

Biochemistry 5700
Fall, 2004
Exam 3

INSTRUCTIONS:

Do not begin until 10:30 AM. The exam contains six questions on six pages. Work any five of six questions (pages) for 20 points each. Draw a huge "X" and write "do not grade" across the one page/problem you choose not to answer. *If you answer all six questions, and do not indicate which question is to be discarded, I will count the lowest five point totals for the six questions to calculate your exam score.*

If you do not complete the exam by the end of class time (11:20 AM), you may take additional time to finish the exam at one of the tables in the foyer outside the classroom. The exam must be turned in by 12 noon.

Equations: $\Delta G' = \Delta G^{\circ'} + RT \ln Q$ $\Delta E' = \Delta E^{\circ'} - \frac{RT}{nF} \ln Q$ $\Delta G' = -nFE'$

Constants: $F = 96.5 \text{ kJ/V} \cdot \text{mol}$ $R = 8.3144 \text{ J/mol} \cdot \text{K}$

TABLE 13-7 Standard Reduction Potentials of Some Biologically Important Half-Reactions, at pH 7.0 and 25 °C (298 K)

Half-reaction	E'° (V)
$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$	0.816
$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	0.771
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{NO}_2^- + \text{H}_2\text{O}$	0.421
Cytochrome <i>f</i> (Fe^{3+}) + $\text{e}^- \longrightarrow$ cytochrome <i>f</i> (Fe^{2+})	0.365
$\text{Fe}(\text{CN})_6^{3-}$ (ferricyanide) + $\text{e}^- \longrightarrow \text{Fe}(\text{CN})_6^{4-}$	0.36
Cytochrome <i>a</i> ₃ (Fe^{3+}) + $\text{e}^- \longrightarrow$ cytochrome <i>a</i> ₃ (Fe^{2+})	0.35
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2$	0.295
Cytochrome <i>a</i> (Fe^{3+}) + $\text{e}^- \longrightarrow$ cytochrome <i>a</i> (Fe^{2+})	0.29
Cytochrome <i>c</i> (Fe^{3+}) + $\text{e}^- \longrightarrow$ cytochrome <i>c</i> (Fe^{2+})	0.254
Cytochrome <i>c</i> ₁ (Fe^{3+}) + $\text{e}^- \longrightarrow$ cytochrome <i>c</i> ₁ (Fe^{2+})	0.22
Cytochrome <i>b</i> (Fe^{3+}) + $\text{e}^- \longrightarrow$ cytochrome <i>b</i> (Fe^{2+})	0.077
Ubiquinone + $2\text{H}^+ + 2\text{e}^- \longrightarrow$ ubiquinol + H_2	0.045
$\text{Fumarate}^{2-} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{succinate}^{2-}$	0.031
$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ (at standard conditions, pH 0)	0.000
Crotonyl-CoA + $2\text{H}^+ + 2\text{e}^- \longrightarrow$ butyryl-CoA	-0.015
$\text{Oxaloacetate}^{2-} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{malate}^{2-}$	-0.166
$\text{Pyruvate}^- + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{lactate}^-$	-0.185
Acetaldehyde + $2\text{H}^+ + 2\text{e}^- \longrightarrow$ ethanol	-0.197
$\text{FAD} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{FADH}_2$	-0.219*
Glutathione + $2\text{H}^+ + 2\text{e}^- \longrightarrow$ 2 reduced glutathione	-0.23
$\text{S} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{S}$	-0.243
Lipoic acid + $2\text{H}^+ + 2\text{e}^- \longrightarrow$ dihydrolipoic acid	-0.29
$\text{NAD}^+ + \text{H}^+ + 2\text{e}^- \longrightarrow \text{NADH}$	-0.320
$\text{NADP}^+ + \text{H}^+ + 2\text{e}^- \longrightarrow \text{NADPH}$	-0.324
Acetoacetate + $2\text{H}^+ + 2\text{e}^- \longrightarrow \beta$ -hydroxybutyrate	-0.346
α -Ketoglutarate + $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow$ isocitrate	-0.38
$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ (at pH 7)	-0.414
Ferredoxin (Fe^{3+}) + $\text{e}^- \longrightarrow$ ferredoxin (Fe^{2+})	-0.432

(1) 20 points. Pot pourri of definitions.

Name the product of the reaction catalyzed by
glyceralde-3-phosphate dehydrogenase

Name the products of the reaction catalyzed by aldolase

The oxidative portion of the pentose phosphate pathway
is intended to produce what two molecules ?

What is the general name for the class of enzymes that
transfer a phosphoryl group to water?

Name a specific enzyme that catalyzes a nonoxidative
decarboxylation reaction **NOT requiring TPP**

Name the two specific enzymes from glycolysis that
catalyze substrate level phosphorylation of ADP

What molecule is the initial electron acceptor of the
pyruvate dehydrogenase enzyme complex?

Name a cofactor used to facilitate homolytic bond
cleavage

Name an enzyme that can discriminate between the two
prochiral arms of its substrate

What compound is exhaled in the breath of diabetic
individuals?

How does biochemical standard state differ from
chemical standard state?

What is the final product of beta-oxidation of an odd-
chain saturated fatty acid?

Dietary fat is transported through the bloodstream in
particles called what?

Name a dehydrogenase that uses FAD rather than
NAD⁺ as electron acceptor.

The reaction catalyzed by citrate synthase is an example
of _____ condensation

What cofactor is used by Propionyl-CoA carboxylase?

Which enzyme has a lower K_m for glucose: hexokinase
in the muscle, or glucokinase in the liver?

Name a high energy compound from central metabolism
that is an acylphosphate

Name a high energy compound that is an enolphosphate

Name a high energy compound that is a thioester

(2) (20 points total)

(a) The reactions catalyzed by succinyl-CoA synthetase and phosphoglycerate mutase each involve phosphoenzyme intermediates.

(a.i.) (4 points) Write the net reactions catalyzed by these two enzymes.

(a.ii.) (10 points) For one of the two enzymes above (you choose which one) write a complete reaction mechanism, showing all necessary general acids, bases, intermediates, and correct electron pushing.

(b.i) (6 points) Draw the structures of the key intermediates formed during conversion of substrate to product by the following enzymes:

(a) aconitase

(b.ii) triose phosphate isomerase

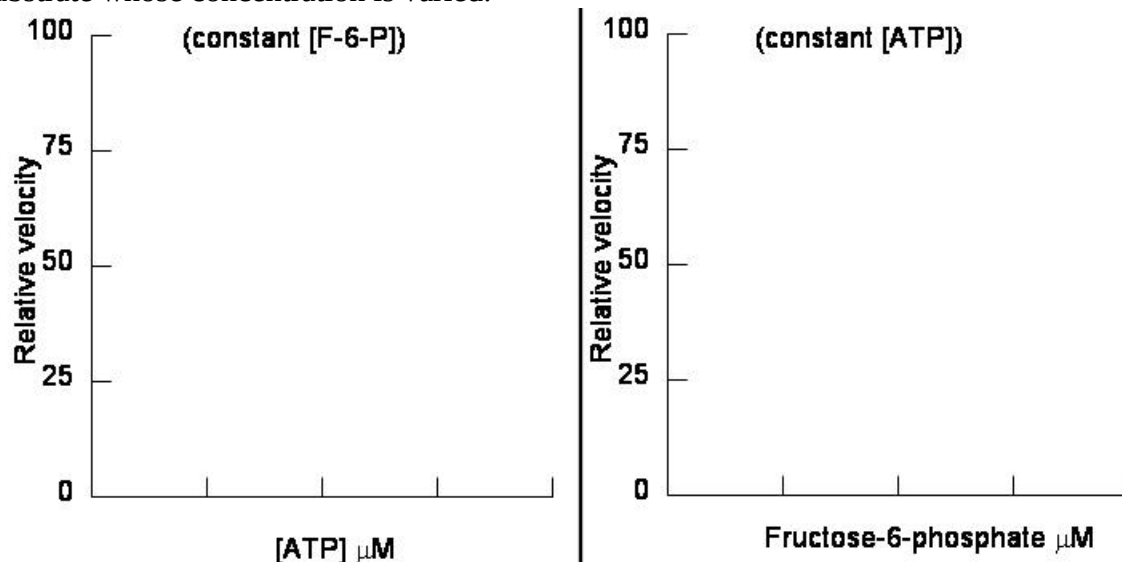
(3) (20 points total)

(a) (6 points) What events and reactions result in the production of cAMP in the liver, muscle, or adipose tissue? Describe in detail.

(b) (4 points) How does cAMP activate protein kinase?

(c) (4 points) Glycogen phosphorylase in the liver is a glucose/AMP (circle one) sensor, and binds this metabolite in the phosphorylated/unphosphorylated (circle one) form. In contrast, glycogen phosphorylase in the muscle is a glucose/AMP (circle one) sensor and binds this metabolite in the phosphorylated/unphosphorylated (circle one) form.

(d) (6 points) Recall that ATP is both a substrate and allosteric effector of phosphofructokinase. Draw the v vs. S plots for phosphofructokinase, focusing on either ATP or fructose-6-phosphate as the substrate whose concentration is varied:



(4) (a) (10 points) Use information from the first page of the exam to calculate ΔG° and K_{eq} for the following reaction:



(b) (10 points) Diagram the reaction mechanism by which lactate dehydrogenase catalyzes this reaction in the direction written, showing all necessary cofactors, general acids, bases, intermediates, and correct electron pushing. You may abbreviate the ADP-ribose portion of NAD^+ and NADH as "R", as shown for NADH on the cofactors sheet (page 2).

(5) (20 points total)

(a) (5 points) Draw the structure of isocitrate. Circle the carbon atoms on isocitrate that are released as CO_2 during one turn of the citric acid cycle.

(b) (3 points) Write the balanced chemical equations for conversion of one molecule glucose to pyruvate by glycolysis.

(c) (3 points) Write the balanced chemical equation for one turn of the citric acid cycle (starting with acetyl-CoA).

(d) (3 points) Write the balanced chemical equation for the oxidation of one molecule of oleic acid (saturated C18 fatty acid) to CO_2 by beta oxidation and the Citric Acid Cycle (your answer to part (c) above should help you here).

(e) (6 points) For each of the general terms below, write a reaction from central metabolism that illustrates that process, and name the enzyme involved:

(e.i) Phosphorolysis

(e.ii) Hydrolysis

(e.iii) Thiolytic

(6) (20 points)

(a) 10 points) You have just eaten a big juicy, fatty hamburger. Explain (feel free to diagram) how the portion of the hamburger that is fat eventually arrives in your muscle cell (i.e., what is the biochemical/molecular path from intestine to muscle?

(b) 10 points) Diagram the pathway by which fatty acids are transported from the cytosol to the mitochondrial matrix.