Notes 12/4

Tuesday, December 04, 2007
10:00 AM

Notes 124 - 2

Audio recording started: 10:05 AM Tuesday, December 04, 2007

FINAL SLIDES:

Electron Transport

Dec. 4, 2007

Electron Transport

Dec. 4, 2007

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Reminder

- All students in section 1D, Tuesday 1-2pm with Midge will have a room change for next week Dec 4th. Please join Rebecca and section 2D in WGYH CS24 at the same time.
  There is plenty of room!!!

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Overview

- Reduction Potentials
- Phosphorylation and Oxidation
- Electron transport system

Overview

- Reduction Potentials
- Phosphorylation and Oxidation
- Electron Transport System

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- Slide 3 Missing: biochemical Hal -Reactions Are Physiologically Improtant
  - If the standard reduction potential is large positive value then the oxidized form is a strong e^- acceptor (strong oxidizing agent)
  - Its conjugant reduced form is a weak e^- donor (reducing agent)
- Slide 4 Missing Table 16-4A Standard Reduction Potentials of Some Biochemically Important half - reactions
  - Oxygen is best oxidizing agent/electron acceptor (large positive V)
  - NADH is not a good oxidizing agent (better reducing agent)
- Cytochromes
  - Iron is atom that gets reduced

Biochemical Half-Reactions Are Physiologically Important

- $A_{ox}^{n+} + ne^- \Longleftrightarrow A_{red}$
- If standard reduction potential is large positive value then the oxidized form is a strong e^- acceptor (strong oxidizing agent)
- Its conjugant reduced form is a weak e^- donor (reducing agent)

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Table 16-4b Standard Reduction Potentials of Some Biochemically Important Half-reactions

Half-Reaction	$\mathcal{E}°'$ (V)
$FAD + 2H^+ + 2e^- \rightleftharpoons FADH_2$ (*in flavoproteins*)	−0.040
$Oxaloacetate^- + 2H^+ + 2e^- \rightleftharpoons malate^-$	−0.166
$Pyruvate^- + 2H^+ + 2e^- \rightleftharpoons lactate^-$	−0.185

Acetaldehyde + $2H^+$ + $2e^-$ ⇌ ethanol	−0.197
FAD + $2H^+$ + $2e^-$ ⇌ $FADH_2$ (*free coenzyme*)	−0.219
S + $2H^+$ + $2e^-$ ⇌ H_2S	−0.23
Lipoic acid + $2H^+$ + $2e^-$ ⇌ dihydrolipoic acid	−0.29
NAD^+ + H^+ + $2e^-$ ⇌ NADH	−0.315
$NADP^+$ + H^+ + $2e^-$ ⇌ NADPH	−0.320
Cystine + $2H^+$ + $2e^-$ ⇌ 2 cysteine	−0.340
$Acetoacetate^-$ + $2H^+$ + $2e^-$ ⇌ β-hydroxybutyrate	−0.346
H^+ + e^- ⇌ $\frac{1}{2}H_2$	−0.421
$Acetate^-$ + $3H^+$ + $2e^-$ ⇌ acetaldehyde + H_2O	−0.581

Source: Mostly from Loach, P.A., *in* Fasman, G.D. (Ed.), *Handbook of Biochemistry and Molecular Biology* (3rd ed.), *Physical and Chemical Data*, Vol. I, *pp.* 123–130, CRC Press (1976).

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Table 16-4a Standard Reduction Potentials of Some Biochemically Important Half-reactions.

Half Reaction	$\mathcal{E}^{\circ\prime}$ (V)
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
FAD + $2H^+$ + $2e^-$ ⇌ $FADH_2$ [illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
FAD + $2H^+$ + $2e^-$ ⇌ $FADH_2$ [illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Biochemical Half-Reactions Are Physiologically Important

- $A_{ox}^{n+} + ne^- \leftrightarrow A_{red}$
- If standard reduction potential is large then the oxidized form is a strong e^- acceptor (oxidizing agent)
- Its conjugant reduced form is a weak e^- donor (reducing agent)

Thermodynamics of Electron Transport

- NADH oxidation is highly exergonic
- Electron transport is thermodynamically efficient

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Thermodynamics of Electron Transport

- NADH oxidation is highly exergonic
- Electron transport is thermodynamically efficient

NADH Oxidation Is a Highly Exergonic Rxn

- Half-rxns for O_2 oxidation of NADH

Half Reaction	$\mathcal{E}^{\circ\prime}$ (V)
[illegible]	[illegible]
[illegible]	[illegible]

- Write the overall rxn
- Solve for $\Delta\mathcal{E}^{\circ\prime}$
- Solve for $\Delta G^{\circ\prime}$

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Electron transport system is more energy efficient than cars on the 405

- Electrons passes through protein complexes (not directly to O_2)
- Protein complexes contain redox centers
- Overall NADH (or $FADH_2$) free energy is broken up amongst protein complexes
- ATP is made via coupled oxidative phosphorylation
- Physiological thermodynamic efficiency = about 70%

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NADH Oxidation Is a Highly Exergonic Rxn

- Half-rxns for O_2 oxidation of NADH

½ Rxn	$\mathcal{E}^{\circ\prime}$(V)
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	0.815
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	-0.315

1) • Write overal Rxn

$$\frac{1}{2}O_2 + H^+ + NADH \rightleftharpoons H_2O + NAD^+$$

2) • Solve for $\Delta\mathcal{E}^{\circ\prime}$

$$\Delta\mathcal{E}^{\circ\prime} = \mathcal{E}^{\circ}_{(e^-\ acceptor)} - \mathcal{E}^{\circ}_{(e^-\ donor)} = 0.815V + 0.315V = 1.13V$$

3) Solve for $\Delta G^{\circ\prime}$

$$\Delta G^{\circ\prime} = -nF\Delta\mathcal{E}^{\circ\prime}$$

$$(-2)(96485)(1.13)$$

$$= -218\ kJ/mol$$

$F = 96,485\ C/mol$

$V = J/C$

$n = mol\ e^-$

The Sequence of Electron Transport

- Series of 4 protein complexes
- Electrons pass from lower to higher standard reduction potentials

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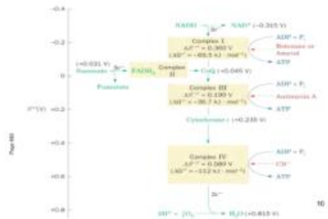
Electron transport system is more energy efficient than cars on the 405

- Electrons passes through protein complexes (not directly to O_2)
- Protein complexes contain redox centers Redox centers carry e⁻ through system
- Overall NADH free energy is broken up amongst three protein complexes, $FADH_2$ is broken up amongst four (need to double check)
- ATP is made via coupled oxidative phosphorylation
- Physiological thermodynamic efficiency = about 70%
  - Automobile engine 30% efficient

Figure 22-9
The mitochondrial electron-transport chain.



Phosphorylation and Oxidation are Tightly Coupled

- Oxidation of NADH by O_2 yields 3 ATP (3 ADP are phosphorylated)
- Oxidation of $FADH_2$ by O_2 yields 2 ATP (2 ADP are phosphorylated)
- P/O ratio is used to describe stoichiometry
- P/O indicates that oxidation in mitochondria can only occur if ADP is phosporylated at the same time

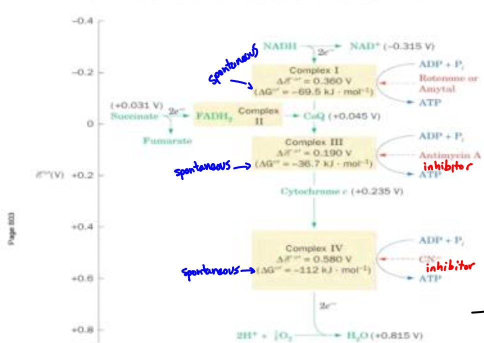
The Sequence of Electron Transport

- Series of 4 protein complexes
- Electrons pass from lower to higher standard reduction potentials

However, P/O Ratio Values Depend on the Biochemist You Ask

3 ATP/NADH x 10 NADH/glucose	2.5 ATP/NADH x 10 NADH/glucose
2 ATP/$FADH_2$ x 2 $FADH_2$/glucose	1.5 ATP/$FADH_2$ x 2 $FADH_2$/glucose
2 ATP/glucose from glycolysis	2 ATP/glucose from glycolysis
2 ATP/glucose from TCA cycle	2 ATP/glucose from TCA cycle
= 38 ATP	= 32 ATP

Figure 22-9
The mitochondrial electron-transport chain.



Oxygen is terminal electron acceptor

Complex 1 Reaction

$NADH + CoQ_{(ox)} \rightarrow NAD^+ + CoQ_{(RED)}$

Complex 1 does not directly make ATP
Rotenone or Amytal are inhibitors of complex 1

Complex 3 Reaction

$CoQ_{(RED)} + 2\,cytochrome\ c_{(ox)} \rightarrow CoQ_{(OX)} + 2\,cytochrome\ c_{(RED)}$

Complex 4 Reaction

$2\,cyto\ c_{(RED)} + \frac{1}{2}O_2 \rightarrow 2\,cyto\ c_{(ox)} + H_2O$

Complex 2 Reaction

$FADH_2 + CoQ_{(ox)} \rightarrow FAD + CoQ_{(RED)}$

Closer Look at the Components of the Electron-Transport Chain

- Inner mitochondrial membrane proteins complexes
- Each complex = several proteins + prosthetic groups
- Laterally mobile
- Don't form higher order structure(s)
- Transfer electrons between each other

Phosphorylation and Oxidation are Tightly Coupled

- Oxidation of NADH by O_2 yields 3 ATP (3 ADP are phosphorylated)
- Oxidation of $FADH_2$ by O_2 yields 2 ATP (2 ADP are phosphorylated)
- P/O ratio is used to describe stoichiometry
- P/O indicates that oxidation in mitochondria can only occur if ADP is phosporylated at the same time

P/O stands for phosphorylation
3/1 ratio for NADH to ATP

Team members of electron-transport chain

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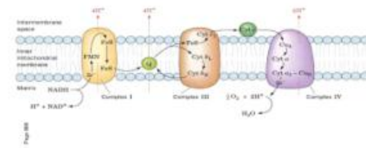
Figure 22-14
The mitochondrial electron-transport chain.



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The P/O Ratio Values Depend on the Biochemist You Ask

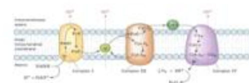
will use these values

- 3 ATP/NADH
- 2 ATP/$FADH_2$
- 10 NADH/glucose
- 2 $FADH_2$/glucose
- 2 ATP/glucose from glycolysis
- 2 ATP/glucose from TCA cycle
- 38 ATP

- 2.5 ATP/NADH
- 1.5 ATP/$FADH_2$
- 32 ATP

$3\times10 + 2\times2 + 2 + 2 = 38$

Complex I



- Passes electrons from NADH to CoQ
- 850 kD
- Flavin mononucleotide (FMN)
- Iron-sulfur clusters
- Iron-sulfur clusters are redox active

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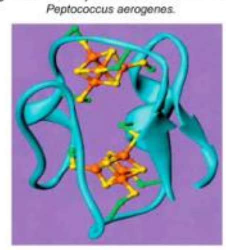
*Alternative slide title: Closer look at components of ETC

Components of the Electron-Transport Chain

- Inner mitochondrial membrane proteins complexes
- Each complex = several proteins + prosthetic groups
- Laterally mobile
- Don't form higher order structure(s)
- Transfer electrons between each other

Figure 22-16 X-Ray structure of ferredoxin from *Peptococcus aerogenes.*



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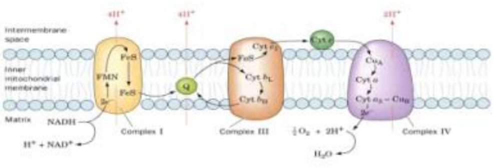
- Slide 14: Missing Team members of electron transport chain
  - Complex 1: NADH-Coenzyme Q Reductase
  - Complex II: Succinate-Coenzyme Q Reductase)
  - Complex III: Coenzyme Q-Cytochrome C Reductase
  - Cytochrome c
  - Complex IV: Cytrochrom c Oxidase
- Slide 16: Complex 1: Slide Missing

END LECTURE… RAN OUT OF TIME.

Figure 22-14
The mitochondrial electron-transport chain.



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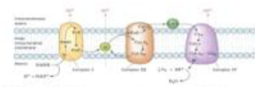
What does each electron-transport chain component look like?

- Complex I (NADH-Coenzyme Q Reductase)
- Complex II (Succinate-Coenzyme Q Reductase)
- Complex III (Coenzyme Q-Cytochrome c Reductase)
- Cytochrome c
- Complex IV (Cytochrome c Oxidase)

Complex I

- Passes elctrons from NADH to CoQ
- 850 kD
- Flavin mononucleotide (FMN)
- Iron-sulfur clusters
- Iron-sulfur clusters are redox active

The Coenzymes of Complex I



- FMN and CoQ can accept one or two electrons
- FMN and CoQ bridge the 2-electron donor NADH to cytochromes (one-electron acceptors)

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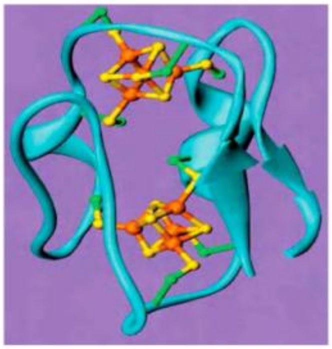
Figure 22-16 X-Ray structure of ferredoxin from *Peptococcus aerogenes*.



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The Coenzymes of Complex I

- FMN and CoQ can accept one or two electrons
- Why?
- FMN and CoQ bridge the 2-electron donor NADH to cytochromes (one-electron acceptors)

Figure 22-17a
Oxidation states of the coenzymes of complex I. (*a*) FMN.

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Figure 22-17b
Oxidation states of the coenzymes of complex I. (*b*) CoQ.

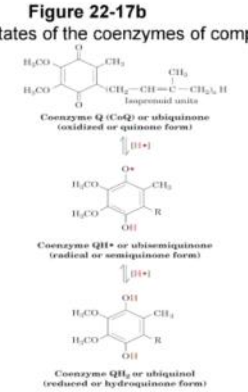

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Figure 22-22a Porphyrin rings in cytochromes. (*a*) Chemical structures.

Figure 22-29 Coupling of electron transport (*green arrow*) and ATP synthesis.

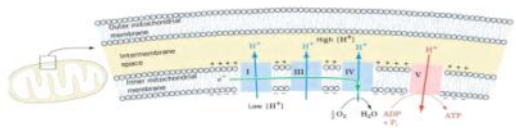

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Figure 22-31 The Q cycle.

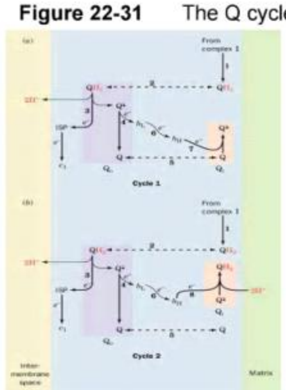

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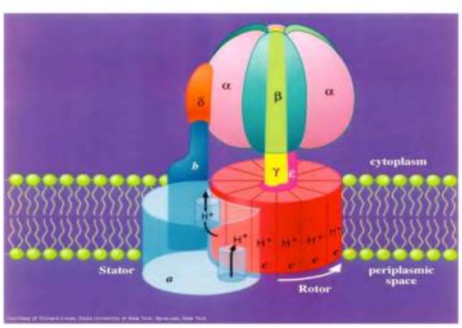
Figure 22-43 Model of the *E. coli* F_1F_0–ATPase.



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