This test is take-home and open book, and it is intended that all members of the group contribute to completing it. Only one copy is to be submitted by the group, and all members who participated should sign their names below. **Test is due at the noon on Monday, September 11.**

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1. Plants, but not animals, can convert acetyl-CoA to glucose. To accomplish this, it is necessary that the acetyl-CoA be converted to phosphoenolpyruvate (PEP) in a net manner, and plants have two enzymes that animals do not which enable this conversion.

(a) Show a pathway, including structures of all intermediates, by which the following metabolic conversion can be achieved. **Circle the steps of the pathway that are peculiar to plants.**

\[
2 \text{ Acetyl-CoA} \rightarrow \text{PEP} + \text{CO}_2 + 2 \text{ CoASH}
\]

(b) Complete the overall stoichiometric balance of the above reaction, showing the total consumption or production of ATP, GTP, NADH, CoQH\(_2\), and Pi. (Show on your pathway where these coenzymes are being used or produced.)
2. Upon starvation, your body begins to break down muscle protein to provide energy and to produce glucose needed by the brain for fuel. As an example, glutamate is oxidized by an enzyme called glutamate dehydrogenase, producing $\alpha$-ketoglutarate by the following reaction:

$$\text{glutamate} + \text{NAD}^+ \rightarrow \alpha\text{-ketoglutarate} + \text{NH}_4^+ + \text{NADH}$$

Give a pathway by which glutamate can be completely degraded to $\text{CO}_2$ in order to produce energy. Identify steps in which substrate coenzymes (NADH, ATP, GTP, CoQH$_2$) are either used or produced, and write an equation giving the overall stoichiometry of the net reaction.
(12) 3. You have studied three reactions involving malic acid: malate dehydrogenase, malate synthase, and malic enzyme. Give the reaction catalyzed by each enzyme (structure or name of reactants and products) and the function served by each enzyme in metabolism.

(10) 4. You have studied two enzymes with covalently bound prosthetic groups which act as carriers for intermediates in the enzymatic reaction. Identify by name these prosthetic groups, and give the structures which each cycles through during the course of the reaction.

(8) 5. Starting with [1-\(^{14}\)C]-glucose, trace the labeled carbon through the glycolytic and TCA cycle intermediates. Don't give all the intermediate structures here, but give the structure and circle the labeled carbon(s) for each of the following:

(a) Pyruvate
(b) Oxaloacetate formed from pyruvate by pyruvate carboxylase.
(c) Succinate, formed in the first turn of the TCA cycle.
(d) Oxaloacetate, formed in the first turn of the TCA cycle.
Use the standard reduction potentials found in Table 21.1, page 677, and $\Delta G^\circ$ of hydrolysis of ATP as $-30.5$ kJ/mol. Use the following constants in your calculations: $R = 8.3 \times 10^{-3}$ kJ mol$^{-1}$ K$^{-1}$; $T = 310$ K; $F = 96.5$ kJ volt$^{-1}$ equiv.$^{-1}$

6. (a) Calculate $\Delta G^\circ$ for the following reaction:

$$\text{NADH} + \text{fumarate} \rightleftharpoons \text{NAD}^+ + \text{succinate}$$

(b) This reaction can be catalyzed by submitochondrial particles, created by sonication of mitochondria in which the inner mitochondrial membrane recloses inside out to form closed spherical vesicles. Diagram such a particle, showing the location and orientation of each protein complex involved in the catalysis and how they participate in the reaction. Identify the intermediate electron carriers (A,B,C,D,E in the following scheme) involved in the reaction.

$$\text{NADH} \rightarrow A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow \text{fumarate}$$

(c) Such vesicles as described above should pump protons from the solution to the interior of the vesicle. Assuming the proton stoichiometry proposed for the complexes involved, calculate the energy of the electrochemical gradient that would be created if the NADH/NAD$^+$ and fumarate/succinate ratios were each maintained at 1:1.

Energy of electrochemical gradient:

$$\Delta G = 2.3nRT\Delta pH + nF\Delta \Psi$$

where $n =$ # protons
7. Mitochondria, or "right-side out" submitochondrial particles can carry out the following reaction, the oxidation of cytochrome c by oxygen coupled to the synthesis of ATP.

\[
2 \text{ cyt c (red)} + \frac{1}{2} \text{O}_2 + \text{ADP} + \text{Pi} \rightleftharpoons 2 \text{ cyt c (ox)} + \text{H}_2\text{O} + \text{ATP}
\]

Why would this reaction not work with the "inside-out" particles described in problem 6?

Calculate \( \Delta G^\circ \) for this coupled reaction (all reactants and products in standard states).

How would the following inhibitors affect this reaction:

- cyanide
- antimycin
- dinitrophenol
- rotenone
- oligomycin
- valinomycin

8. Identify which of the respiratory complexes I, II, III, or IV fit the following descriptions (more than one may apply).

- ______ contains cytochromes
- ______ contains Cu
- ______ contains Fe/S proteins
- ______ reduces CoQ
- ______ acts as a proton pump
- ______ interacts with cyt c