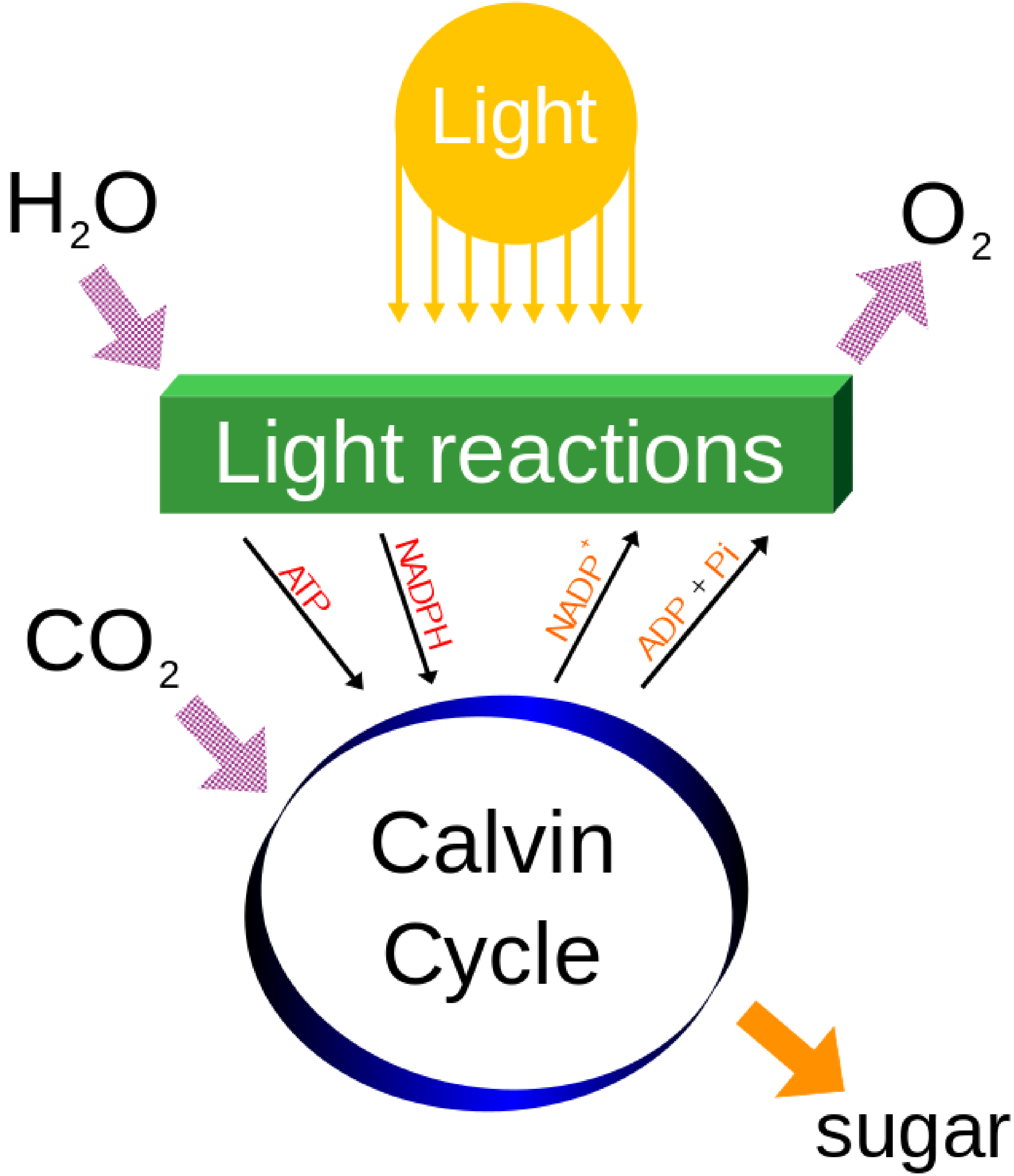
Chemistry 201

Bioenergetics

NC State University

Biochemical reduction potentials

Half-reaction	Δξ°'(V)
$CH_3COOH + 2 H^+ + 2 e^- \rightarrow CH_3CHO + H_2O$	-0.58
$2 H^+ + 2 e^- \rightarrow H_2$	-0.42
$NAD^+ + H^+ + 2 e^- \rightarrow NADH$	-0.320
$NADP^+ + H^+ + 2 e^- \rightarrow NADPH$	-0.320
$FAD + 2 H^+ + 2 e^- \rightarrow FADH_2$	-0.04
$O_2 + 2 H^+ + 2 e^- \rightarrow H_2O_2$	+0.30
$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$	+0.82
$P680^+ + e^- \rightarrow P680$	~ +1.0



Light
H_2O
O_2
Light reactions
ATP
NADPH
$NADP^+$
ADP + Pi
CO_2
Calvin Cycle
sugar

Bioenergetics: Photosynthesis

Biological oxidation-reduction occurs in photosynthesis.
The overall equation for the photosynthetic process may be expressed as:

$$6\ CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2\ \text{(glucose)}$$

The equation is the net result of two processes. One process involves the splitting of water. This process is really an oxidative process that requires light, and is often referred to as the **"light reaction“** in photosynthesis. This reaction may be written as:

$$12\ H_2O \rightarrow 6\ O_2 + 24\ H^+ + 24e^-$$

Bioenergetics: Photosynthesis

The oxidation of water is accompanied by a reduction reaction resulting in the formation of a compound, called nicotinamide adenine dinucleotide phosphate (NADPH). This reaction is shown below:

$$2\ NADP^+ + 2\ H_2O \rightarrow 2\ NADPH + 2\ H^+ + O_2$$

This reaction is linked or coupled to yet another reaction resulting in the formation of adenosine triphosphate, (ATP).

$$ADP + P_i \rightarrow ATP$$

The latter process is called **photophosphorylation** and requires the coupling of a proton gradient, which is generated by the light reactions.

Bioenergetics: Photosynthesis

Think of the **light reaction**, as a process by which organisms "capture and store" radiant energy as they produce oxygen gas. This energy is stored in the form of chemical bonds of compounds such as NADPH and ATP. The energy contained in both NADPH and ATP is then used to reduce carbon dioxide to glucose, a type of sugar ($C_6H_{12}O_6$). C

$$6\ CO_2 + 24\ H^+ + 24\ e^- \rightarrow C_6H_{12}O_6 + 6\ H_2O$$

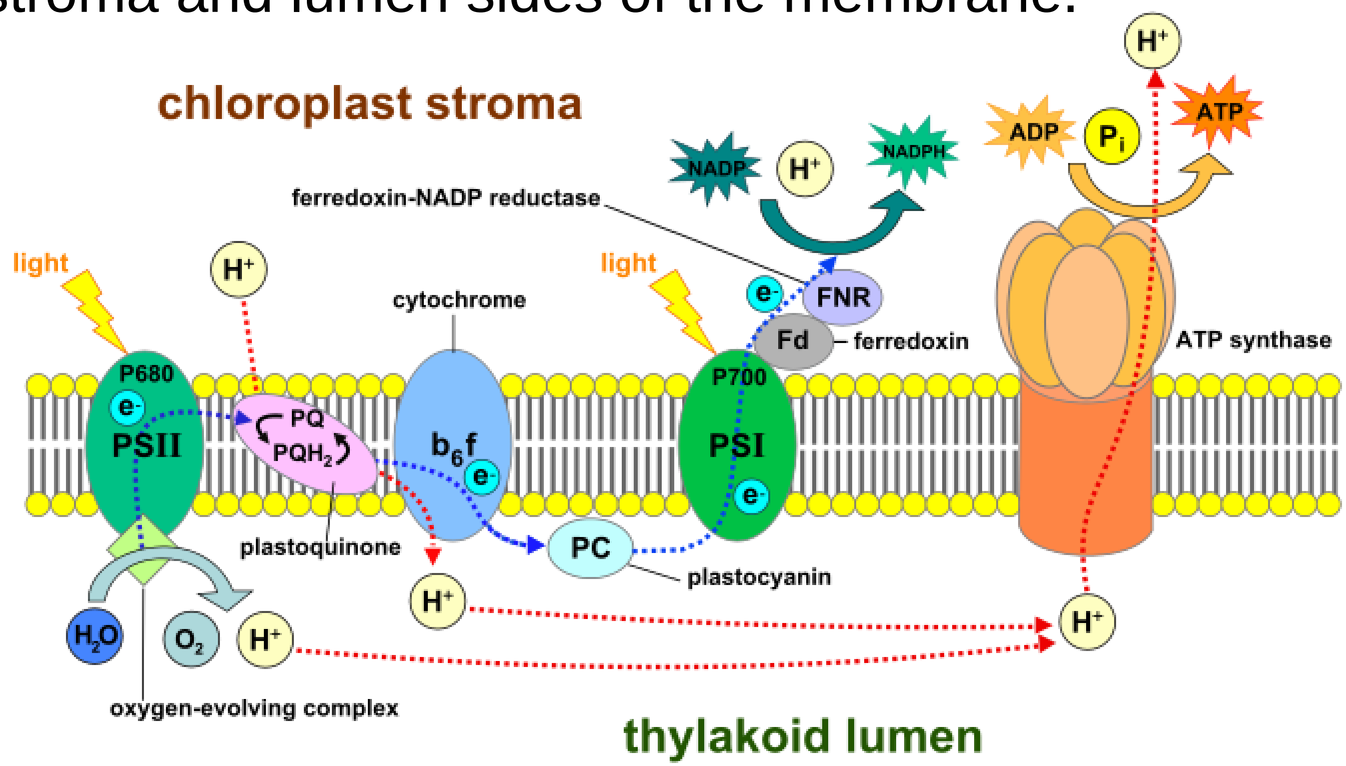
This is called the **dark reaction**.

The energy conversion is managed by the pumping hydrogen ions across a membrane. In plants this is called the thylakoid membrane and in photosynthetic bacteria it is the inner membrane.

Free energy of proton pumping across the thylakoid membrane

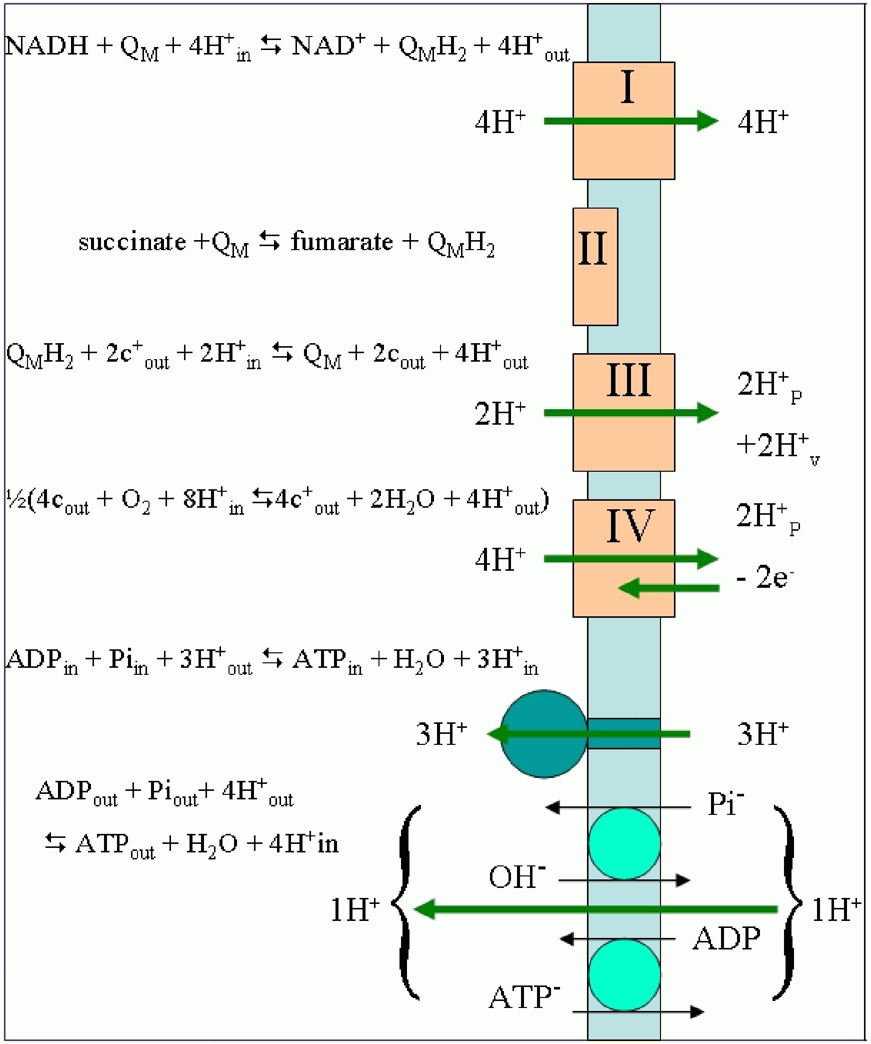
During photosynthesis, light energy from the sun is converted into a proton gradient across a membrane (the thylakoid membrane) . We can express the [H+] concentration as a pH on the stroma and lumen sides of the membrane.

Low pH



High pH

Proton pumps as the essence of energy storage in life



Application of the Nernst equation to membrane potential

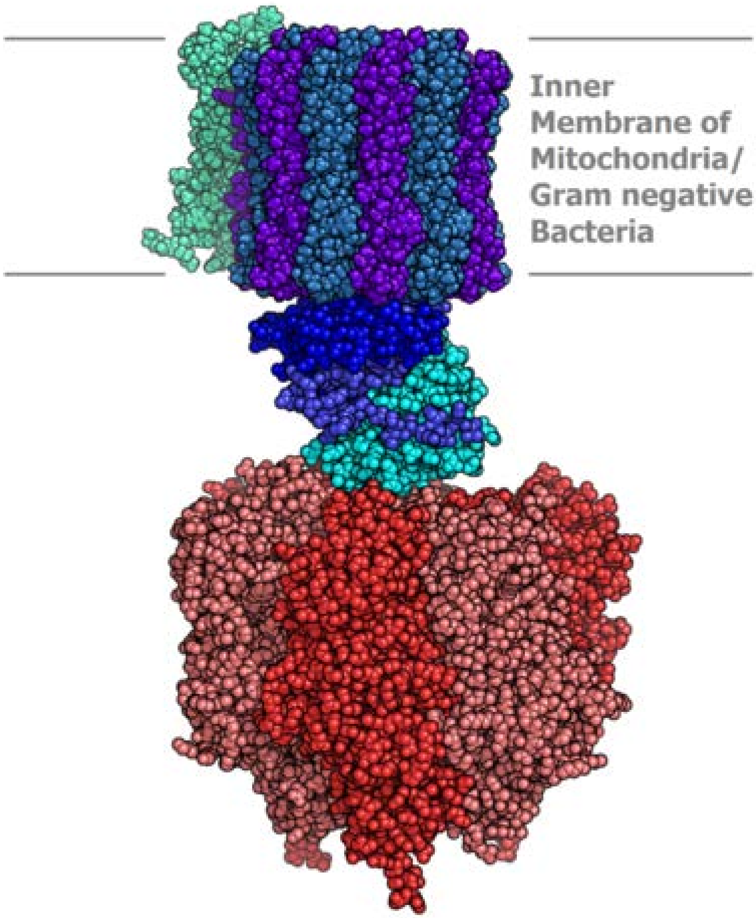
The free energy per mole of solute moved across the membrane ΔG_{conc} = -RTln(C_o/C_i) where C_o is the concentration outside the membrane and C_i is the concentration inside the membrane. The difference in charge concentration results in a free energy contribution from the voltage difference ΔG_{volt} = -FΔE (assuming n=1). The balance of forces at equilibrium requires that $\Delta G_{volt} = \Delta G_{conc}$ so that the trans-membrane potential is obtained as follows.

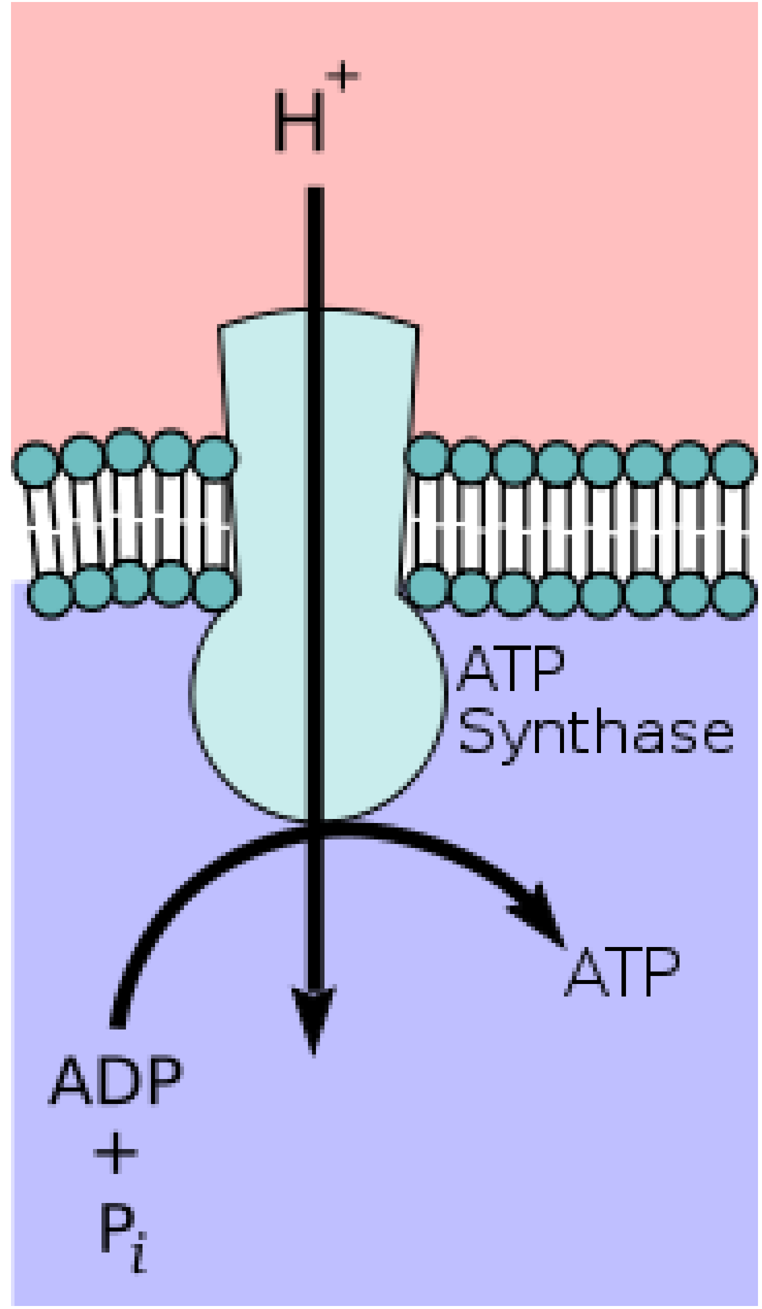
$$\Delta G_{volt} = \Delta G_{conc}$$

$$-F\Delta E = -RT \ln\left(\frac{C_o}{C_i}\right)$$

$$\Delta E = \frac{RT}{F} \ln\left(\frac{C_o}{C_i}\right)$$

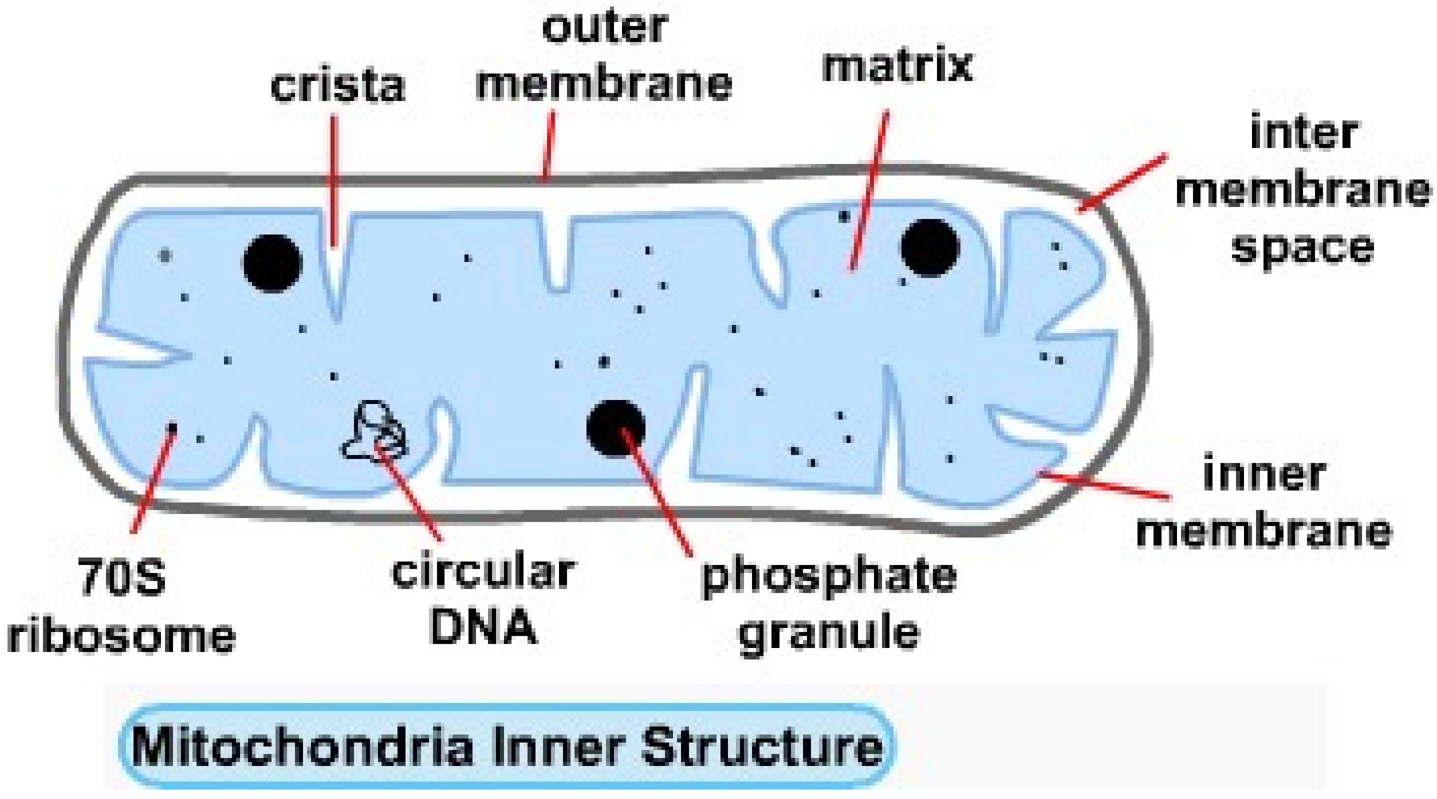
Structure of F_0-F_1 ATP Synthase





"ATP-Synthase" by Mitochondriale_Elektronentransportkette.svg. Licensed under Public Domain via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:ATP-Synthase.svg#/media/File:ATP-Synthase.svg

Mirochondrial respiration



Bioenergetics of respiration

The reduction potential of dark reaction is -0.42 V

$$6\, CO_2 + 24\, H^+ + 24\, e^- \rightarrow C_6H_{12}O_6 + 6\, H_2O \qquad E^0_{red} = -0.42\, V$$

In respiration, this process is linked to the consumption of oxygen to produce energy for the cell. We can estimate the amount of free energy that is available from respiration of one mole of glucose. The reduction potential of the oxygen half reaction is +0.82 V.

$$O_2 + 2\, H_2O + 4\, e^- \rightarrow 4\, OH^- \qquad E^0_{red} = +0.84\, V$$

These two reactions can be coupled by writing one of them as an oxidation.

The cell potential for respiration

We apply the same procedure as previously for inorganic reactions in an electrochemical cell. We write one of the reactions as an oxidation find the least common factor.

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 24\ H^+ + 24\ e^- \qquad E^0_{ox} = +0.42\ V$$

$$6(O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-) \qquad E^0_{red} = +0.82\ V$$

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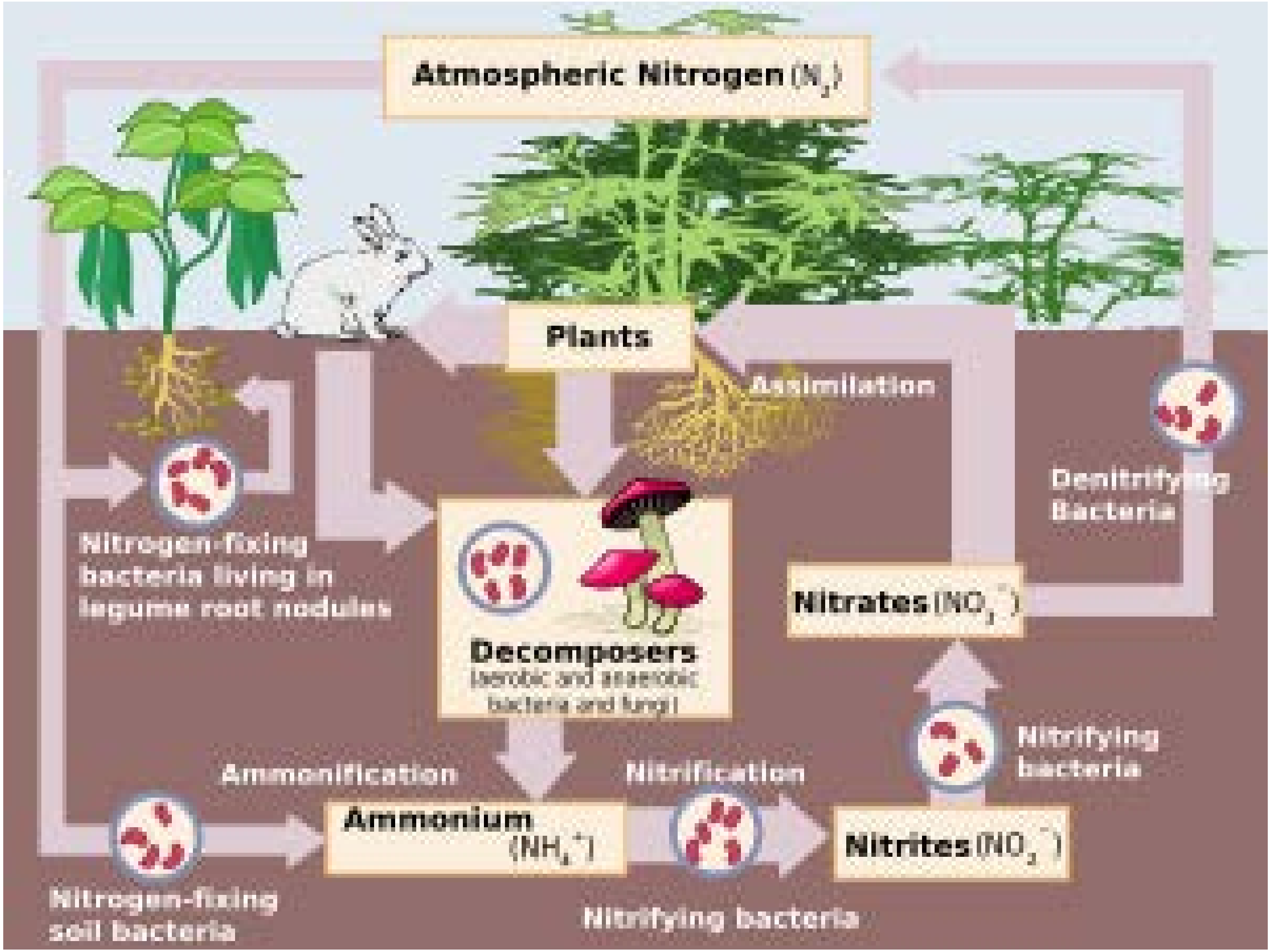
$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \qquad E^0_{cell} = +1.24\ V$$

From this electrochemical potential we can calculate the free energy change associated with respiration.

Nitrogen chemistry in living systems



Nitrogen fixation

Nitrogen is the most abundant element in our atmosphere. Nitrogen is a primary nutrient for all green plants and photo-synthetic bacteria, but it must be reduced to ammonia before it can be readily utilized by most living systems.

Nitrogen fixation is one process by which molecular nitrogen is reduced to form ammonia. This complex process is carried out by nitrogen-fixing bacteria present in the soil. Although nitrogen-fixation involves a number of oxidation-reduction reactions that occur sequentially, that reaction which describes its reduction can be written in a simplified way as:

$N_2 + 6\ e^- + 8H^+ \text{--->}\ 2\ NH_4^+$ (ammonium ion)

This reaction has a reduction potential of +0.092 V.

The role of ammonia

The ammonium ion (the conjugate acid of ammonia, NH_3) that is produced by this reaction is the form of nitrogen that is used by living systems in the synthesis of bio-organic compounds.

Another way by which ammonia may be formed is by the process called **nitrification**. In this process compounds called nitrates and nitrites, released by decaying organic matter are converted to ammonium ions by **nitrifying bacteria** present in the soil.

The Haber-Bosch process that we have discussed previously is an analog of these reactions developed by humans for use In production of fertilizer.

Nitrification

The process of nitrification carried out by bacteria is a complex series of oxidation-reduction reactions involving nitrate and nitrite ions, which can be simplified as:

$NO_3^- + 2e^- + 2H^+$ -----------> $NO_2^- + H_2O$

$NO_2^- + 6e^- + 2H^+$ ----------> $NH_4^+ + 2\ H_2O$

Another way in which molecular nitrogen is modified is via the discharge of lightning. The tremendous energy released by the electrical discharges in our atmosphere breaks bonds between nitrogen atoms, causing them to react with oxygen. Note in this process, nitrogen is oxidized and oxygen is reduced.

lightning $N_2 + O_2$ -------------> 2 NO (nitric oxide)

2 NO + O_2 ---------------> $2NO_2$ (nitrogen dioxide)

The nitrogen cycle

Nitrogen dioxide readily dissolves in water to product nitric and nitrous acids;

$2\ NO_2 + H_2O$ -------> $HNO_3 + HNO_2$

These acids readily release the hydrogen forming nitrate and nitrite ions which can be readily utilized by plants and micro-organisms.

HNO_3 --------> $H^+ + NO_3^-$ (nitrate ions)
HNO_2 --------> $H^+ + NO_2^-$ (nitrite ions)

Denitrifying bacteria, act on ammonia as well as nitrates produced by death and decay, recycling these compounds as free nitrogen (N_2).

The nitrogen cycle

The nitrogen that is fixed by the processes described above is eventually returned to the atmosphere by denitrification. This process completes the "nitrogen cycle".