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Chapter 20: The Electron Transport Chain

Do Problems 1,2,4,6,8-13,16,17,19.

Overview of oxidative phosphorylation

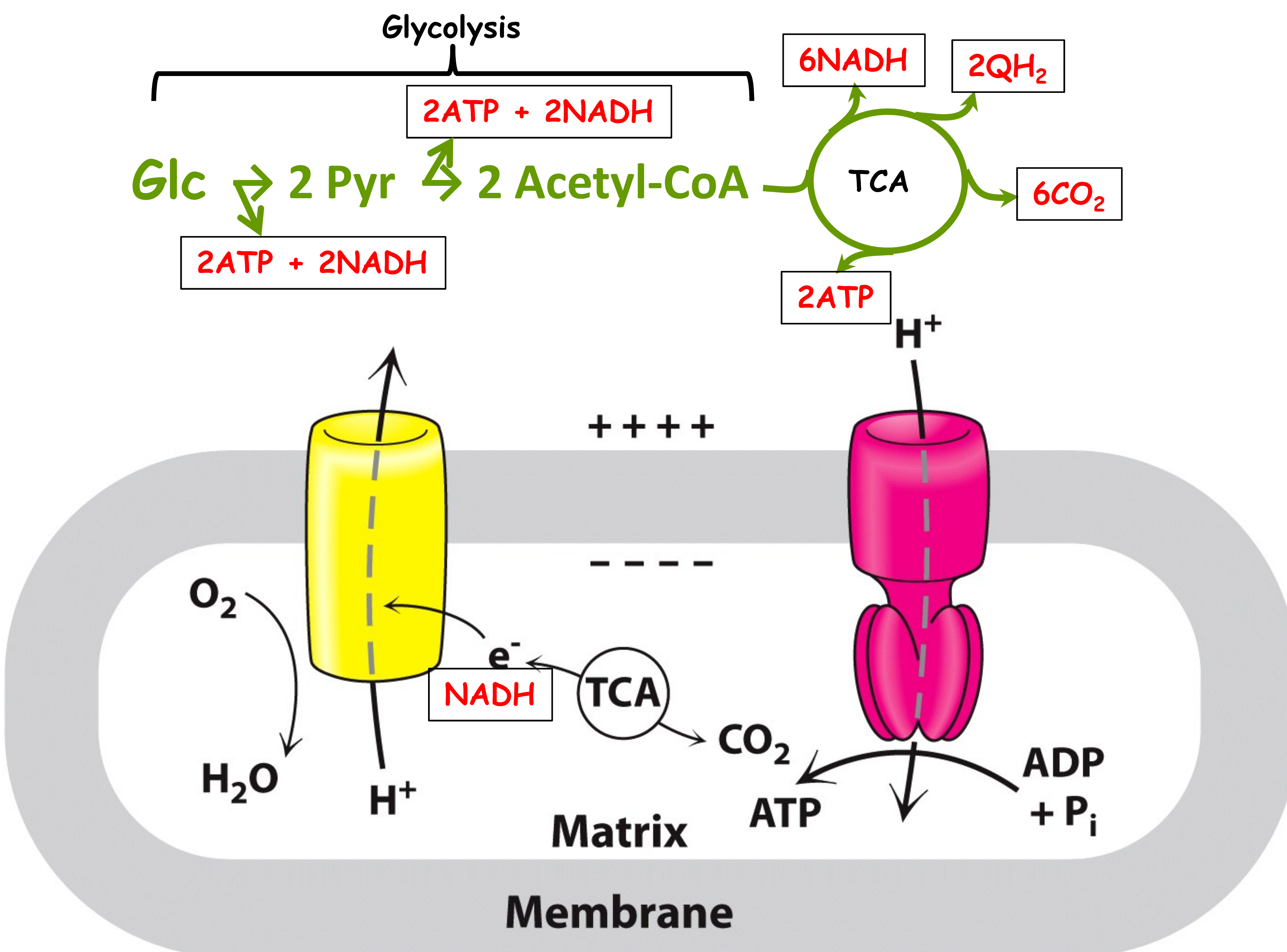

Figure 20.1
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20.1 OxPhos Takes Place in The Mitochondrion

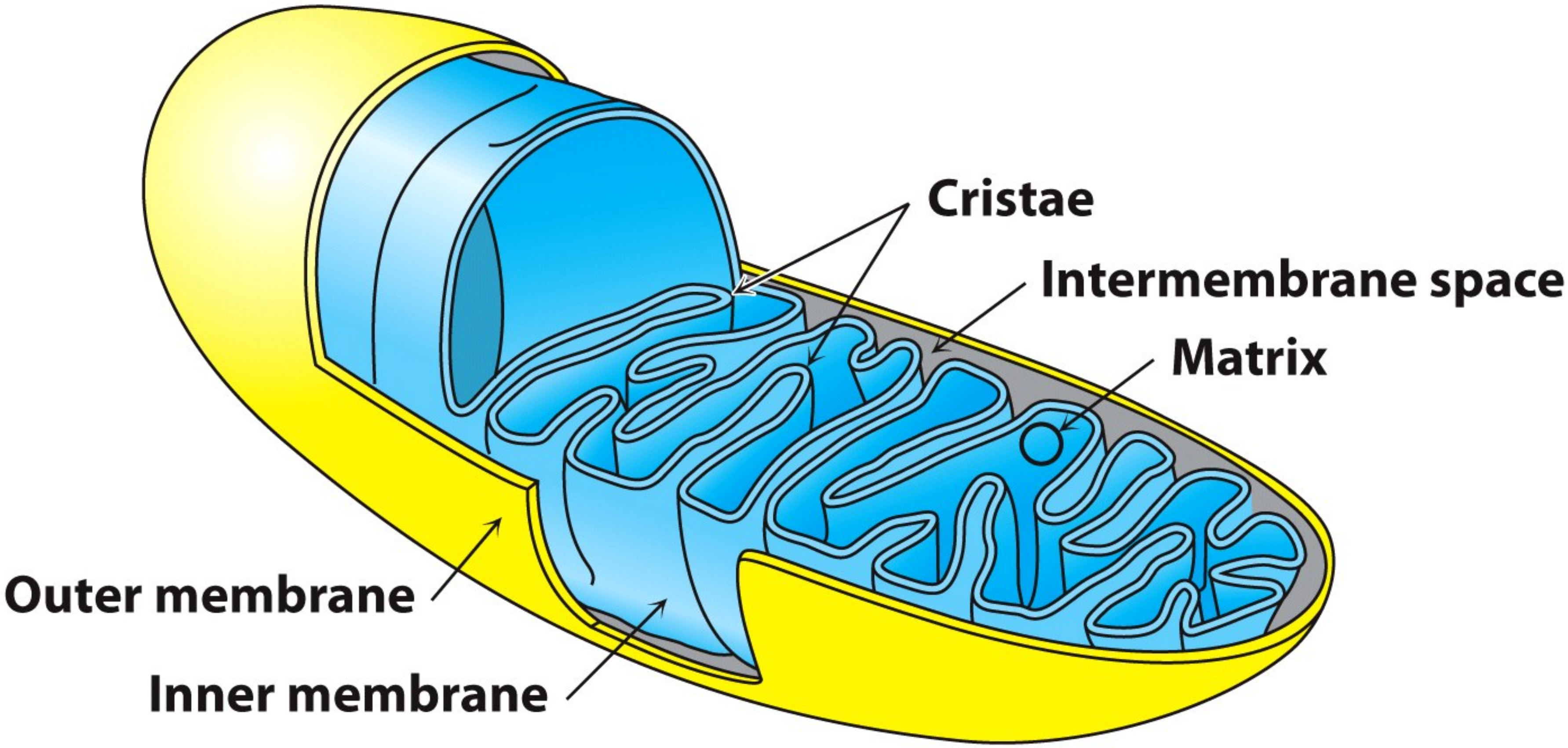

Figure 20.2b
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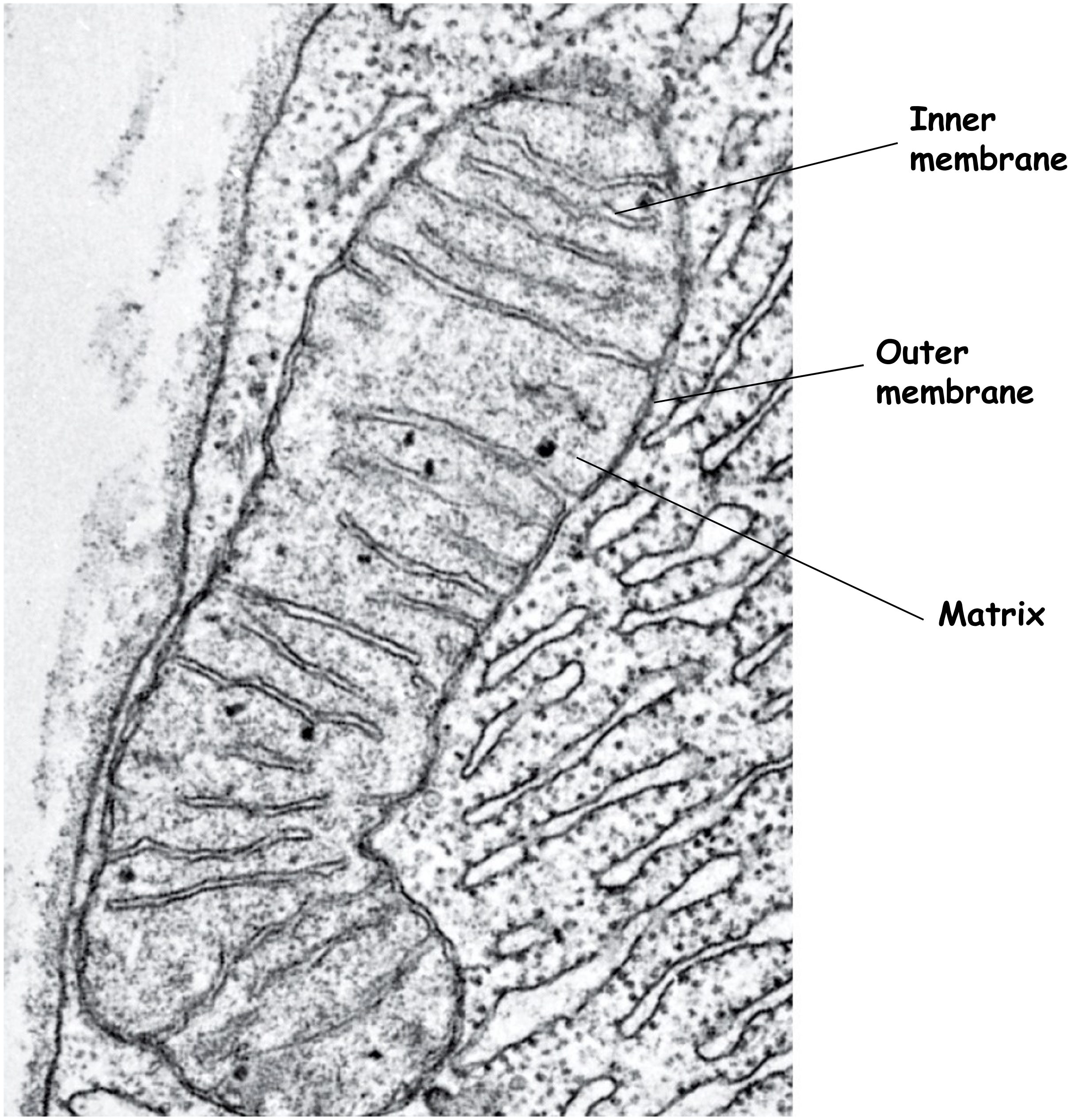

Figure 20.2a
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20.2 OxPhos Depends on e- Transfer

- **Protonmotive force** is the energy created by the proton concentration gradient formed across the mitochondria inner membrane.

- H^+ flow forms a circuit (similar to an electrical circuit).

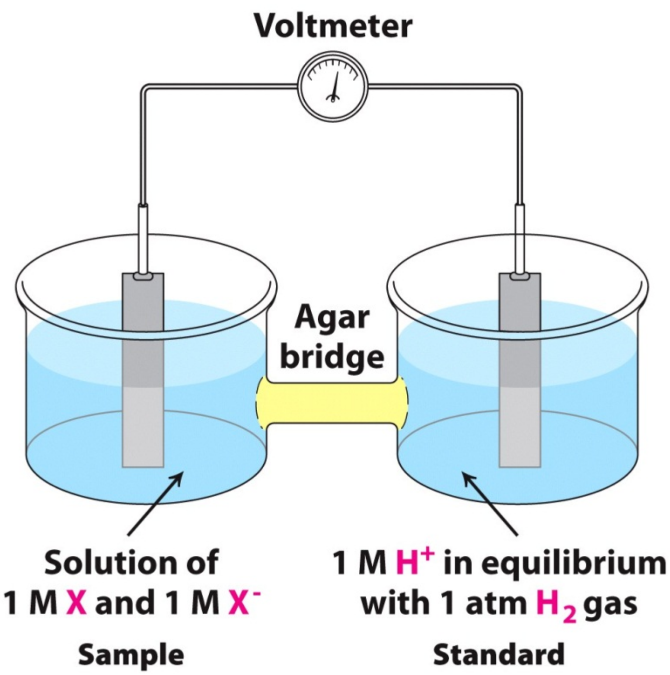

Figure 20.4
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Energy Potential Across Membrane is Formed by a Proton Gradient

$X^- + H^+ \rightarrow X + \frac{1}{2}H_2$

$$\boxed{\begin{array}{l} X^- \rightarrow X + e^- \\ H^+ + e^- \rightarrow H_2 \end{array}}$$

$\Delta G^{o\prime} = -nF\Delta E'_0$

n = number of electrons translocated; 2

F = Faraday's Constant, 96.48 kJ/mol/V, or 23.06 kcal/mol/V

e^- Transport Chain Components and Energetics

Downhill Energy Process

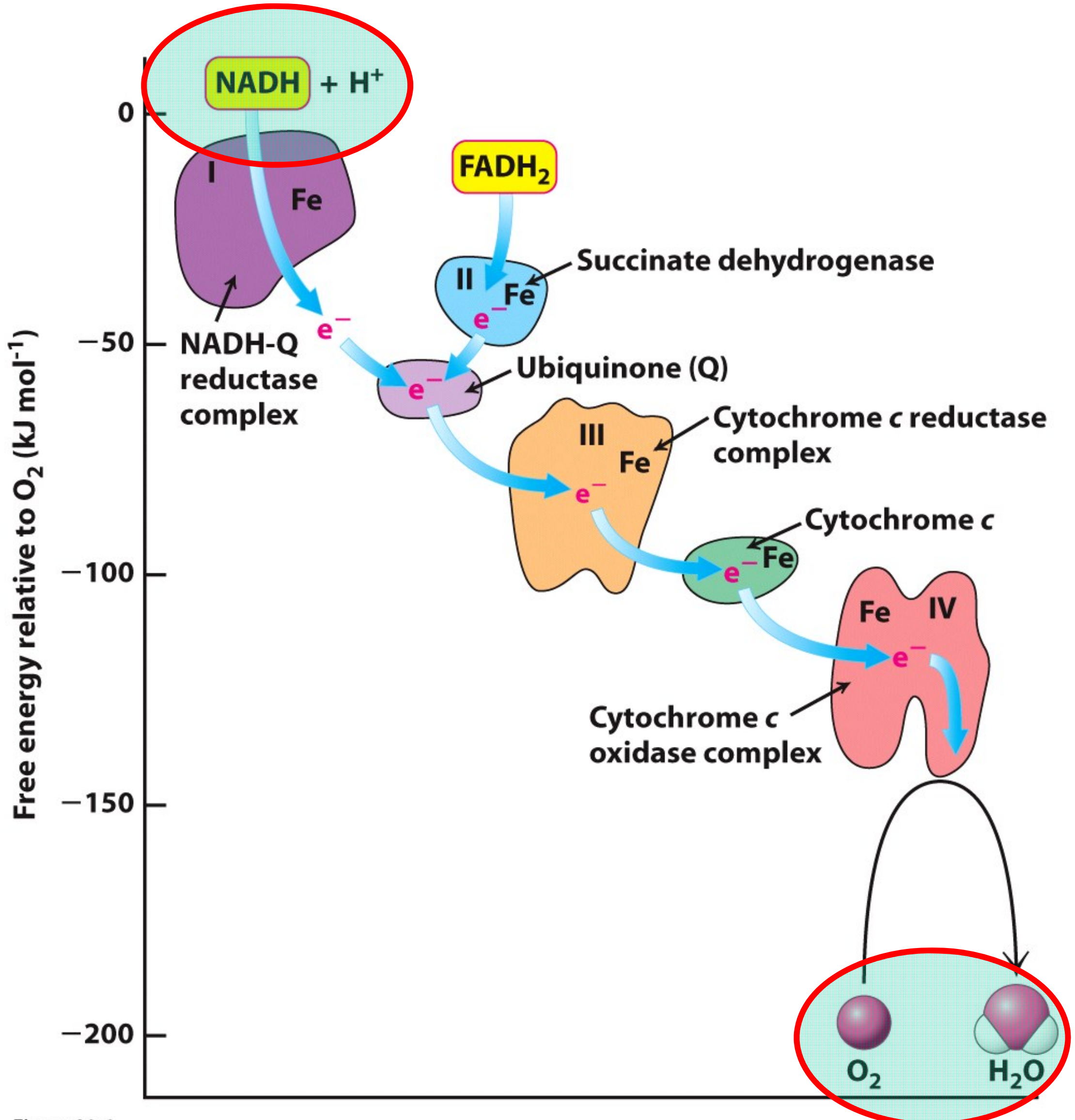

Figure 20.6
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Overall Net Reaction

$$NADH + \tfrac{1}{2}O_2 + H^+ \rightarrow H_2O + NAD^+$$

		$\underline{E'_0}$
$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$		$+0.82V$
$NAD^+ + H^+ + 2e^-$	$NADH$	$-0.32V$

Table 20.1 Standard reduction potentials of some reactions

Oxidant	Reductant	*n*	E'_0(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[1]
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
$^1/_2\, O_2 + 2\, H^+$	H_2O	2	+0.82

Note: E'_0 is the standard oxidation–reduction potential (pH 7, 25°C, except where noted) and *n* is the number of electrons transferred. E'_0 refers to the partial reaction written as

Oxidant + $e^- \rightarrow$ reductant

[1]Standard oxidation–reduction potential at pH = 0.

Table 20.1
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$$\Delta G^{o\prime} = -nF\Delta E'_0$$

$$= -2(96.48 \text{ Kj/mol/V})$$

$$(0.82V - (-0.32V))$$

$$= -2(96.48\text{Kj/mol/V})(1.14V)$$

$$= -220\text{Kj/mol} = 52.6\text{kcal/mol}$$

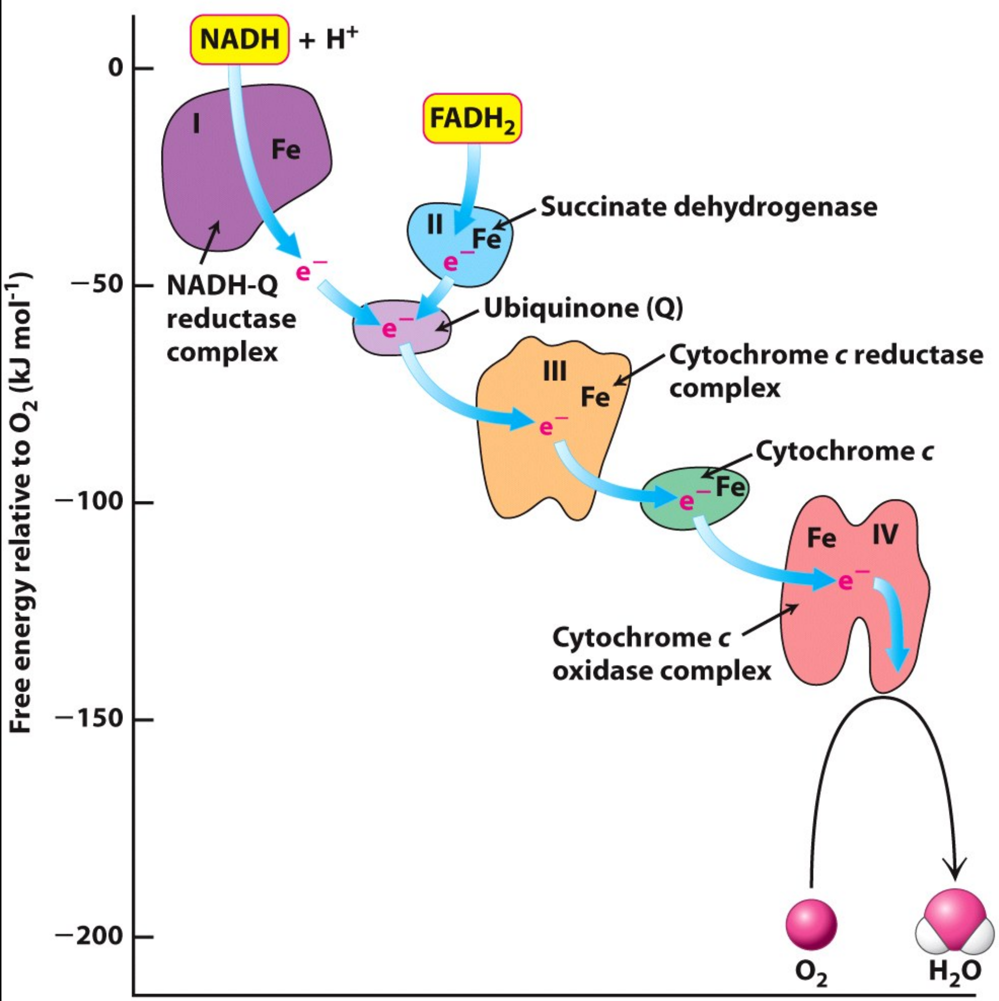

Figure 20.6
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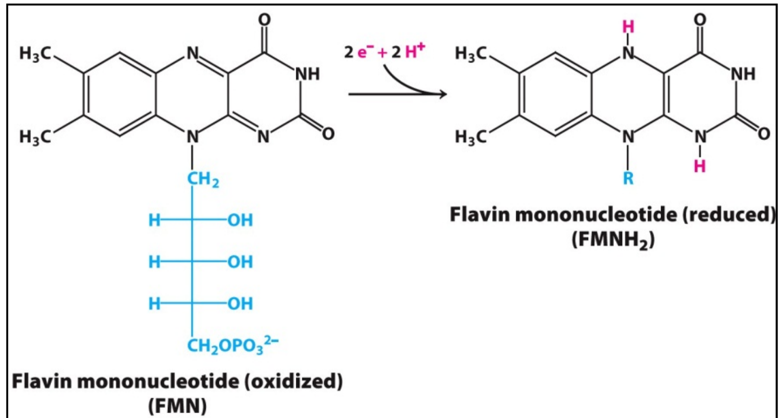

Figure 20.5
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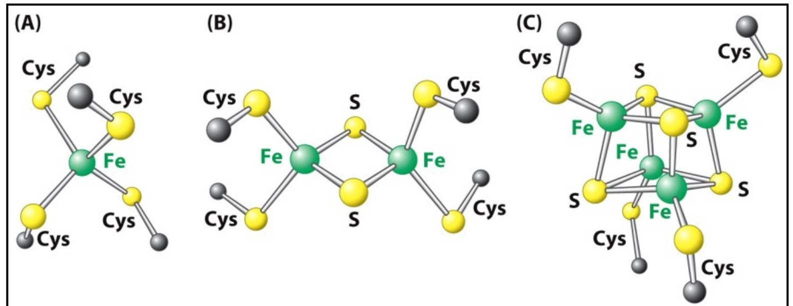

Figure 20.7
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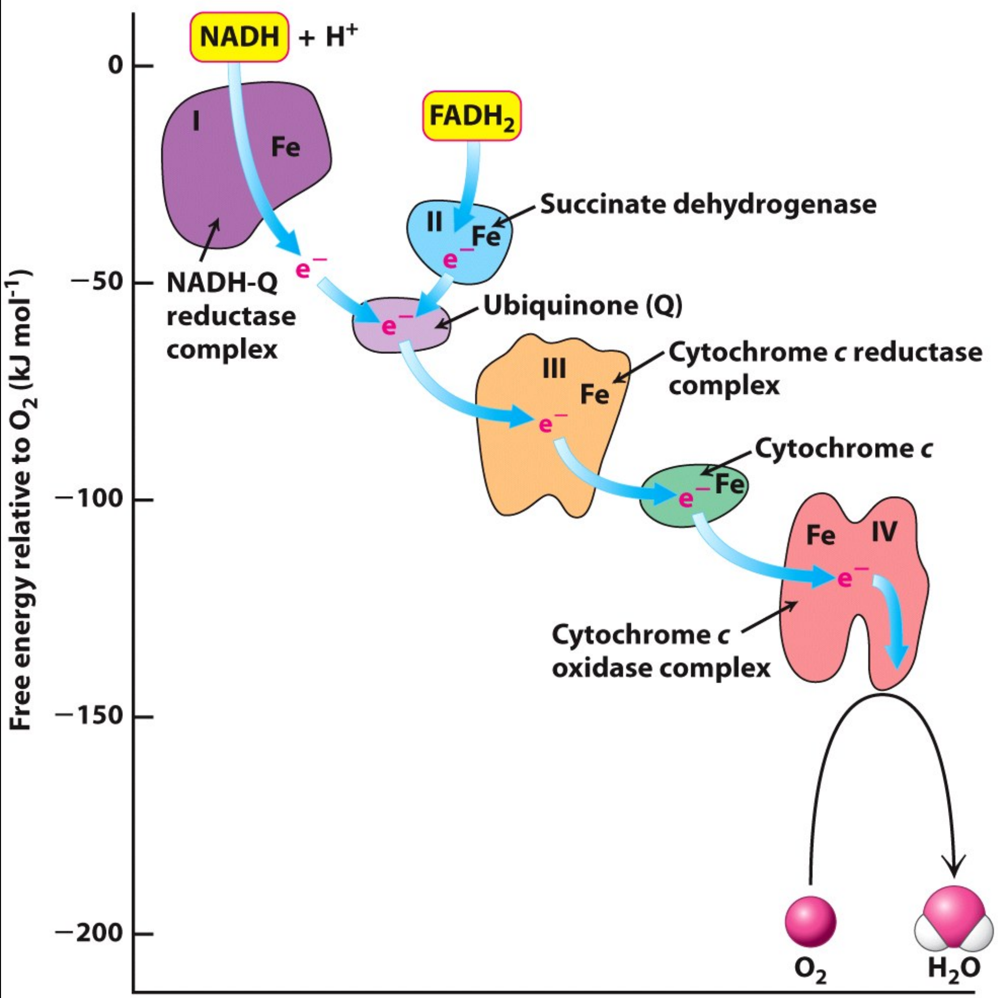
Iron-sulfur proteins: non-heme, different chemical environments = different electrochemical potentials

$$Fe^{2+} \rightleftarrows Fe^{3+} + e^-$$
$$Cu^{+} \rightleftarrows Cu^{2+} + e^-$$



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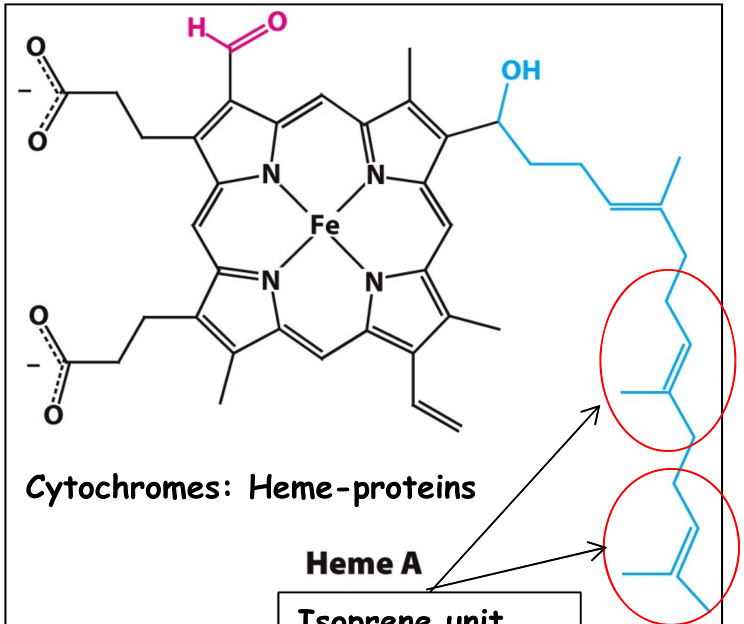

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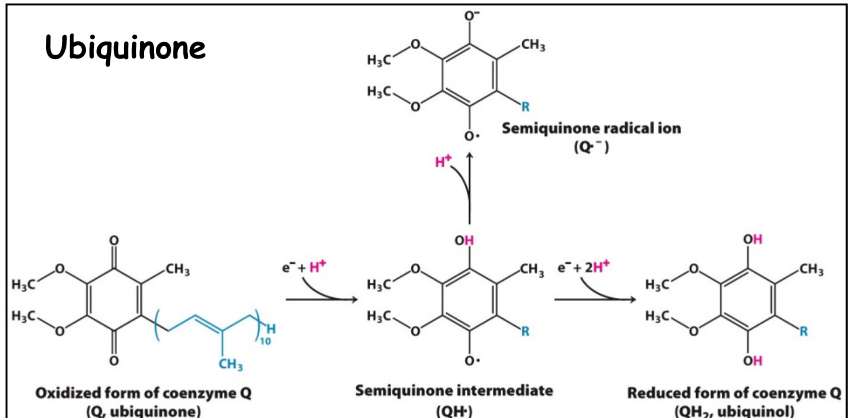

Figure 20.9
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20.3 ETC, Proton Pumps & Citric Acid Cycle

$NADH + Q + 5H^+_{MATR} \rightarrow NAD^+ + QH_2 + 4H^+_{IM}$

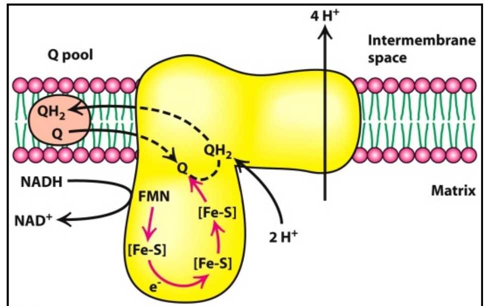

Figure 19.11
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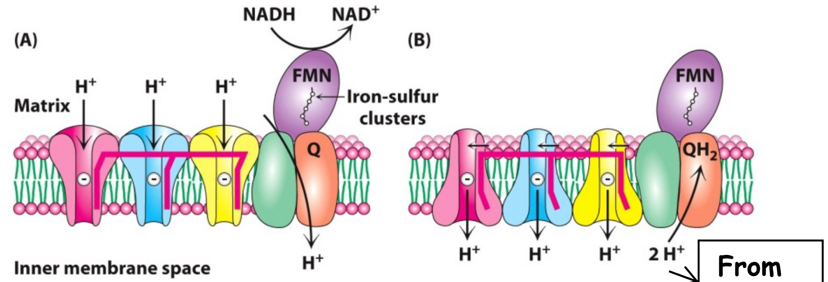

From matrix

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4 protons transported

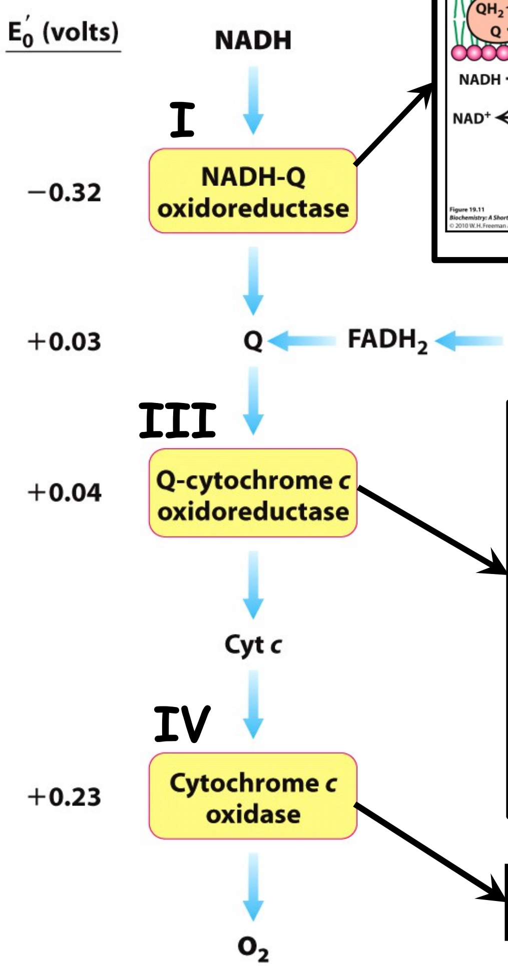

Figure 20.10
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II
Succinate-Q reductase

From citric acid cycle

$QH_2 + 2Cytc_{ox} + 2H^+_{MATR} \rightarrow Q + 2Cytc_{red} + 4H^+_{IM}$

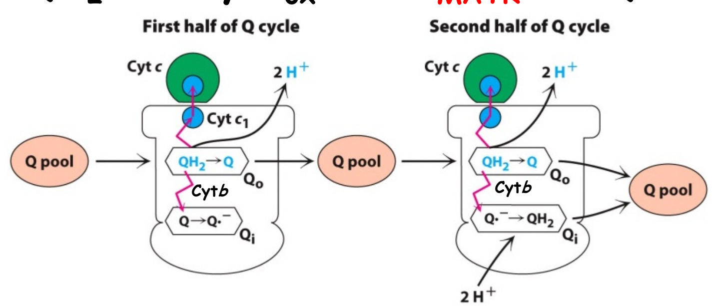

Figure 20.12
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$2QH_2 + Q + 2Cytc_{ox} + 2H^+_{MATR}$

$\downarrow$

$2Q + QH_2 + 2Cytc_{red} + 4H^+_{IM}$

2 protons used from matrix and 4 transported

$4Cytc_{red} + 8H^+_{MATR} + O_2 \rightarrow 4Cytc_{ox} + 2H_2O + 4H^+_{IM}$

4 protons/2e⁻ used from matrix and 2 protons/2e⁻ transported to IM

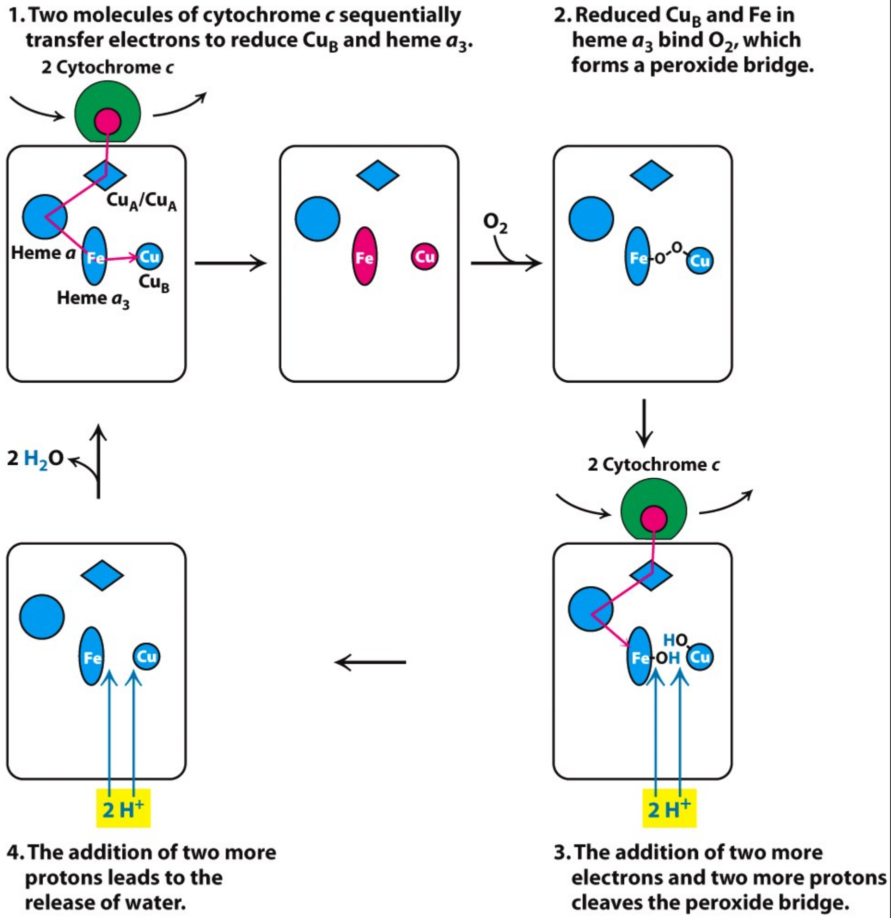

Figure 20.13
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Summary

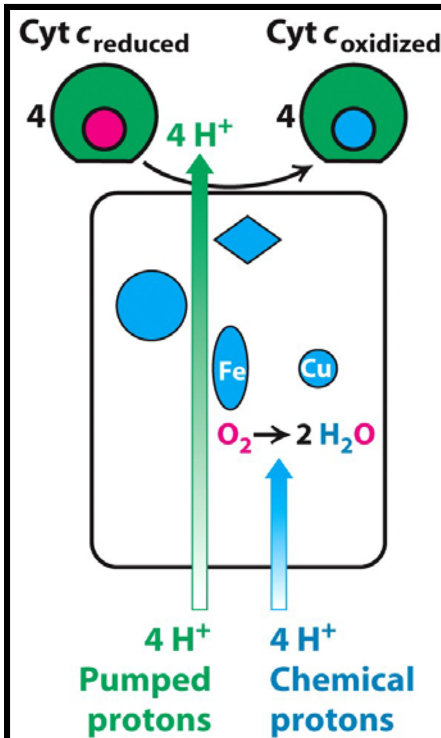

Figure 20.14
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$\Delta G^{o\prime} = -nF\Delta E'_0$ = -231.8 kJ/mol

$$\boxed{4H^+_{MATR} + O_2 \rightarrow 2H_2O}$$

$\Delta G^{o\prime} = -nF\Delta E'_0$ = -4(96.48 kJ/mol/V)(0.82V) = -316.45 kJ/mol.

Cytc oxidase uses extra energy to transport 4 protons to IM

Overall Summary of ETC

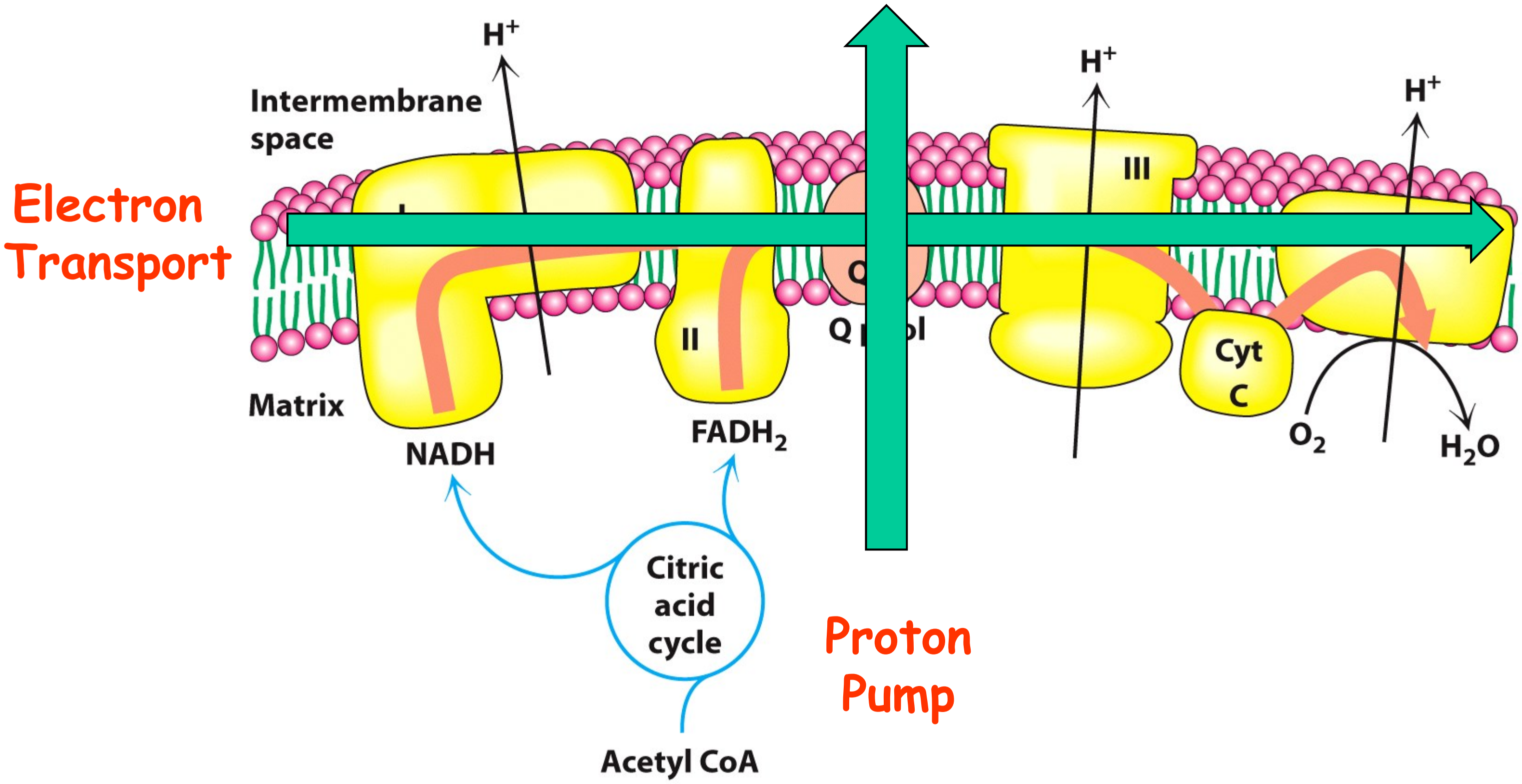

Figure 20.15
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ETC Leads to Toxic Reactive Oxygen Species (ROS)

$O_2 \xrightarrow{e^-} O_2^{-\cdot} \xrightarrow{e^-} O_2^{2-}$

Superoxide ion   Peroxide

Reacts with and damages:
Proteins, nucleotide bases, membranes, etc.

$2O_2^{-\cdot} + 2H^+ \rightarrow O_2 + H_2O_2$ Superoxide dismutase

$2H_2O_2 \rightarrow 2O_2 + 2H_2O$ Catalase

Antioxidants: vitamin E, C, ubiquinol, etc.

ROS: Signal Transduction, Channels, TSs, etc., pathogen defense

Table 20.3 Pathological and other conditions that may be due to free-radical injury

Atherogenesis	Acute renal failure
Emphysema; bronchitis	Down syndrome
Parkinson disease	Retrolental fibroplasia (conversion of the retina into a fibrous mass in premature infants)
Duchenne muscular dystrophy	Cerebrovascular disorders
Cervical cancer	Ischemia; reperfusion injury
Alcoholic liver disease	
Diabetes	

Source: After D. B. Marks, A. D. Marks, and C. M. Smith, *Basic Medical Biochemistry: A Clinical Approach* (Williams & Wilkins, 1996), p. 331.

Table 20.3
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