Instructions: Please read all questions carefully. Use structures if they are called for. **Unless noted otherwise, please draw them in the correct protonation state for pH 7.4.** Do not use acronyms unless specifically directed. If you need more space, use the back of your paper. No calculators or electronic devices. Answers should be short and to the point. If you have extra material that is incorrect, points will be deducted. This is a one hour exam, but you have two hours to complete it. Good luck.

1) **6 pts** Draw the structure and show the mechanism for conversion of ubiquinone to ubiquinol.

![Mechanism for conversion of ubiquinone to ubiquinol](image)

2) **6 pts total** Here are some common biological half reactions. Going in the forward direction, please note if they are reductions, oxidations, or neither and state the number of electrons involved in the transformation.

   2 pts a) **oxidation** number electrons **2**

   \[ 2 \text{RSH} \rightleftharpoons \text{RS} - \text{SR} \]

   4 pts (1,3) b) **oxidation** number electrons **6**

   \[ \text{CH}_3 \]

   \[ \rightarrow \]

   \[ \text{HO} \]

   + HCOOH

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C483 Exam 2 2014

Name
3) **4 pts** What four basic roles do lipids play?

- Energy Source
- Constituent of membranes
- Signalling molecules
- Membrane anchor for proteins

4) **8 pts** Dialkyl fluorophosphates are excellent irreversible inhibitors of serine proteases. Draw a mechanism for this inhibition. Why are such molecules better inhibitors than acylfluorides? (give two reasons).

![Chemical structures and mechanism](image)

5) **5 pts** What is the role of the carboxylate (Asp or Glu, depending on the enzyme) in the catalytic triad of serine proteases? (Use structures and appropriate diagrams to explain this.)

![Chemical structures](image)

6) **7 pts** The $k_{cat}$ for hydrolysis of a series of ester substrates catalyzed by serine proteases, is usually about the same, regardless of the nature of the leaving group being cleaved. However, $k_{cat}$ usually varies for amide substrates and is substantially slower, changing even more as a function of leaving group. Explain this phenomenon and draw a free energy profile that accounts for this.

![Free energy profile](image)
7) 6 pts The three forms of metabolic pathways are: Give an example of each.

linear ______________ example __glycolysis__
cyclic ______________ example __krebs cycle__
spiral ______________ example __fatty acid synthesis / breakdown__

8) (2 pts each, 10 pts total) Answer the following short answer questions

a) A nonphotosynthetic organism that requires an organic carbon source such as glucose, is called a/an __autotroph (or chemoautotroph)__

b) __anabolic__ reactions are those by which the cell synthesizes needed materials, such as proteins and nucleic acids, while __catabolic__ reactions are those by which the cell degrades material for energy and building blocks.

c) A moiety common in the head group of all phosphotidates is __phosphate (phosphoester)__

d) Three common amino alcohols found in phosphotidates are __serine__, __choline__ and __ethanolamine__

e) Enzymes responsible for the phosphorylation of alcohols are called __kinases__

9. (2 pts each, 10 pts total) True or false

a) __F__ Relatively strong binding of reactants in the enzyme active site is necessary for efficient catalysis

b) __F__ Vitamin K is a lipid vitamin with antioxidant activity

c) __F__ Dihydroxyacetone could be described as a ketotetrose

d) __F__ Amylopectin is an entirely linear polymer of D-glucose units found in natural starch

e) __T__ Epimers are two carbohydrates that differ only in in the configuration of groups at a single chiral center
10. (2 pts each, 20 pts total) Fill in the blank

a) Monosaccharides that form six-membered rings are called __pyranose__

b) Glycolysis is the principle mode of energy generation in the muscle under __anaerobic__ conditions.

c) __Zymogens__ are inactive enzyme precursors activated by removal of one or more portions of the precursor molecule.

d,e) Activation of an enzyme by a substrate-initiated conformation change is called __induced fit___. __Hexokinase__ is an enzyme that utilizes this strategy.

f) For a substrate with a positive charge, __aspartate__ or __glutamate__ might be present near the binding site on an enzyme to aid in substrate binding.

g) Rate enhancement by the binding of reactants close to each other in the enzyme active site is called the __proximity effect__

h) The most frequently found residue in the active site of enzymes is __His__

i) The cofactor(s) that links one electron and two electron redox processes is(are) called __flavin__

j) Draw the structure of sphingosine__

NB: Glycolysis graded in 2-4 point segments. 1 free error in each segment omission of step -2pts. Use of acronym -1 pt.

11. 8 pts Draw the transformations of glycolysis starting with glucose and ending with pyruvate. You must use structures. You get two free mistakes and then one point off for each additional error. Omission of a structure, step, or product, will count as two errors. Do NOT use acronyms.
NB - CoA thioesters **CANNOT** go through membranes. Look up the structure of CoA please.

**12. 10 pts.** Suggest a process by which a fatty acid is converted to a thioester. Why do we need such a process?

\[
R-\text{COO}^- + \text{CoA-SH} \rightarrow R-\text{CO-S-CoA} \rightarrow R-\text{CO-PR}_{1} + \text{AMP} + \text{PPi} (2 \text{ P})
\]

There are two problems:

1. Kinetic: carboxylates are poor electrophiles and must be activated.
2. Thermodynamic: thioesters are high-energy compounds to drive rxn to completion.

**Extra credit 15 pts.** Each error costs 3 pts.

Give the overall equation and draw the mechanism for the pyruvate dehydrogenase reaction. You must draw enough of the structure of ALL cofactors involved in the reaction so that the chemistry they undergo is obvious. Omission of a required cofactor will count as two mistakes.