Chemistry 786
Exam II
February 25, 1998

- Print you name on all sheets of the exam.
- Show all work. Partial credit cannot be given without evidence of work. No credit will be given for incorrect answers without work.
- Do work in the space provided. If additional space is needed, use the opposite side of the page and make note of your additional work in the given space.
- The exam is worth 100 points total. Questions 1-10 are worth 5 points each. Questions 11-15 are worth 10 points each.

1. Describe briefly the chemiosmotic theory for coupling oxidation to phosphorylation in mitochondria.

    1. Electrons flow through membrane bound enzyme complexes supplying the energy needed to create a proton gradient across the matrix membrane.

    2. The proton motive force (electrochemical gradient) drives protons back into the matrix via proton channels.

    3. The energy of proton flow back into the gradient is transferred to the conversion of ADP and Pi to ATP.

2. List three (3) ways in which the proton gradient formed by the mitochondrial electron transport system can be put to use.

    1. Conversion of ADP and Pi to ATP

    2. Transport of ADP into the matrix

    3. Transport of cytosolic NADH into the matrix.

3. The standard reduction potential, $E^{0'}$, for ubiquinone (Q) is 0.045 V and the standard reduction potential for FAD is -0.219 V. Solve for the standard free-energy change ($\Delta G^{0'}$) for the oxidation of $FADH_2$ by ubiquinone. Faraday's constant, $\mathcal{F}$, is 96.48 kJ/V·mol.

$$\Delta E^{0'} = E^{0'}(\text{red}) - E^{0'}(\text{ox}) = 0.045\ \text{V} - (-0.219\ \text{V}) = 0.264\ \text{V}$$

$$\Delta G^{0'} = -n\,\mathcal{F}\Delta E^{0'}$$

$$\Delta G^{0'} = -2\ (96.48\ \text{kJ/V·mol})\ (0.264\ \text{V}) = 50.9\ \text{kJ/mol}$$

4. Schematically show how glycogen phosphorylase and glycogen ~~phosphatase~~ synthase are affected by phosphorylation. Explain how this phosphorylation regulates glycogen storage/breakdown.

Phosphorylation of glycogen synthase causes it to become inactive while phosphorylation of glycogen phosphorylase causes it to become active. The net effect is glycogen degradation without any counteractive synthetic processes to detract form the production of glucose for energy production.

5. In the biosynthesis of glucose from pyruvate, name all of the enzymes that are not also participants in glycolysis.

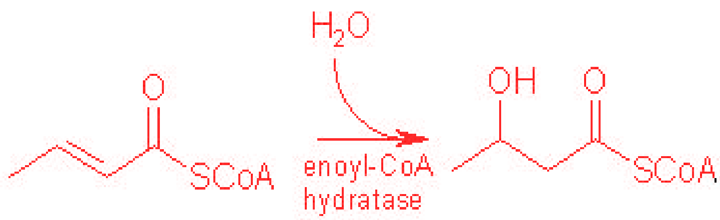
Pyruvate carboxylase, PEP carboxykinase, Fructose-1,6-bisphosphatase, Glucose-6-phosphatase

6. What are the compounds produced by the pentose phosphate pathway and what is the purpose of these compounds?

Ribose-6-phosphate: precursor for nucleotide biosynthesis

NADPH: reductive cofactor for lipid biosynthesis

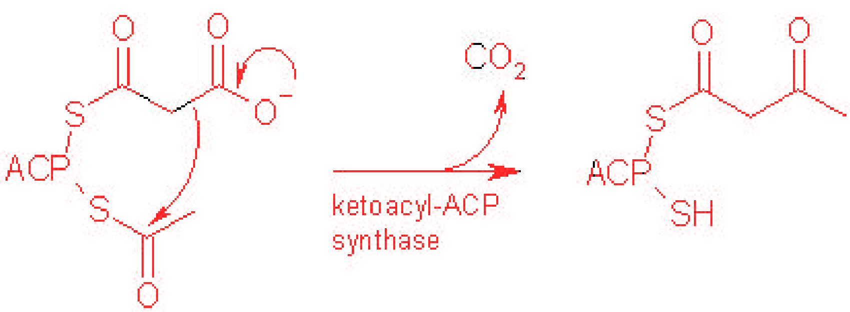
7. Draw the hydration step in the β-oxidation of fatty acids if butanoyl-CoA (C_4) was utilized as the initial starting material.



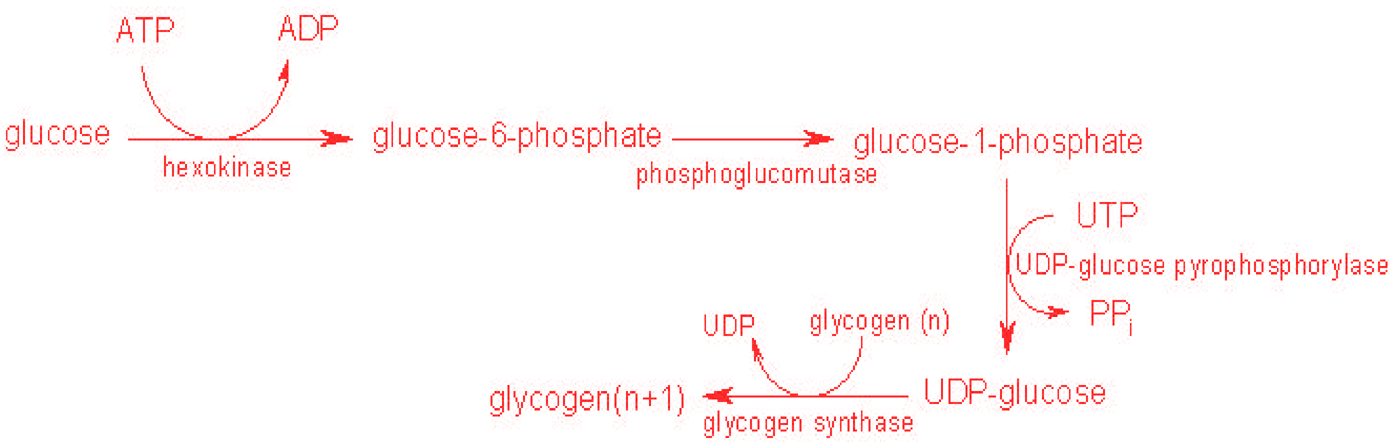
8. Explain the role of the enzymes biotin carboxylase and transcarbamoylase in the process of fatty acid synthesis.

Biotin carboxylase activates the carbon in bicarbonate ion by binding it to the biotin cofactors a -COO- functional group. Transcarbamoylase transfers the COO- functional group to acetyl-CoA to form malonyl-CoA for fatty acid biosynthesis.

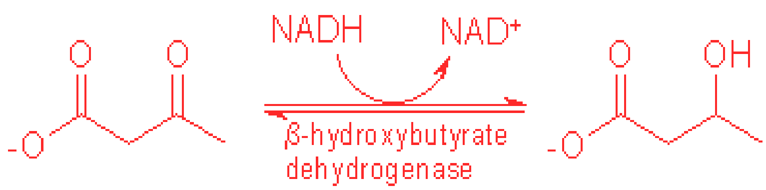
9. Draw out the condensation step of fatty acid biosynthesis using acetyl/malonyl-ACP as your starting material. Include any cofactors and enzyme name in your reaction.



10. Starting with glucose, explain how a monosaccharide unit can be incorporated into a pre-existing polymer of glycogen (structures optional).

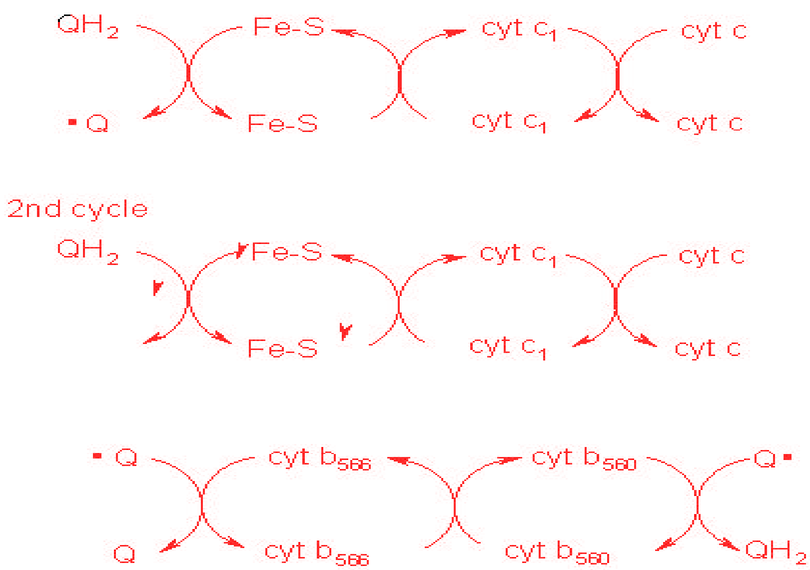


11. Write out the reaction catalyzed by the enzyme, β-hydroxybutyrate dehydrogenase (including structures) and explain the conditions under which you expect this reaction to occur.



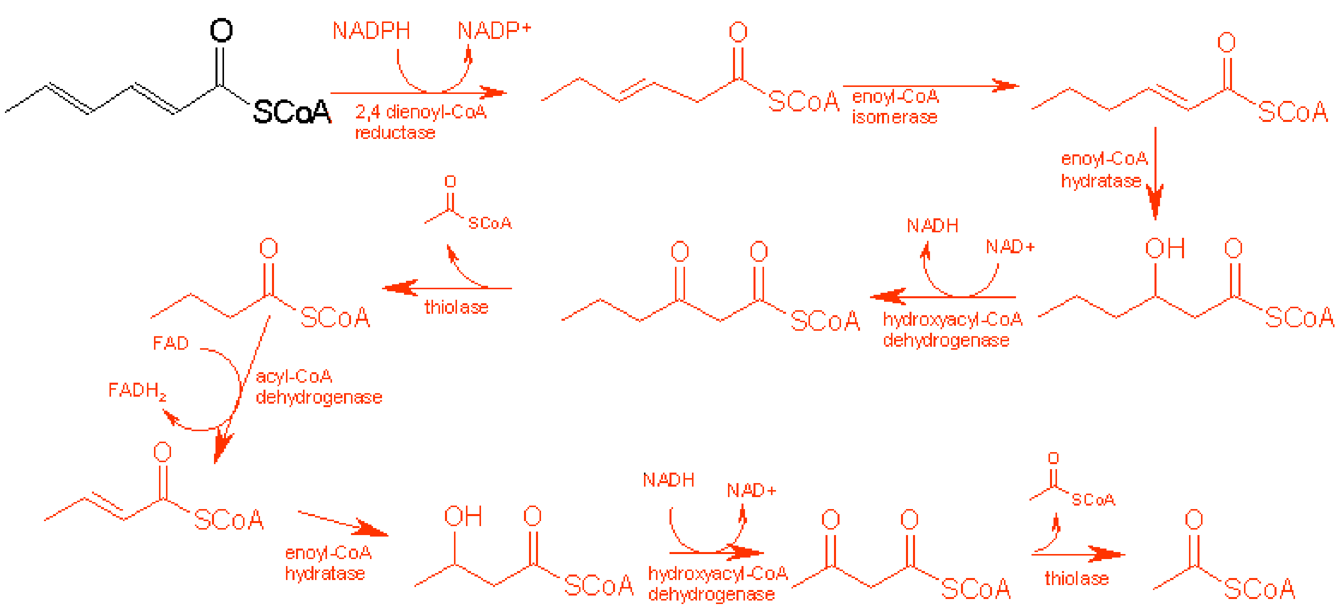
Such chemistry is expected under starvation or fasting conditions leading to the formation of such ketone bodies. Chemically, this occurs when oxaloacetate is used up for gluconeogenesis and cannot carry acetyl-CoA through the citric acid cycle.

12. Show the path of electron flow in the Q cycle (starting with the first QH_2) and explain why it is necessary to use 2 molecules of QH_2, which carries 4 electrons, to transport only 2 electrons to cytochrome *c*.

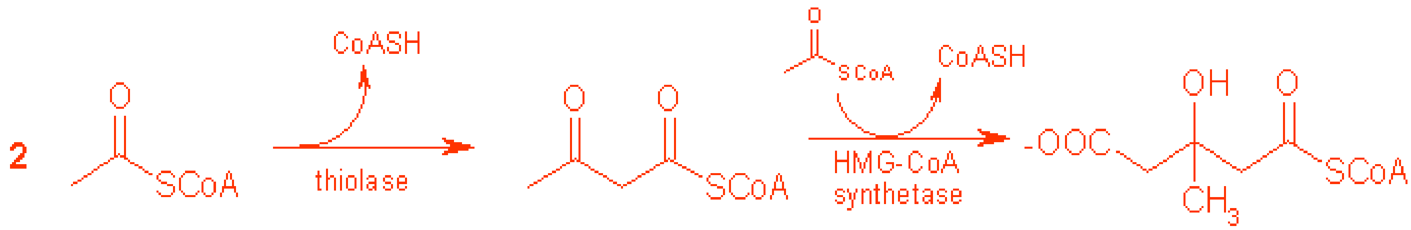


2 QH2 molecules are required to pass 2 electrons since the transfer of an individual electron results in a free radical. The second QH2 provides the means for scavenging the free radical.

13. For the molecules shown below, complete the degradation pathway until only acetyl-CoA remains. Include all enzymes and cofactors.



14. Write out the reactions leading to the formation of HMG-CoA and list the roles of this intermediate in lipid metabolism.



HMG-CoA can be used for the formation of ketone bodies for fuel during starvation/fasting or can serve as a precursor to activated isoprenes, which lead to the synthesis of cholesterol.

15. For the reaction shown below, provide the names of the compounds and enzyme and show how the compounds will react to form squalene.