Biochemistry 411
Section ______

Exam 2

1. (10 points) A. What is the overall reaction catalyzed by the pyruvate dehydrogenase complex?

pyruvate + NAD\(^+\) + CoASH \rightarrow \text{acetyl CoA} + \text{NADH} + \text{CO}_2

B. What are the names of the individual enzymes in the complex? For each list the cofactor(s) in that enzyme.
E1-pyruvate dehydrogenase; thiamine pyrophosphate
E2-dihydrolipoyl transacetylase; lipoic acid
E3-dihydrolipoyl dehydrogenase; FAD

2. (10 points) What enzymes of the glyoxylate pathway are not also found in the citric acid cycle? For one of these, give the names and structures of the substrates and products.

isocitrate lyase

\[
\text{isocitrate} \quad \overset{\text{H-C}}{\xrightarrow{\text{CO}_2}} \quad \text{glyoxylate}
\]

\[
\text{CO}_2 \quad \overset{\text{H-C}}{\xrightarrow{\text{CH}_2}} \quad \text{glyoxylate}
\]

malate synthase

\[
\text{H}_3\text{C-C-SCoA} \quad \overset{\text{O-H}}{\xrightarrow{\text{CO}_2}} \quad \text{malate}
\]

\[
\text{H}_3\text{C-C-SCoA} \quad \overset{\text{O-H}}{\xrightarrow{\text{CO}_2}} \quad \text{malate}
\]
3. (14 points) For the following enzymes, give the names and structures of the substrates and products. You need not give structures of nucleotides.

A. succinyl CoA synthetase

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\[\text{succinyl-CoA} \quad \text{succinate}\]
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\[
\text{CO}_2^2 \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{O} = \text{C} \quad \text{SCoA} + \text{GDP} + \text{Pi} \quad \text{CO}_2^2 \\
\text{CH}_2 \quad \text{CH}_2 \quad \text{CO}_2^2 \\
\text{GTP} + \text{CoASH} \quad \text{succinate}
\]
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B. isocitrate dehydrogenase

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\[\text{isocitrate} \quad \text{a-ketoglutarate}\]
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\[
\text{CO}_2^2 \quad \text{H} - \text{C} - \text{CO}_2^2 \\
\text{HO} - \text{CH} \quad \text{O} = \text{C} \\
\text{CH}_2 \quad \text{CO}_2^2 \\
\text{NAD}^+ \quad \text{NADH, CO}_2 \\
\text{isocitrate} \quad \text{a-ketoglutarate}
\]
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4. (8 points) Given the $E^\prime\prime$ values of the two half cells below, determine whether the following reaction is favorable under standard conditions. Clearly explain your reasoning.

$$\text{FAD} + \text{NADPH} + H^+ \rightleftharpoons \text{FADH}_2 + \text{NADP}^+$$

$$\begin{align*}
\text{FAD} + 2 e^- + 2 H^+ & \rightleftharpoons \text{FADH}_2 & E^\prime\prime = -0.219 \text{ V} \\
\text{NADP}^+ + 2 e^- + H^+ & \rightleftharpoons \text{NADPH} & E^\prime\prime = -0.320 \text{ V}
\end{align*}$$

The $\Delta E^\prime\prime$ value is simply the difference between the $E^\prime\prime$ value of the acceptor, FAD, and the electron donor, NADP$^+$, $-0.219 - (-0.320) = 0.101 \text{ V}$. A positive $\Delta E^\prime\prime$ value indicates that the reaction is favorable as written under standard conditions.

Give the equation you would use to determine the standard free energy change for this reaction.

$$\Delta G^\prime\prime = -nF\Delta E^\prime\prime$$

5. (4 points) Describe the role of thioredoxin.

It is involved in the regulation of enzymes in the Calvin cycle. It must be reduced to activate the enzymes. It is reduced by reduced ferredoxin.

6. (6 points) What is the overall reaction of the citric acid cycle?

$$\text{acetyl CoA} + 3 \text{ NAD}^+ + \text{GDP} + P_i + \text{FAD} \rightarrow 2 \text{ CO}_2 + \text{CoASH} + 3 \text{ NADH} + \text{GTP} + \text{FADH}_2$$
7. (16 points) Show the structure of the intermediate in the rubisco reaction which can react with either CO$_2$ or O$_2$.

Show the structure of the active site base in rubisco.

Give the names and the structures of the products when rubisco reacts with CO$_2$.

Give the names and the structures of the products when rubisco reacts with O$_2$. 

3-phosphoglycerate + phosphoglycolate
8. (12 points) A. Which of the electron transport complexes in mitochondria are proton pumps?

Complex I
Complex III
Complex IV

B. Where are the complexes located in mitochondria?
inner mitochondrial membrane

C. In what direction are the protons pumped?
From the matrix to the intermembrane space.

D. What is the role of the proton gradient formed by these complexes? Name a protein which utilizes the proton gradient.

The proton gradient is used to drive the formation of ATP from ADP and phosphate. The enzyme is ATP synthase.

9. (10 points) Describe the reaction of Photosystem II.

When Photosystem II absorbs a proton, the energy is transferred from antenna pigments to P680 in the reaction center. This results in the loss of an electron from P680 to form P680\(^{+}\). The electron is replaced by an electron removed from water by the water splitting complex. The electron lost from P680 travels through a series of electron acceptors until it reaches plastoquinone. Plastoquinone can accept 2 electrons to form reduced plastoquinone (PQH\(_2\)).
10. (10 points) What is the purpose of the malate-aspartate shuttle? Describe how it works. In your answer give the names of all the substrate and enzymes involved. You need not give structures.

The malate-aspartate shuttle forms NADH in the mitochondrion at the expense of NADH in the cytoplasm, effectively transferring NADH from the cytoplasm to the mitochondrion.

1. In the cytoplasm, NADH reacts with oxaloacetate in the malate dehydrogenase reaction to form malate and NAD$^+$.  
2. The malate then enters the mitochondrion.  
3. Mitochondrial malate dehydrogenase then catalyzes the formation of oxaloacetate from malate, consuming NAD$^+$ and forming NADH.  
4. Aspartate aminotransferase then catalyzes the reaction between oxaloacetate and glutamate to form aspartate and α-ketoglutarate.  
5. The aspartate is transported to the cytoplasm.  
6. In the cytoplasm, aspartate aminotransferase catalyzes formation of oxaloacetate from the aspartate, converting α-ketoglutarate to glutamate.