

## Chem 352 - Spring 2013 - Exam III

Use constants: Ideal gas law constant,  $R = 0.08206 \text{ (l}\cdot\text{atm)} / (\text{mol}\cdot\text{K}) = 8.314 \text{ (J)} / (\text{mol}\cdot\text{K})$ ; Faraday's constant,  $\mathcal{F} = 9.659 \times 10^4 \text{ J/(V}\cdot\text{mol)}$ ; Planck's constant,  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ .

1. The light reactions of photosynthesis and the electron transport chain in plants share many common features.
- a. Identify the components of each that fit the following descriptions:

	Photosynthesis	Electron Transport Chain
The initial donor of electrons		
The final acceptor of electrons		
The mobile 1-electron carrier		
The mobile 2-electron carrier		
The complex that is site of the Q-cycle		
In what form does each store energy used for phosphorylation of ADP by ATP Synthase		
Cellular location of each in eukaryotes		

- b. Considering only the initial electron donor and final electron acceptor identified above, write the *net balanced reaction equation* for the light reactions of photosynthesis in plants

- c. Using the appropriate reduction potentials provided in the table below, calculate the change in the standard free energy per mole of  $\text{NADH} + \text{H}^+$  for this overall reaction. (Show your calculations.)

Reduction half-reaction	$E^\circ \text{ (V)}$
Acetyl CoA + $\text{CO}_2 + \text{H}^+ + 2e^- \rightarrow$ Pyruvate + CoA	-0.48
Ferredoxin (spinach), $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	-0.43
$2 \text{H}^+ + 2e^- \rightarrow \text{H}_2$ (at pH 7.0)	-0.42
$\alpha$ -Ketoglutarate + $\text{CO}_2 + 2 \text{H}^+ + 2e^- \rightarrow$ Isocitrate	-0.38
Lipoyl dehydrogenase (FAD) + $2 \text{H}^+ + 2e^- \rightarrow$ Lipoyl dehydrogenase (FADH <sub>2</sub> )	-0.34
$\text{NADP}^+ + \text{H}^+ + 2e^- \rightarrow$ NADPH	-0.32
$\text{NAD}^+ + \text{H}^+ + 2e^- \rightarrow$ NADH	-0.32
Lipoic acid + $2 \text{H}^+ + 2e^- \rightarrow$ Dithiolipoic acid	-0.29
Thioredoxin (oxidized) + $2 \text{H}^+ + 2e^- \rightarrow$ Thioredoxin (reduced)	-0.28
Photosystem I (P700)	0.43
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	0.77
$\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}$	0.82
Photosystem II (P680)	1.1

$\Delta G^\circ =$  \_\_\_\_\_

- d. Is this reaction favorable under standard state conditions (Yes/No)? \_\_\_\_\_  
Explain:
- e. If your answer is “No” to d., identify the source of energy that plants use to make this reaction favorable.
- f. It turns out that the source of energy that you identified in e. delivers considerably more free energy than is required to drive the reaction that you identified in b. What is this excess energy used for?
- g. The energy captured from the light reactions is used to fix CO<sub>2</sub> by converting 3 molecules of ribose 5-phosphate plus 3 molecules of CO<sub>2</sub> into 6 molecules of the glycolytic intermediate, 3-phosphoglycerate. *Using structural formulas for the intermediates*, draw the sequence of *balanced chemical equations* for the four reactions in this pathway. Also, name each of the intermediates.

2. Fatty acids are synthesized by adding two carbon units onto a growing acyl chain.
- a. *Using structural formulas*, show the sequence of reactions involved in elongating an acyl chain by two carbon atoms.
- b. Fatty acid synthesis shares a number of similar features with  $\beta$ -oxidation (the degradation of fatty acids), but in reverse. Identify two features of fatty acid biosynthesis that distinguishes it from the reverse of  $\beta$ -oxidation.
- i.
- ii.
- c. Where in a eukaryotic cell does fatty acid synthesis occur? \_\_\_\_\_
- d. When eukaryotes convert carbohydrates to fatty acids, the glycolytic pathway is used to convert glucose to pyruvate, which is then converted to acetyl-CoA by way of the enzyme pyruvate dehydrogenase. Describe where in the cell this acetyl-CoA is produced and indicate how it is transported to the location where fatty acid biosynthesis takes place.

3. Starting at the glycolytic intermediate pyruvate, it is possible to trace a metabolic pathway that will lead to the synthesis of either the amino acid *serine* or the amino acid *glutamate*.
- a. Pick one of these pathways, and *using structural formulas for the intermediates*, draw the sequence of *balanced chemical equations* for the reactions leading to the synthesis of your chosen amino acid, starting at pyruvate. Also name each of the intermediates in this pathway.
- b. Predict and explain the effect that elevated levels of acetyl-CoA will have on you chosen pathway.

4. Both cytidine monophosphate (CMP) and uridine monophosphate (UMP) contain a pyrimidine ring.
- Draw the chemical structure for UMP
  - In your drawing, label the biochemical origin of each of the atoms in the pyrimidine ring.
  - UMP is used as a building block for the synthesis of RNA molecules. The corresponding nucleotide used to make DNA is deoxythymidine monophosphate (dTMP), which is synthesized by making two chemical modifications to the structure of UMP. To illustrate these modifications, draw the structure of dTMP and circle the two modifications.
  - One of the modifications that you circled above is a methyl group. What was the biochemical source of this carbon atom?
5. Both proteins and nucleic acids contain large quantities of nitrogen. When terrestrial animals have accumulated an excess of nitrogen, they excrete it in the form of *urea*.
- Draw the chemical structure of urea
  - What metabolic pathway is used to synthesize urea? \_\_\_\_\_
  - What is the biochemical source of the two nitrogen atoms that you drew above in your structure of urea? \_\_\_\_\_
  - The pathway that you identified above contains a number of  $\alpha$ -amino acids, but only one of which is a member of the group of 20 standard amino acids used to make proteins. Draw the structure for and label this amino acid.