1

Chem 352 - Lecture 9
Photosynthesis

Question for the Day: How is photosynthesis analogous to a combination of gluconeogenesis, the pentose phosphate pathway, and the electron transport chain?

2

Introduction

The evolution of photosynthesis was a milestone for living system on earth

- It allowed energy to be obtain from an extraterrestrial source.
- This led to the creation of an oxygenated atmosphere along with a food source for non-photosynthesizing organisms.

3

Introduction

There are two parts to photosynthesis

- **Light reactions**
  - Shares much in common with the electron transport chain and ATP synthase.
- **Dark reactions**
  - Fixes atmospheric CO_2 and shares much in common with Gluconeogenesis and the Pentose Phosphate Pathway.

4

Introduction

- The light reactions take place in complex structures called **photosystems**.
- Light energy is used to energetically excite electrons, and that energy is then used to make either ATP or reduced NADPH + H^+.

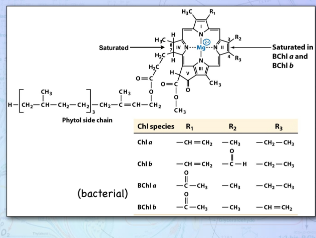
5

Introduction

- The light reactions take place in complex structures called **photosystems**.
- There are two different types of photosystems, PSI and PSII
  - Some organisms have one or the other and some have both.

6

The Light-gathering Pigments



Oxidation and reduction occurs on the tetrapyrrole ring.

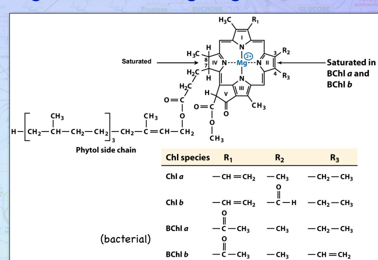
7-1

Light-Harvesting Pigments

- Chlorophylls
- Associated Pigments
  - β-carotene
  - xanthophylls
  - Phycobilins
  - et al.

7-2

Light-Harvesting Pigments



7-3

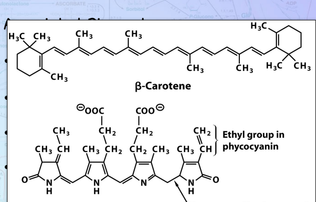
Light-Harvesting Pigments

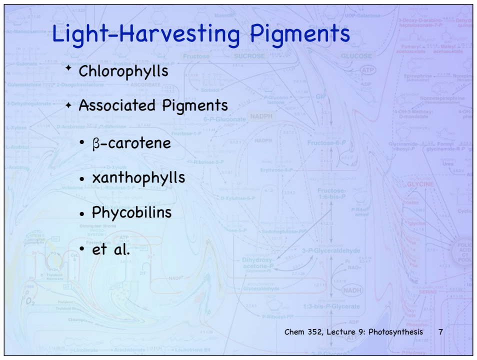
- Chlorophylls
- Associated Pigments
  - β-carotene
  - xanthophylls
  - Phycobilins
  - et al.

7-4

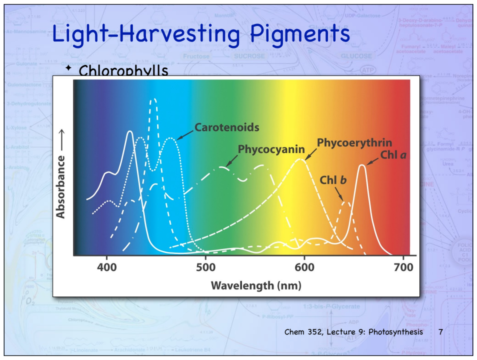
Light-Harvesting Pigments

- Chlorophylls

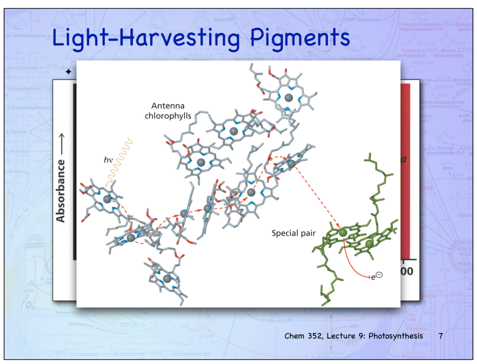



Light-Harvesting Pigments
Chlorophylls
Associated Pigments
β-carotene
xanthophylls
Phycobilins
et al.
Chem 352, Lecture 9: Photosynthesis 7

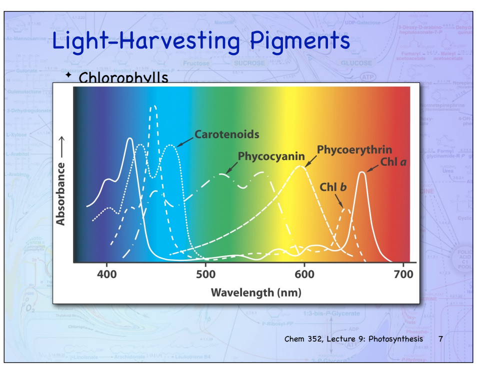
7-5


Light-Harvesting Pigments
Chlorophylls
Carotenoids
Phycocyanin
Phycoerythrin
Chl a
Chl b
Absorbance
400
500
600
700
Wavelength (nm)
Chem 352, Lecture 9: Photosynthesis 7

7-6


Light-Harvesting Pigments
Antenna chlorophylls
hv
Special pair
Absorbance
Chem 352, Lecture 9: Photosynthesis 7

7-7


Light-Harvesting Pigments
Chlorophylls
Carotenoids
Phycocyanin
Phycoerythrin
Chl a
Chl b
Absorbance
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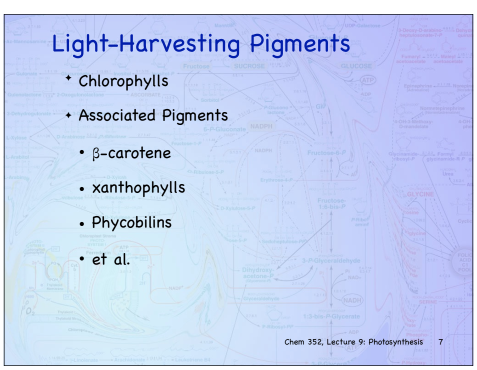
Wavelength (nm)
Chem 352, Lecture 9: Photosynthesis 7

7-8


Light-Harvesting Pigments
Chlorophylls
Associated Pigments
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xanthophylls
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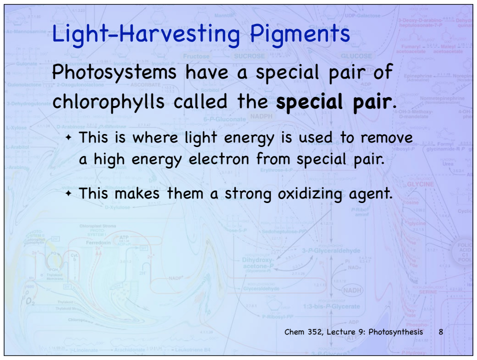
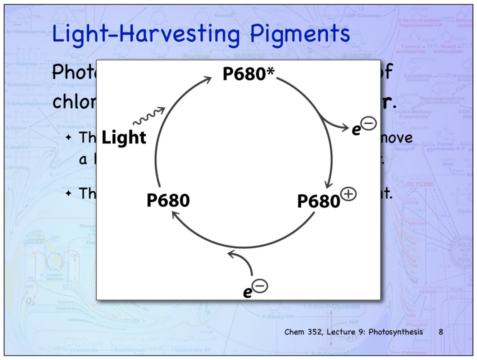
Chem 352, Lecture 9: Photosynthesis 7

7-9

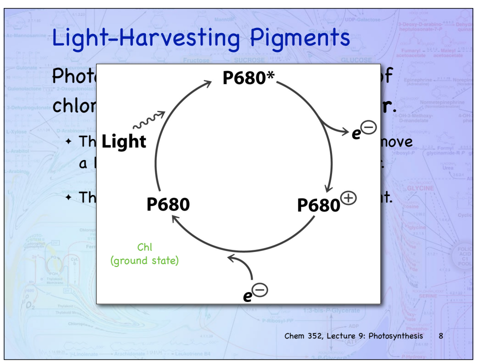
8-1


Light-Harvesting Pigments
Photosystems have a special pair of chlorophylls called the **special pair**.
This is where light energy is used to remove a high energy electron from special pair.
This makes them a strong oxidizing agent.
Chem 352, Lecture 9: Photosynthesis 8

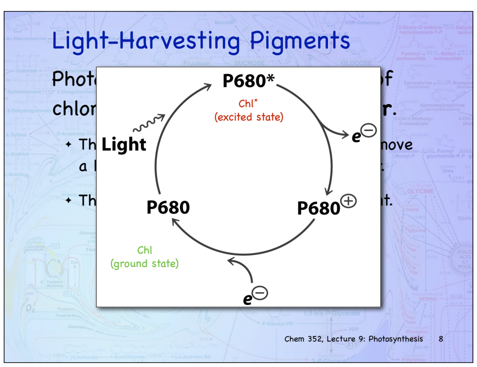
8-2


Light-Harvesting Pigments
P680*
Light
e⊖
P680
P680⊕
e⊖
Chem 352, Lecture 9: Photosynthesis 8

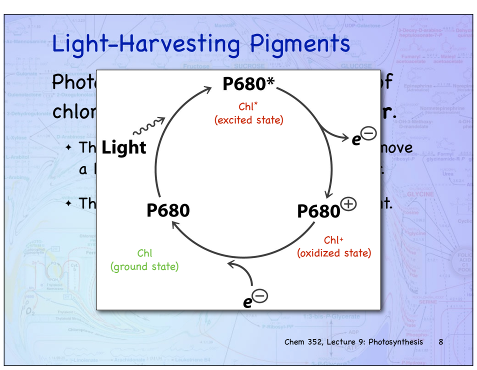
8-3


Light-Harvesting Pigments
P680*
Light
e⊖
P680
P680⊕
Chl
(ground state)
e⊖
Chem 352, Lecture 9: Photosynthesis 8

8-4


Light-Harvesting Pigments
P680*
Chl*
(excited state)
Light
e⊖
P680
P680⊕
Chl
(ground state)
e⊖
Chem 352, Lecture 9: Photosynthesis 8

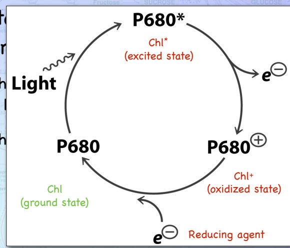
8-5


Light-Harvesting Pigments
P680*
Chl*
(excited state)
Light
e⊖
P680
P680⊕
Chl
(ground state)
Chl+
(oxidized state)
e⊖
Chem 352, Lecture 9: Photosynthesis 8

Light-Harvesting Pigments

Phot ... f
chlor ... r.

- Th ... move
  a ...
- Th ... t.



8-6

Photosystem II (PSII)

Two related photosystems have evolved in the the last 2.8 billion years.

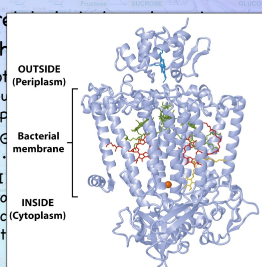
- Photosystem II (PSII)
  - Found in
    - Purple bacteria
    - Green filamentous bacteria
      - both are strict anaerobes
- PSII is combined with cytochrome bc to create a proton gradient that is used to synthesize ATP.
  - cytochrome bc is complex III from the electron transport chain.

9-1

Photosystem II (PSII)

Two re ... volved in
the th

- Phot
  - Fou
- PSII ... reate a
  proto ... ATP.
  - c ... e electron
    t

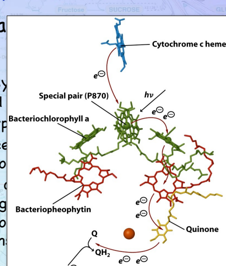


9-2

Photosystem II (PSII)

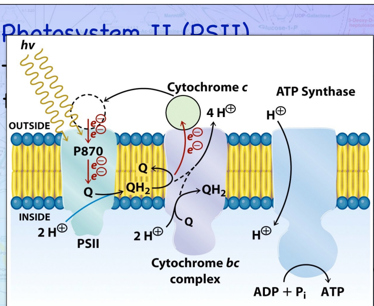
Two rela ... evolved in
the the

- Photosy
  - Found
    - Purp
    - Gree
      - bo
- PSII is ... create a
  proton g ... ze ATP.
  - cyto ... he electron
    tran



9-3

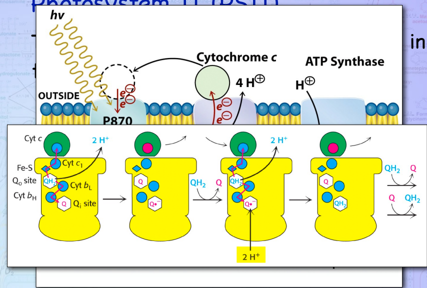
Photosystem II (PSII)



9-4

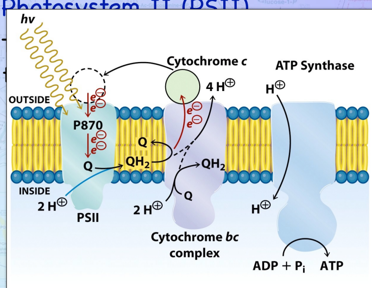
9-5

Photosystem II (PSII)



9-6

Photosystem II (PSII)



9-7

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9-8

Photosystem II (PSII)

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- Photosystem II (PSII)
  - Found in

Table 15.1 Photosystem II reactions

PSII:	$2\ P870 + 2\ photons \longrightarrow 2\ P870^{\oplus} + 2\ e^{\ominus}$
	$Q + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow QH_2$
Cyt bc_1:	$2\ QH_2 + 2\ cyt\ c\ (Fe^{3+}) \longrightarrow 2\ Q + 2\ cyt\ c\ (Fe^{2+}) + 4\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$Q + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow QH_2$
PSII:	$2\ cyt\ c\ (Fe^{2+}) + 2\ P870^{\oplus} \longrightarrow 2\ cyt\ c\ (Fe^{3+}) + 2\ P870$
Sum:	$2\ photons + 4\ H^{\oplus}_{in} \longrightarrow 4\ H^{\oplus}_{out}$

9-9

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10-1

Photosystem I (PSI)

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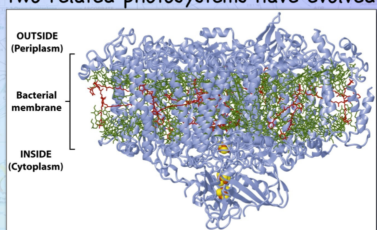
  - Creates either a proton gradient that is used to synthesize ATP.
    - or reduces $NADP^+$ to NADPH + H^+.

10-2

Photosystem I (PSI)

Two related photosystems have evolved



10-3

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10-4

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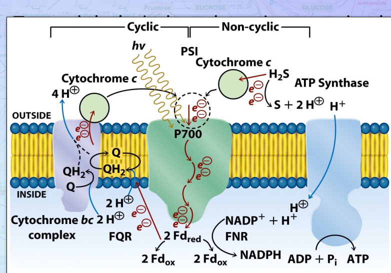


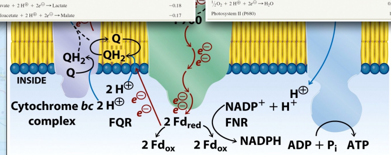
10-5

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

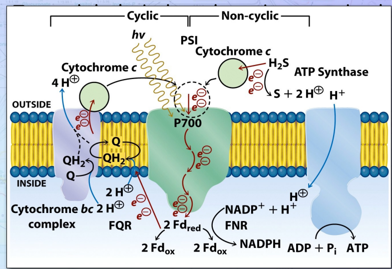
Reduction half-reaction	$E^{\circ\prime}$ (V)
Acetyl CoA + CO_2 + $H^{\oplus}$ + $2e^{\ominus}$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	−0.43
2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^{\oplus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → NADPH + $H^{\oplus}$	−0.32
$NAD^{\oplus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → NADH + $H^{\oplus}$	−0.32
Lipoic acid + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Dihydrolipoic acid	−0.29
Glutathione (oxidized) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → 2 Glutathione (reduced)	−0.23
FAD + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $FADH_2$	−0.22
FMN + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $FMNH_2$	−0.22
Acetaldehyde + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Ethanol	−0.20
Pyruvate + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lactate	−0.18
Oxaloacetate + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Malate	−0.17

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Cytochrome b_5 (microsomal), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.02
Fumarate + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Succinate	0.03
Ubiquinone (Q) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → QH_2	0.04
Cytochrome *b* (mitochondrial), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.08
Cytochrome c_1, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.22
Cytochrome *c*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.23
Cytochrome *a*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.29
Cytochrome *f*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.36
Plastocyanin, Cu^{2+} + $e^{\ominus}$ → Cu^{+}	0.37
$NO_3^{\ominus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $NO_2^{\ominus}$ + H_2O	0.42
Photosystem I (P700)	0.43
Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2O	0.82
Photosystem II (P680)	1.1



Photosystem I (PSI)



10-6

Photosystem I (PSI)

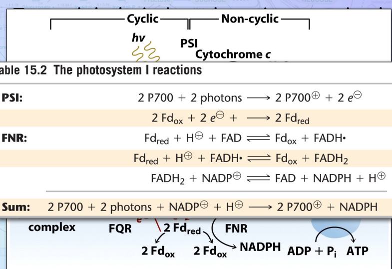
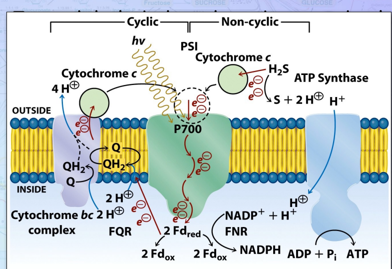


Table 15.2 The photosystem I reactions

PSI:	$2\ \text{P700} + 2\ \text{photons} \longrightarrow 2\ \text{P700}^{\oplus} + 2\ e^{\ominus}$
	$2\ \text{Fd}_{ox} + 2\ e^{\ominus} + \longrightarrow 2\ \text{Fd}_{red}$
FNR:	$\text{Fd}_{red} + \text{H}^{\oplus} + \text{FAD} \rightleftharpoons \text{Fd}_{ox} + \text{FADH}\bullet$
	$\text{Fd}_{red} + \text{H}^{\oplus} + \text{FADH}\bullet \rightleftharpoons \text{Fd}_{ox} + \text{FADH}_2$
	$\text{FADH}_2 + \text{NADP}^{\oplus} \rightleftharpoons \text{FAD} + \text{NADPH} + \text{H}^{\oplus}$
Sum:	$2\ \text{P700} + 2\ \text{photons} + \text{NADP}^{\oplus} + \text{H}^{\oplus} \longrightarrow 2\ \text{P700}^{\oplus} + \text{NADPH}$

10-7

Photosystem I (PSI)



10-8

Photosystem I (PSI)

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    - Green sulfur bacteria
  - Combines PSI with cytochrome bc
    - cytochrome bc is complex III from the electron transport chain.
  - Creates either a proton gradient that is used to synthesize ATP.
    - or reduces $NADP^+$ to NADPH + H^+.

10-9

The Evolution of Photosystems

Cyanobacteria coupled the two systems together.

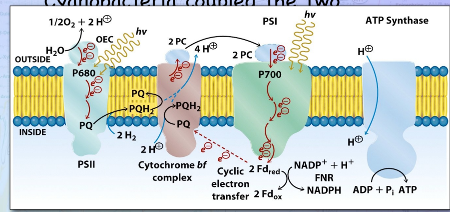
- An oxygen evolving complex evolved to supply the electrons to PSII
- Cytochrome bf (instead of cytochrome bc) is used to reoxidize plastoquinone (instead of ubiquinone) and reduce the blue copper protein, plastocyanin, or cytochrome c
- Plastocyanin (or cytochrome c) then reduces PSI, which in turn reduces $NADP^+$ to NADPH + H^+.

11-1

11-2

The Evolution of Photosystems

Cyanobacteria coupled the two



11-3

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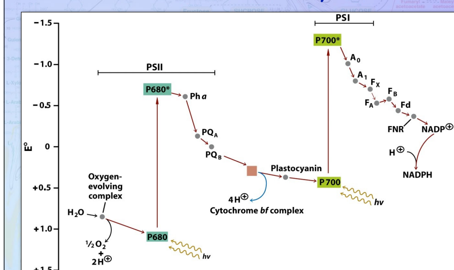
11-4

The Evolution of Photosystems



11-5

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11-6

The Evolution of Photosystems

Cyanobacteria coupled the two

Table 15.3 The photosynthesis reactions in species with both photosystems

PSII:	$2\ P680 + 2\ photons \longrightarrow 2\ P680^{\oplus} + 2\ e^{\ominus}$
	$PQ + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow PQH_2$
OEC:	$H_2O \longrightarrow \frac{1}{2}O_2 + 2\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$2\ P680^{\oplus} + 2\ e^{\ominus} \longrightarrow 2\ P680$
Cyt *bf*:	$2\ PQH_2 + 2\ plastocyanin\ (Cu^{2+}) \longrightarrow 2\ PQ + 2\ plastocyanin\ (Cu^{\oplus}) + 4\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$PQ + 2\ H^{\oplus}_{in} + 2\ e^{\ominus} \longrightarrow PQH_2$
PSI:	$2\ P700 + 2\ photons \longrightarrow 2\ P700^{\oplus} + 2\ e^{\ominus}$
	$2\ Fd_{ox} + 2\ e^{\ominus} \longrightarrow 2\ Fd_{red}$
	$2\ plastocyanin\ (Cu^{\oplus}) + 2\ P700^{\oplus} \longrightarrow 2\ plastocyanin\ (Cu^{2+}) + 2\ P700$
FNR:	$2\ Fd_{red} + H^{\oplus} + NADP^{\oplus} \rightleftharpoons 2\ Fd_{ox} + NADPH$
Sum:	$H_2O + 4\ photons + 4\ H^{\oplus}_{in} + NADP^{\oplus} + H^{\oplus} \longrightarrow \frac{1}{2}O_2 + 6\ H^{\oplus}_{out} + NADPH$

The Evolution of Photosystems

Cyanobacteria coupled the two systems together.

- An oxygen evolving complex evolved to supply the electrons to PSII
- Cytochrome bf (instead of cytochrome bc) is used to reoxidize plastoquinone (instead of ubiquinone) and reduce the blue copper protein, plastocyanin, or cytochrome c
- Plastocyanin (or cytochrome c) then reduces PSI, which in turn reduces $NADP^+$ to NADPH + H^+.

11-7

The Evolution of Photosystems

By coupling the two systems

- Cyanobacteria are able to produces both ATP and reduced NADPH + H^+.
- Use water as as its source of electrons.

12

Plant Photosynthesis

Plant photosynthesis takes place in organelles calls chloroplasts.

- The chloroplasts found in photo-synthesizing eukaryotes are believed to have evolved from cyanobacteria, which established a symbiotic relationship with eukaryotes

13-1

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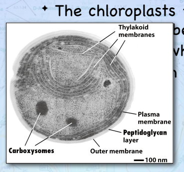

Cyanobacterium

13-2

Plant Photosynthesis

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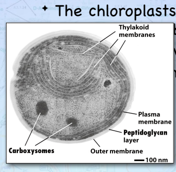
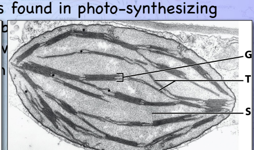
- The chloroplasts found in photo-synthesizing



Cyanobacterium



Chloroplast

13-3

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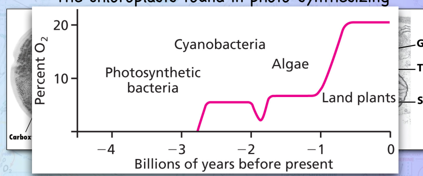
- The chloroplasts found in photo-synthesizing

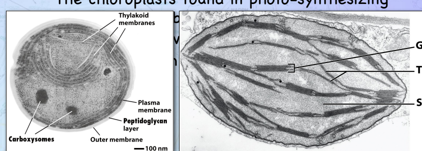


13-4

Plant Photosynthesis

Plant photosynthesis takes place in organelles calls chloroplasts.

- The chloroplasts found in photo-synthesizing



Cyanobacterium

Chloroplast

13-5

Plant Photosynthesis

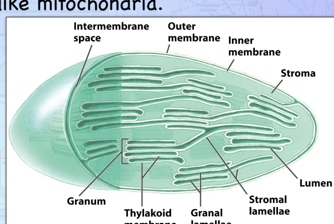
Plant photosynthesis takes place in organelles calls chloroplasts.

- The chloroplasts found in photo-synthesizing eukaryotes are believed to have evolved from cyanobacteria, which established a symbiotic relationship with eukaryotes

13-6

Plant Photosynthesis

- Chloroplasts have double membranes, like mitochondria.



14-1

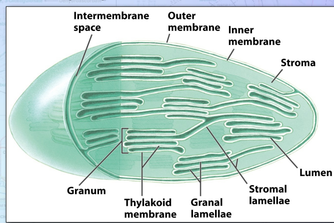
Plant Photosynthesis

- Chloroplasts have double membranes, like mitochondria.

14-2

Plant Photosynthesis

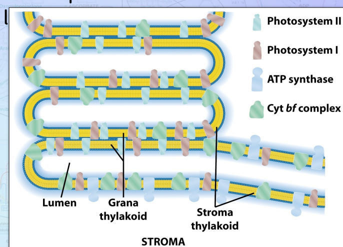
- Chloroplasts have double membranes, like mitochondria.



14-3

Plant Photosynthesis

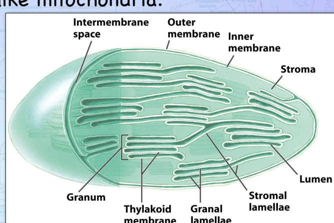
- Chloroplasts have double membranes,



14-4

Plant Photosynthesis

- Chloroplasts have double membranes, like mitochondria.



14-5

The Dark Reactions

- The **dark reactions** of photosynthesis use the ATP and reduced NADPH + H^+ from the light reactions to convert CO_2 and H_2O into glycolytic intermediates.
- Called the **Calvin Cycle**

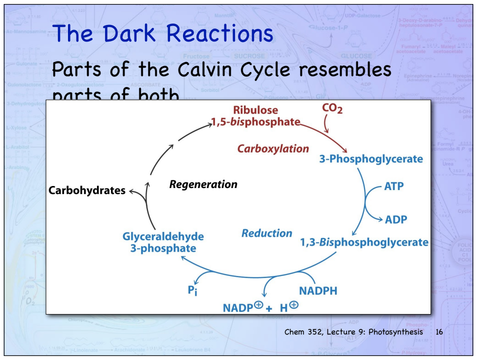
15

The Dark Reactions

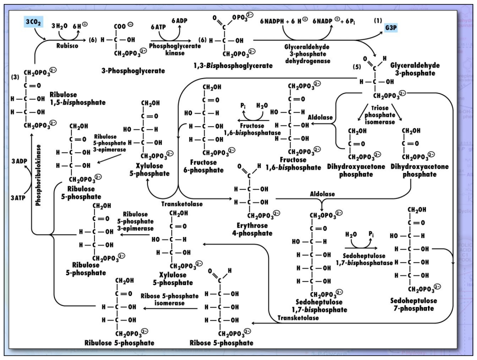
Parts of the Calvin Cycle resembles parts of both

- Gluconeogenesis (Reduction)
- Nonoxidative phase of the Pentose Phosphate Pathway (Regeneration)

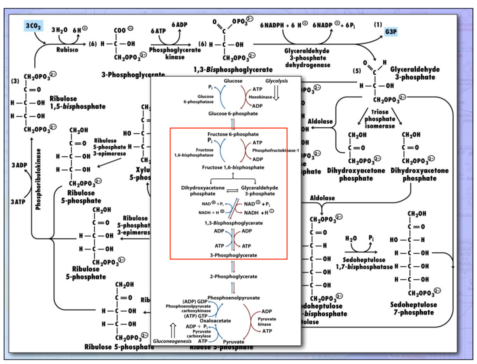
16-1



16-2



16-3



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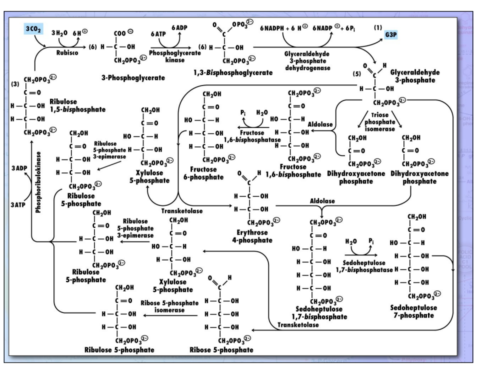
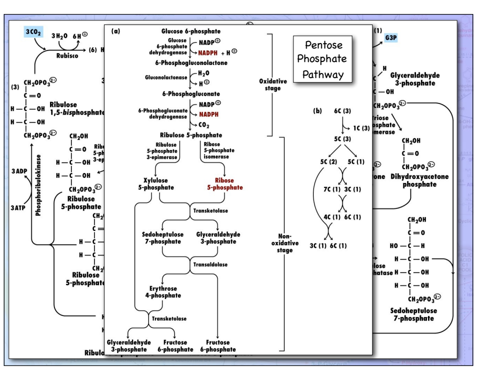
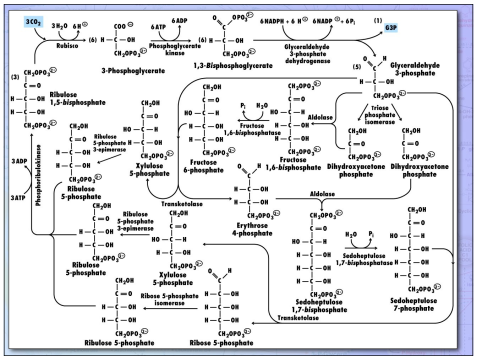


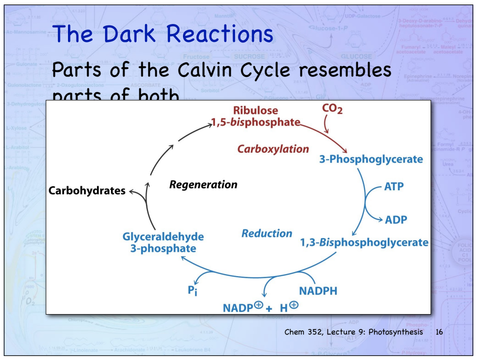
16-5



16-6



16-7



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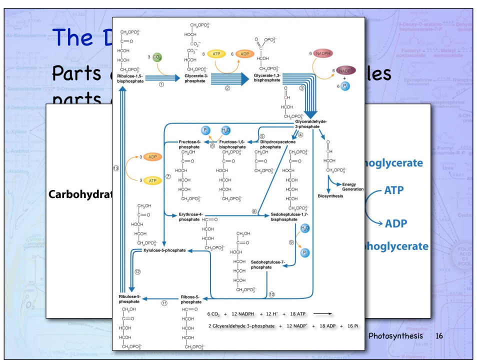
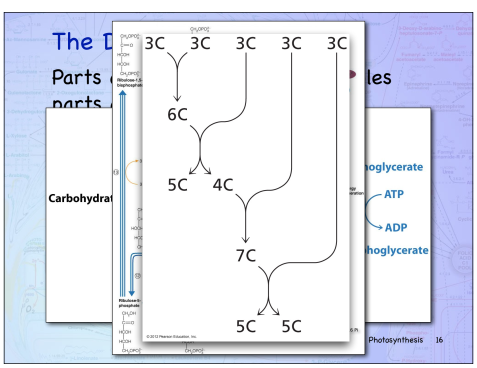
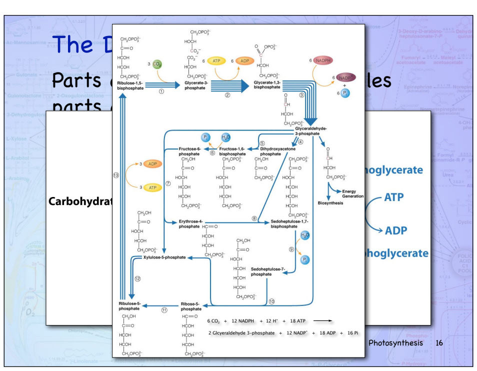


16-9



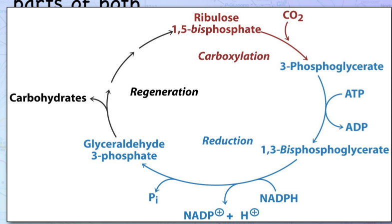
16-10



16-11

The Dark Reactions

Parts of the Calvin Cycle resembles parts of both



Chem 352, Lecture 9: Photosynthesis 16

16-12

The Dark Reactions

Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

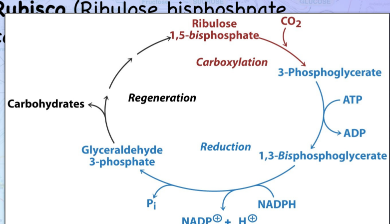
- 50% of soluble protein in leaves is rubisco
- Very inefficient ($k_{cat} \approx 3\ s^{-1}$)
- Nearly every organic-based carbon on earth has passed through the active site of this enzyme.

Chem 352, Lecture 9: Photosynthesis 17

17-1

The Dark Reactions

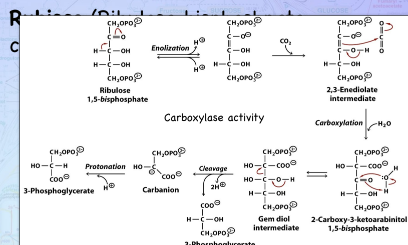
Rubisco (Ribulose bisphoshpate



Chem 352, Lecture 9: Photosynthesis 17

17-2

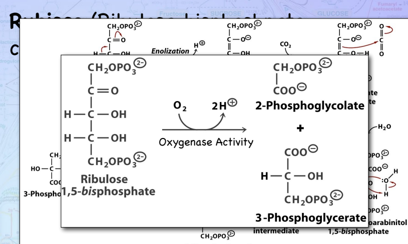
The Dark Reactions



Chem 352, Lecture 9: Photosynthesis 17

17-3

The Dark Reactions



Chem 352, Lecture 9: Photosynthesis 17

17-4

The Dark Reactions

Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

- The oxygenase activity is inefficient
  - It consumes ATP and NADPH + H^+
  - It consumes O_2
  - The metabolism of the 2-Phosphoglycerate leads to the release of CO_2
- Is called **photorespiration**
- Some plants, called C_4 plants, can counteract the oxygenase activity by concentrating CO_2 in the leaf cells.

18-1

The Dark Reactions

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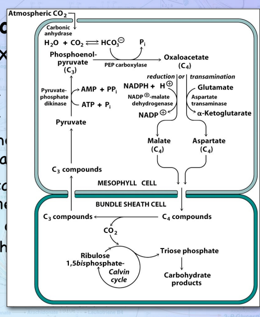

18-2

The Dark Reactions

Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

- The oxygenase activity is inefficient
  - It consumes ATP and NADPH + H^+
  - It consumes O_2
  - The metabolism of the 2-Phosphoglycerate leads to the release of CO_2
- Is called **photorespiration**
- Some plants, called C_4 plants, can counteract the oxygenase activity by concentrating CO_2 in the leaf cells.

18-3

The Dark Reactions

- **Rubisco** (Ribulose bisphoshpate carboxylase/oxygenase
  - The oxygenase activity is inefficient
    - It consumes ATP and NADPH + H^+
    - It consumes O_2
    - The metabolism of the 2-Phosphoglycerate leads to the release of CO_2
  - Is called **photorespiration**
  - Xerophilic plants, such as cactus and pineapples, reduce their H_2O loss during the day by storing up CO_2 during the night using the CAM pathway.

19-1

The Dark Reactions

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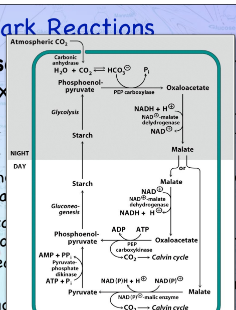

19-2

The Dark Reactions

- **Rubisco** (Ribulose bisphoshpate carboxylase/oxygenase
  - The oxygenase activity is inefficient
    - It consumes ATP and NADPH + H^+
    - It consumes O_2
    - The metabolism of the 2-Phosphoglycerate leads to the release of CO_2
  - Is called **photorespiration**
  - Xerophilic plants, such as cactus and pineapples, reduce their H_2O loss during the day by storing up CO_2 during the night using the CAM pathway.

19-3

Next Up

- Lecture 10 - Lipid Metabolism (Moran et al., Chapter 16)

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