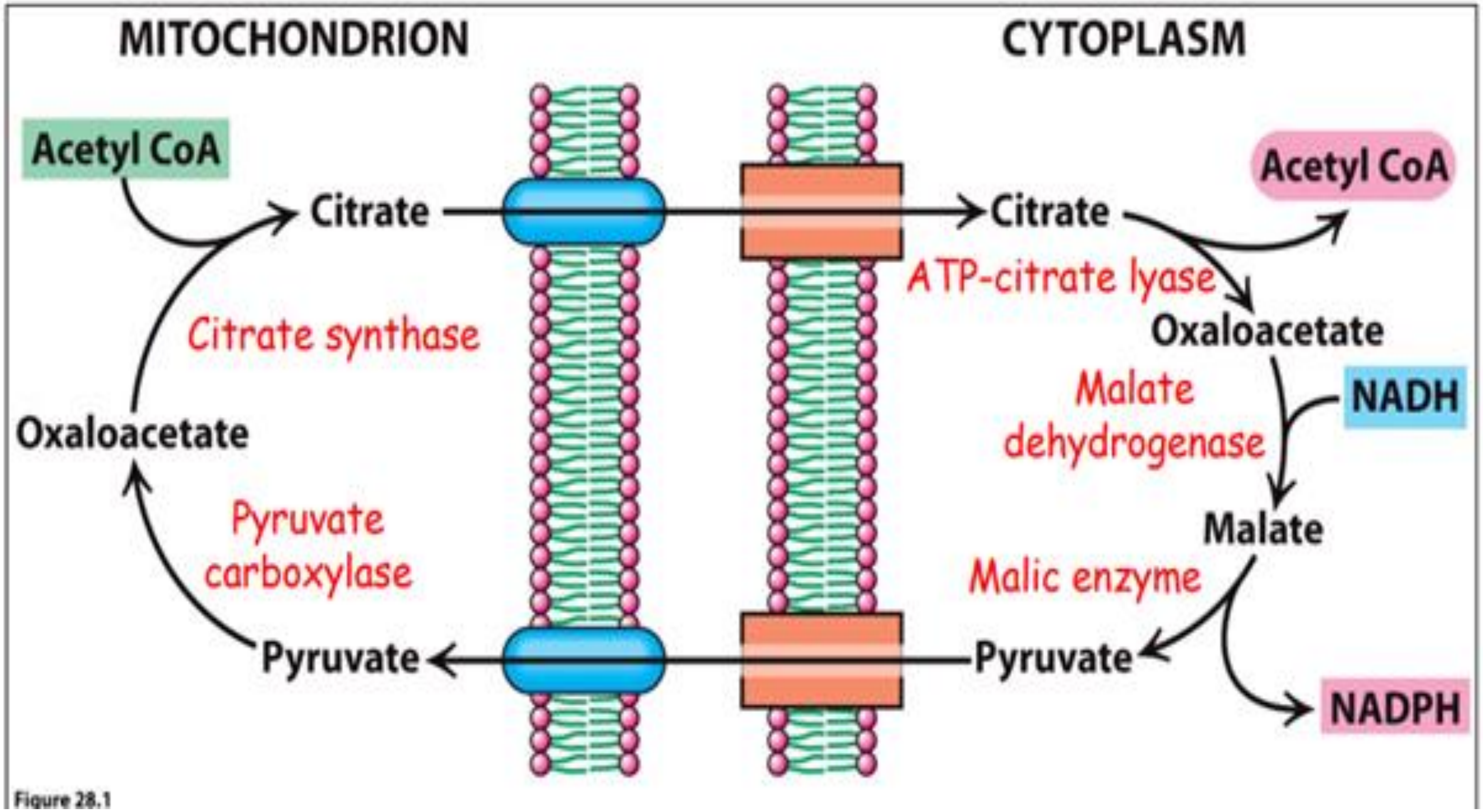
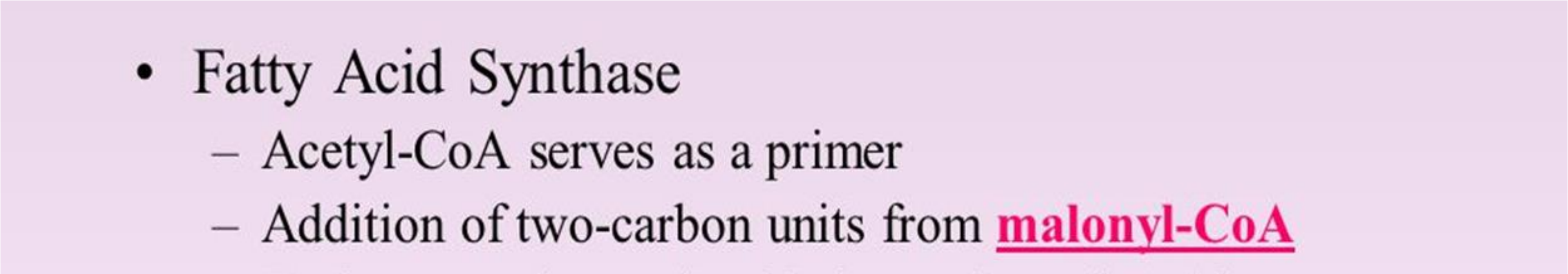
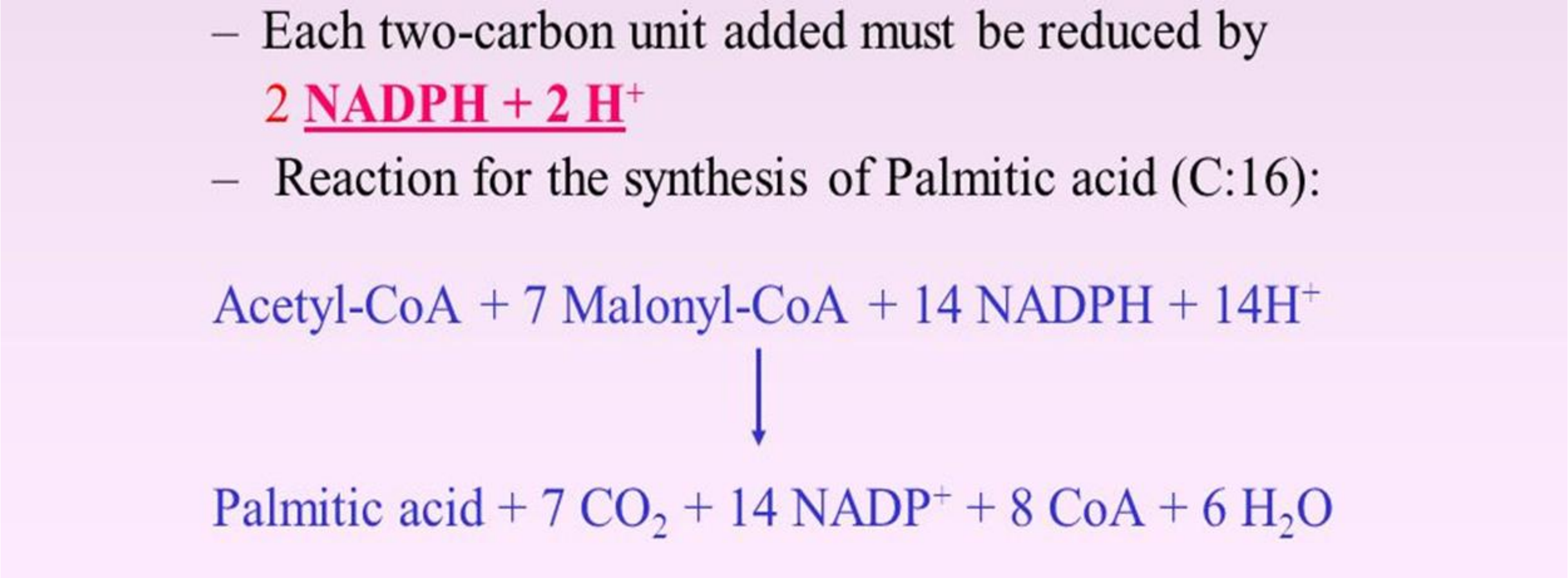


Figure 28.1



- Fatty Acid Synthase
  - Acetyl-CoA serves as a primer
  - Addition of two-carbon units from **malonyl-CoA**

- **Acetyl CoA (2C) → Malonyl CoA (3C)**
- Carboxylation o f Acetyl CoA with bicarbonate (ATP & Acetyl CoA carboxylase)



- Each two-carbon unit added must be reduced by 2 **NADPH + 2 H$^+$**
- Reaction for the synthesis of Palmitic acid (C:16):

$$\text{Acetyl-CoA} + 7\ \text{Malonyl-CoA} + 14\ \text{NADPH} + 14\text{H}^+ \downarrow \text{Palmitic acid} + 7\ CO_2 + 14\ \text{NADP}^+ + 8\ \text{CoA} + 6\ H_2O$$

Summary of palmitic acid synthesis

(i) $\text{Acetyl CoA} + HCO_3 + \text{ATP} \xrightarrow[\text{Mg}^{++}]{\text{①}} \text{Malonyl CoA} + \text{ADP} + \text{Pi}$

(ii) $\text{Acetyl CoA} + \text{ACP - SH} \xrightarrow{\text{②}} \text{Acetyl - S - ACP}$

(iii) $\text{Malonly CoA} + \text{ACP - SH} \xrightarrow{\text{③}} \text{Malonyl - S - ACP}$

(iv) $\text{Malonyl CoA} + \text{Acetyl CoA} \xrightarrow[\text{(Condensation)}]{\text{④}} \text{Acetoacetyl CoA}$

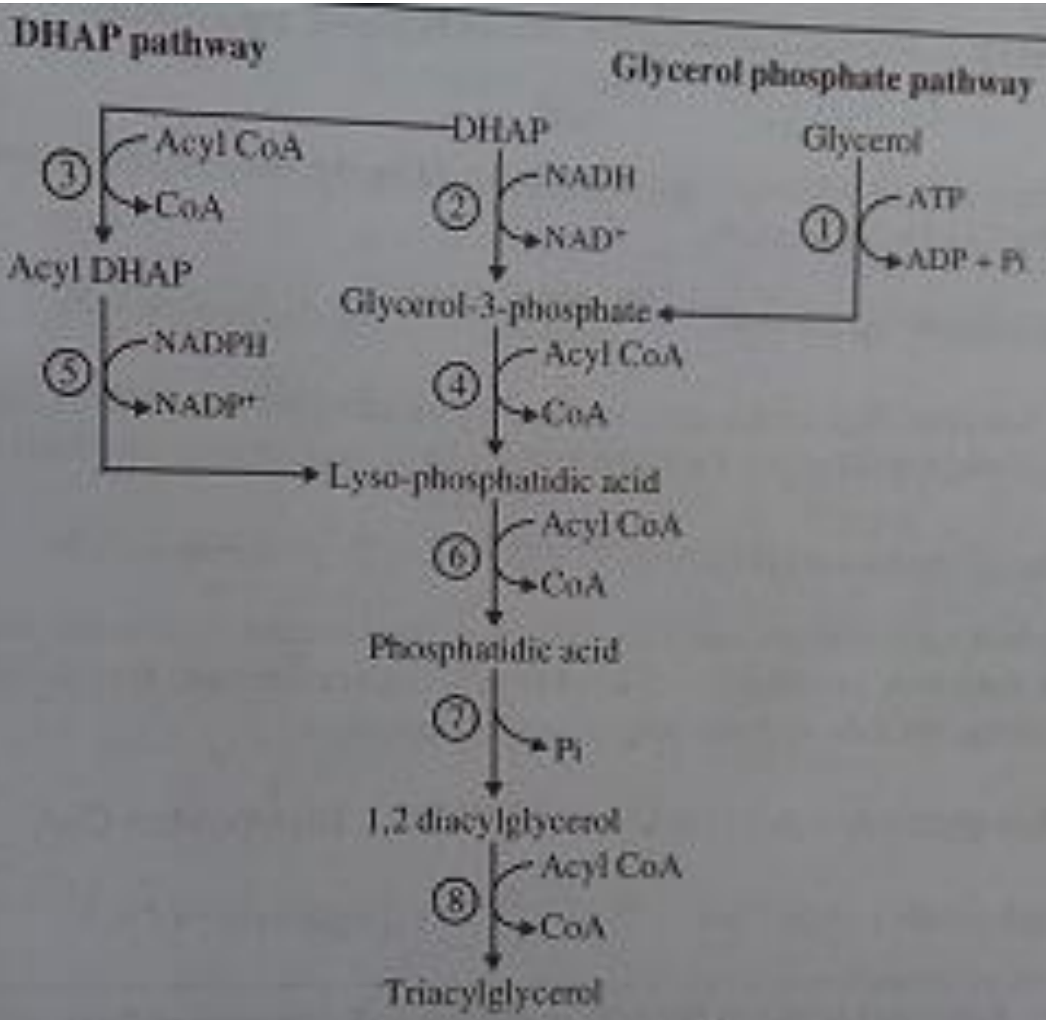
(v) $\text{Acetoacetyl CoA} + \text{NADPH} + H^+ \xrightarrow[\text{(Reduction)}]{\text{⑤}} \beta\text{-hydroxybutyryl CoA.}$

(vi) $\text{Hydroxybutyryl CoA} \xrightarrow[\text{(Dehydration)}]{\text{⑥}} \text{Crotonyl CoA}$

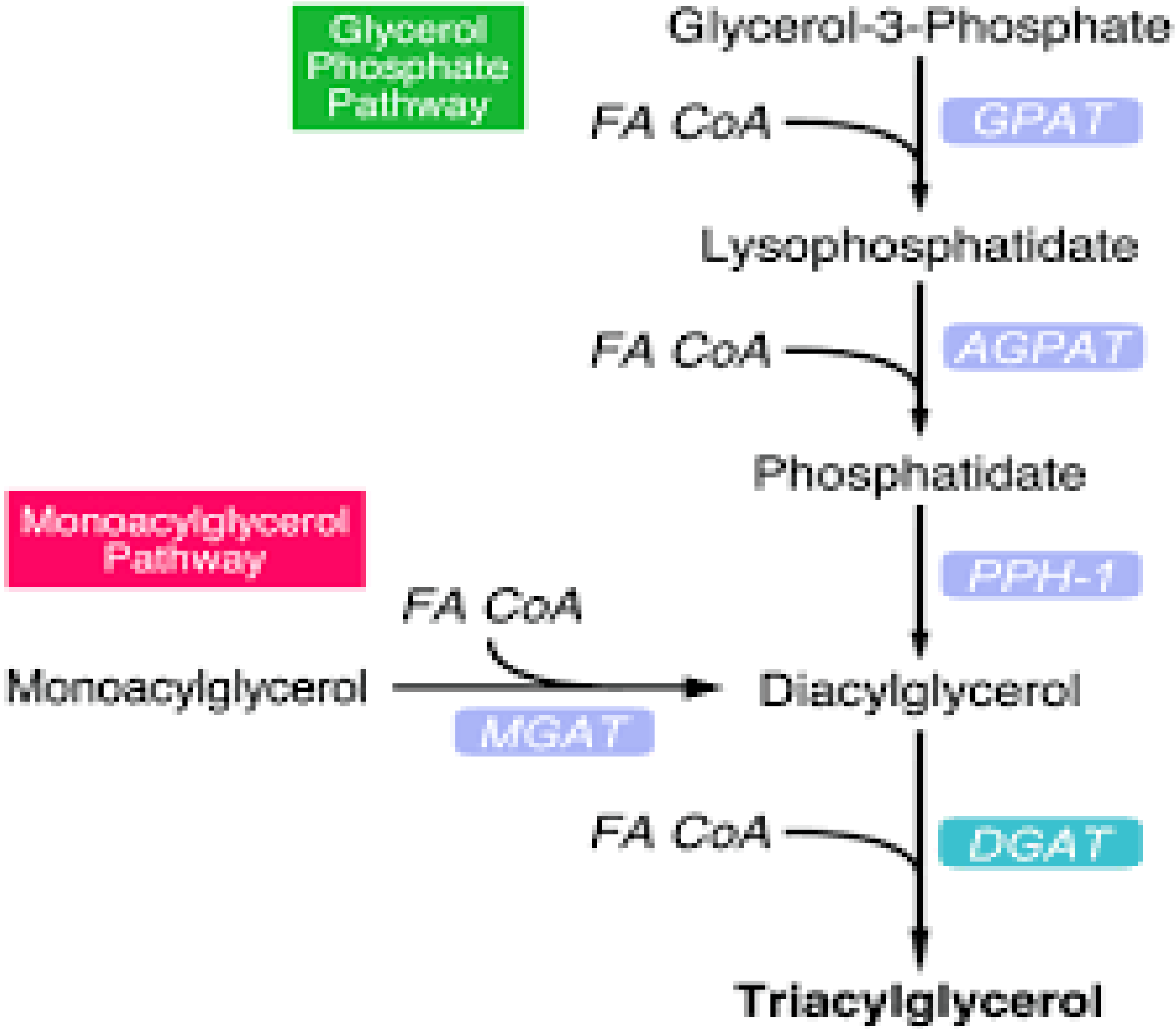
(vii) $\text{Crotonyl CoA} + \text{NADPH} + H^+ \xrightarrow[\text{(Reduction)}]{\text{⑦}} \text{Butyryl CoA}$

(viii) $\text{Polymerisation of butyryl units} \xrightarrow{\text{②}} \text{Palmitic acid}$

(ix) $\text{Enzyme - bound palmitic acid} \xrightarrow[\text{(Cleavage)}]{\text{⑧}} \text{Free palmitic acid} + \text{free enzyme}$



Generalised pathways of triglyceride synthesis



Glycerol Phosphate Pathway

Glycerol-3-Phosphate

FA CoA

GPAT

Lysophosphatidate

FA CoA

AGPAT

Phosphatidate

PPH-1

Monoacylglycerol Pathway

FA CoA

Monoacylglycerol

MGAT

Diacylglycerol

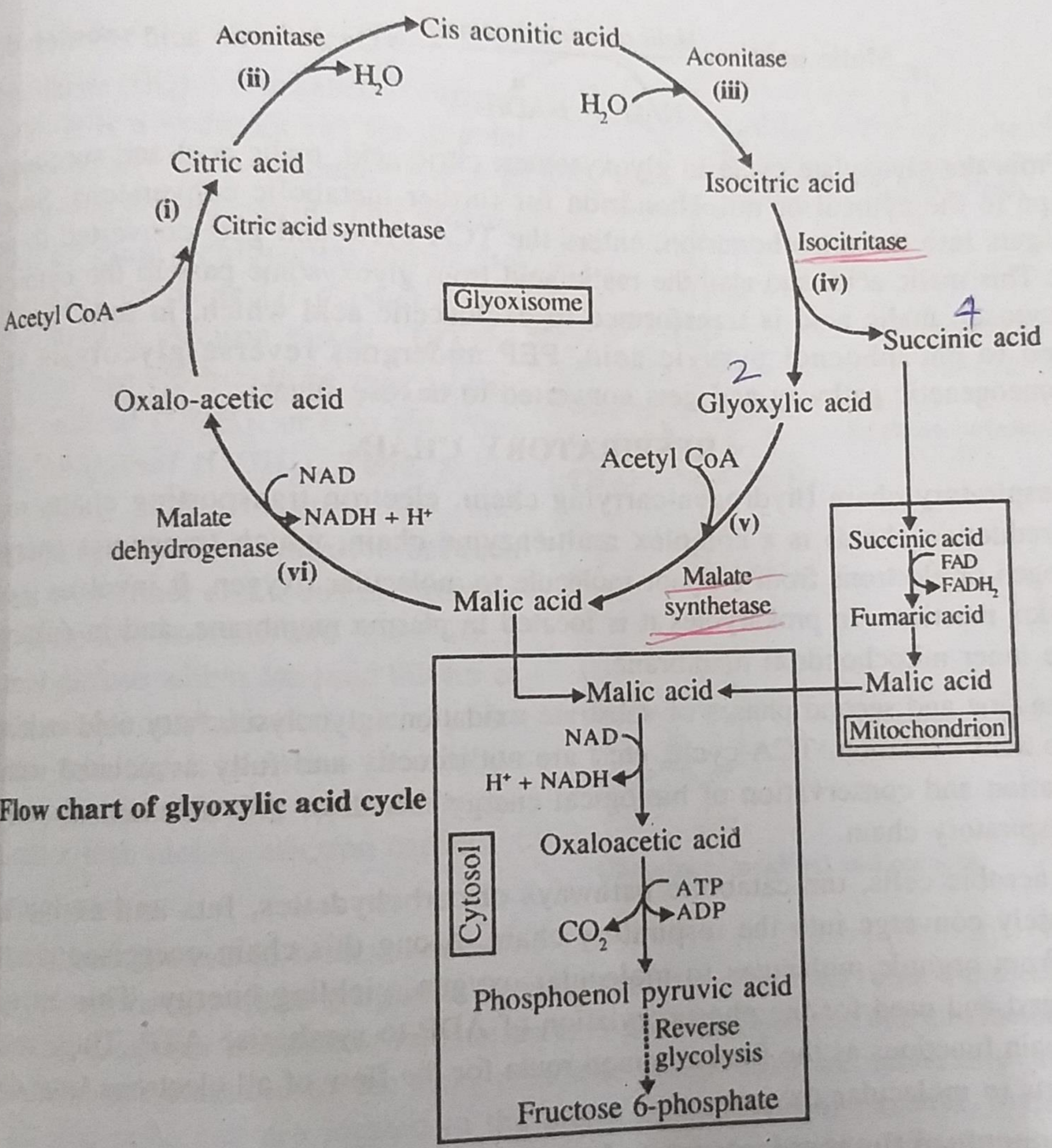
FA CoA

DGAT

Triacylglycerol

β-Oxidation & Fatty Acid Synthesis Compared

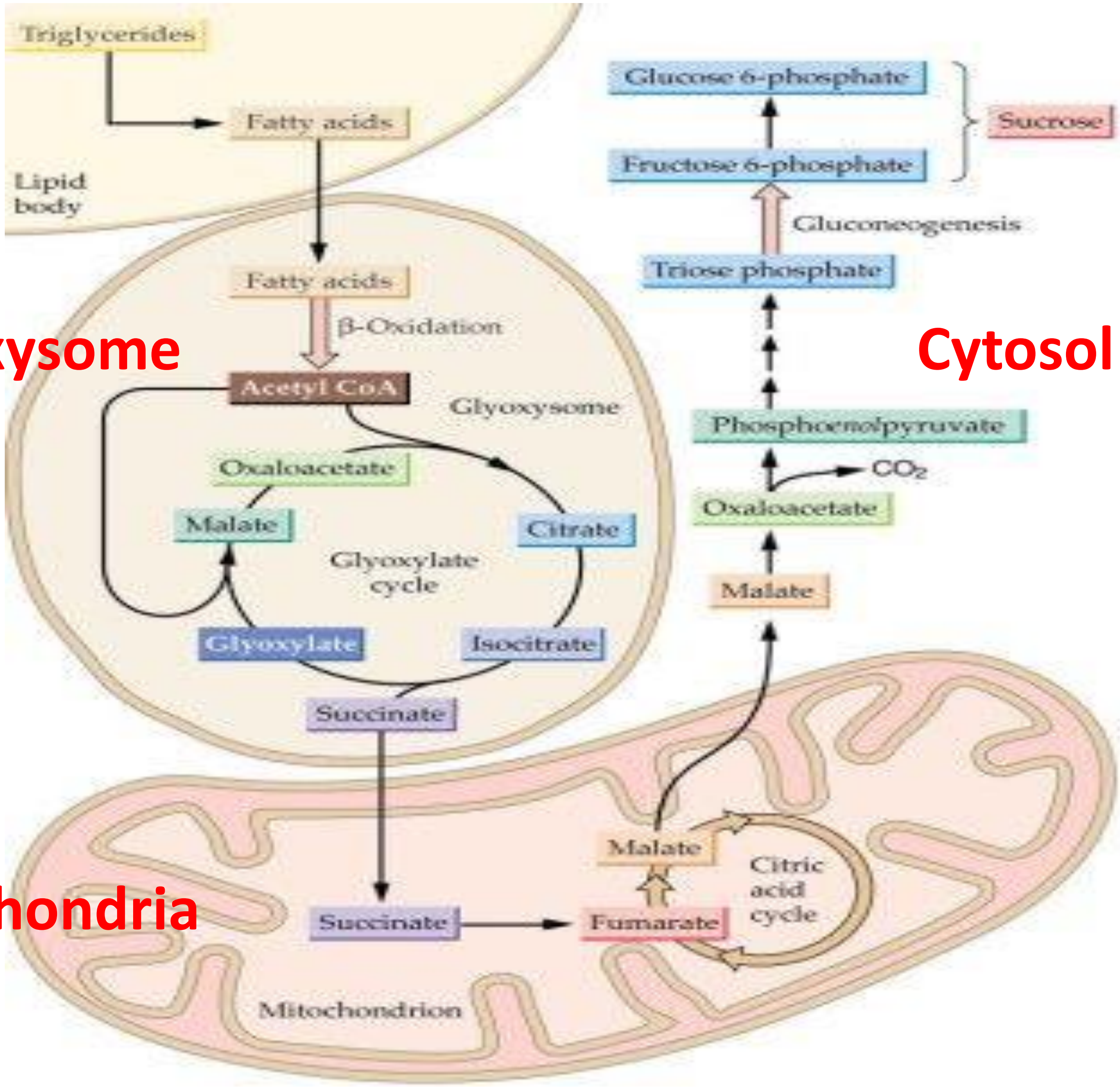
	β Oxidation Pathway	**Fatty Acid Synthesis**
pathway location	mitochondrial matrix	cytosol
acyl carriers (thiols)	Coenzyme-A	phosphopantetheine (ACP) & cysteine
e^- acceptors/donor	FAD & NAD^+	NADPH
-OH intermediate	L	D
2-C product/donor	acetyl-CoA	malonyl-CoA (& acetyl-CoA)



Flow chart of glyoxylic acid cycle

Glyoxysome

Cytosol



Miochondria