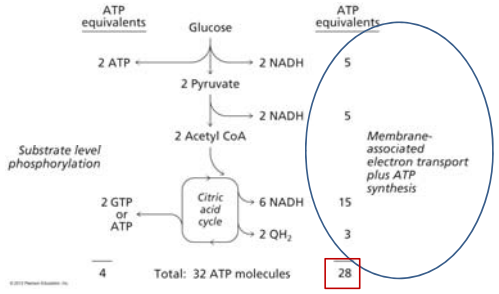
Electron Transport Chain

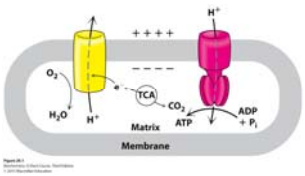
Chapter 20 Stryer Short Course

Substrate Level vs. Oxidative Phosphorylation



Overview

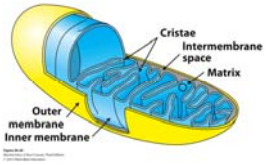
- Redox reactions
- Electron transport chain
- Proton gradient
- ATP synthesis
- Shuttles



Analogy: How does burning coal put flour in the grocery store?

Mitochondria

- Matrix
  - Citric acid cycle
  - NADH
- Inner membrane space



Redox Half Reactions

- Reduction potential written in terms of a reduction half reaction
- $A_{ox} \rightarrow A_{red}$
- Compared to a standard reaction
- Oxygen has high affinity to gain electrons: Reduction potential

$NAD^+ + H_2 \rightarrow NADH + 2\ H^+$

$NAD^+ \rightarrow NADH \quad E_o' = -0.32\ V$

NAD^+ has lower affinity for electrons than H^+
Not spontaneous

$Q + H_2 \rightarrow QH_2 + 2\ H^+$

$Q \rightarrow QH_2 \quad E_o' = +0.10\ V$

Q has higher affinity for electrons than H^+
Spontaneous

Standard Reduction Potential

Table 20.1 Standard reduction potentials of some reactions

Oxidant	Reductant	*n*	E_o' (V)
Succinate + CO_2	α-Ketoglutarate	2	−0.67
Acetate	Acetaldehyde	2	−0.60
Ferredoxin (oxidized)	Ferredoxin (reduced)	1	−0.43
$2\ H^+$	H_2	2	−0.42
NAD^+	NADH + H^+	2	−0.32
$NADP^+$	NADPH + H^+	2	−0.32
Lipoate (oxidized)	Lipoate (reduced)	2	−0.29
Glutathione (oxidized)	Glutathione (reduced)	2	−0.23
FAD	$FADH_2$	2	−0.22
Acetaldehyde	Ethanol	2	−0.20
Pyruvate	Lactate	2	−0.19
$2\ H^+$	H_2	2	0.00†
Cytochrome *b* (+3)	Cytochrome *b* (+2)	1	+0.07
Dehydroascorbate	Ascorbate	2	+0.08
Ubiquinone (oxidized)	Ubiquinone (reduced)	2	+0.10
Cytochrome *c* (+3)	Cytochrome *c* (+2)	1	+0.22
Fe (+3)	Fe (+2)	1	+0.77
$½\ O_2 + 2\ H^+$	H_2O	2	+0.82

Note: is the standard oxidation–reduction potential (pH 7, 25°C, except where noted), and *n* is the number of electrons transferred. refers to the partial reaction written as Oxidant + $e^- \rightarrow$ reductant
†Standard oxidation–reduction potential at pH = 0.

Table 20.1
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Redox Reactions

- Using standard half reactions, can determine spontaneity of any redox reaction
- Determine $\Delta E_o'$
- Determine $\Delta G^{o\prime}$

$$A_{oxidized} + B_{reduced} \rightleftharpoons A_{reduced} + B_{oxidized}$$

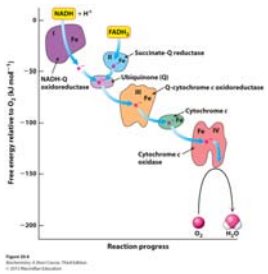
$$FADH_2 \text{ (reduced)} + Q \text{ (oxidized)} \rightleftharpoons FAD \text{ (oxidized)} + QH_2 \text{ (reduced)}$$

FAD → $FADH_2$ $E_o' = -0.22$ V
Flip
$FADH_2$ → FAD $E_o' = +0.22$ V
Q → QH_2 $E_o' = +0.10$ V

$FADH_2 + Q \rightarrow FAD + QH_2$ $E_o' = +0.32$ V

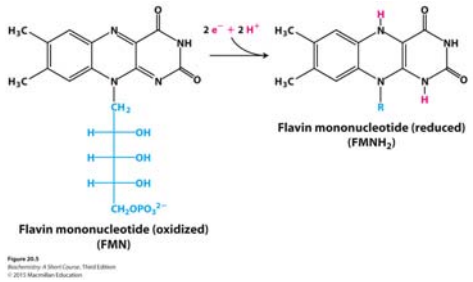
$\Delta G^{o\prime} = -n\ F\ \Delta E_o'$ where n = # e- and F = 96.48 kJ/mol V

Passing electrons down the wire



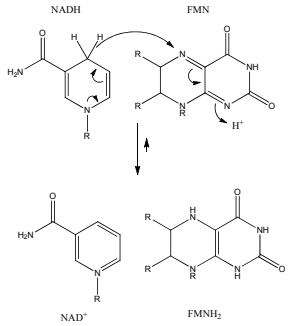
- O_2: high "reduction potential"
- Substrates
  - Organic cofactors
  - Metals (iron/sulfur clusters)
  - cytochromes

FMN



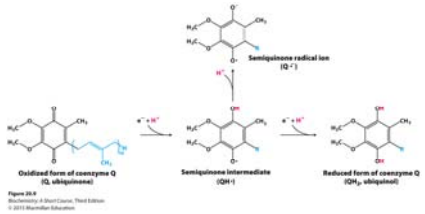
Redox reactions: electricity

- 2 e- transfer



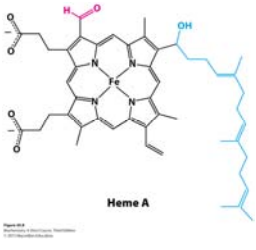
Coenzyme Q: Mobile Carrier

- $FADH_2$ is a one e- donor
- Many reactions, including metals
- Ubiquinone is a key intermediate
- Can diffuse through nonpolar regions easily



Metals

- Iron clusters
- cytochromes
- Accept/donate 1 electron at a time



Oxygen: the final electron acceptor

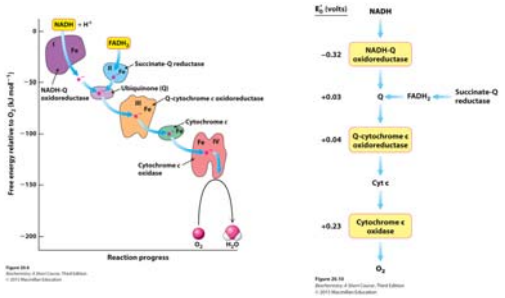
- Water is produced—has very low reactivity, very stable
- Superoxide, peroxide as Reactive Oxygen Species
- Superoxide dismutase, catalase, vitamin E

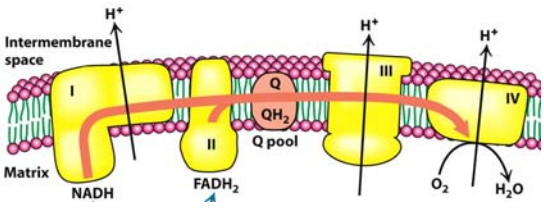
$$O_2 + 4\,e^{\ominus} + 4\,H^{\oplus}_{in} \longrightarrow 2\,H_2O$$

- Overall reaction

  $NADH + H^+ + ½\ O_2 \rightarrow NAD^+ + H_2O$

Electron Transport Chain

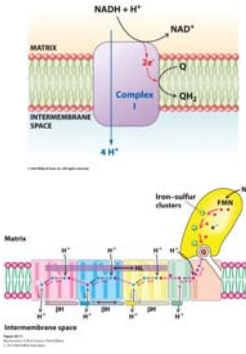




- $NADH + H^+ + ½\ O_2 \rightarrow NAD^+ + H_2O$ + 10 H^+ pumped
- $succinate + ½\ O_2 \rightarrow fumarate + H_2O$ + 6 H^+ pumped

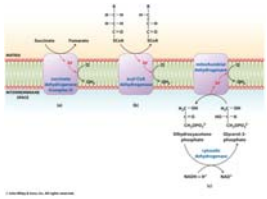
Complex I

- NADH → Q through
  - FMN
  - Iron-sulfur clusters
- "Q pool"
- 4 protons pumped through conformational change induced by Q → QH2



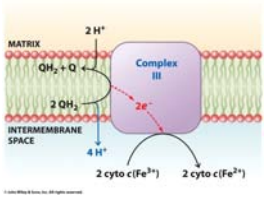
Complex II

- Non-NADH sources
  - Complex II (citric acid cycle)
  - Fatty acid oxidation and Glycerol-3-phosphate shuttle: next chapter
- Bypasses Complex I
  - Loss of 4 protons pumped
- Electrons into Q pool



Complex III

- QH_2 → cytochrome c in the intermembrane space
- 4 protons pumped
- Through Q cycle



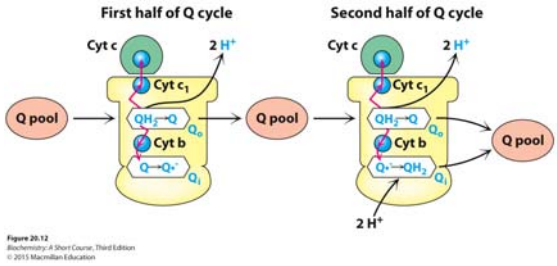


Figure 20.12
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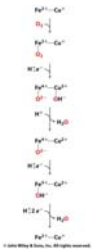
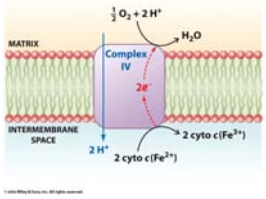
Complex IV

- Cytochromes → O_2
- Stoichiometry of half of an oxygen atom





Overall

- 10 protons shuttled from matrix to intermembrane space
- Makes pH gradient and ion gradient
- Store of potential energy to run ATP-making machine