 Name _____

Biochemistry 5700
Fall, 2002
Exam 3

INSTRUCTIONS:

Do not begin until 10:30 AM. The exam should have 6 questions, with one question on each page. **Answer any five of the six questions**; **write "do not grade" on the one question you choose to skip.** Each graded problem will count 20 points each. Answer questions completely. When drawing mechanisms, push all electrons properly, and draw/show the roles of all necessary general acids/bases, metal ions, and other cofactors. Good Luck!!

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

Constants: F = 96.5 kJ/V•mol R = 8.3144 J/mol•K

(1) (a) 10 points. Some chemolithoautotrophic bacteria gain all their energy from the oxidation of nitrite (NO_2^-) to nitrate (NO_3^-). In theory at least (biochemical standard state conditions), the free energy provided by the oxidation of <u>one mol</u> nitrite in the presence of O_2 is sufficient to form how many ATP molecules? DO NOT ROUND your answer like you did on the quiz- report answer to two significant figures. ($E^{\circ\prime}$= +0.43 V for the NO_3^-/ NO_2^- couple, $E^{\circ\prime}$= +0.816 V for the O_2/H_2O couple, $\Delta G'$= -30.5 kJ/mol for ATP hydrolysis).

(b) 10 points. The free energy of hydrolysis of creatine phosphate is -43 kJ/mol, while that of ATP is -30.5 kJ/mol. What would be the concentration of creatine in equilibrium with ATP, creatine, ADP, and phosphate in a muscle cell where [ATP] = 2.0 mM, [ADP] = 0.05 mM, and [phosphocreatine] = 0.5 mM?

(2) 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?

What is the general name for the class of enzymes that use inorganic phosphate to break an O-glycosidic bond?

Name a specific enzyme from the citric acid cycle that catalyzes substrate level phosphorylation

Name the enzyme from β-oxidation that produces acetyl-CoA as a product

Name a cofactor used to facilitate homolytic bond cleavage

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

Name an enzyme from the citric acid cycle catalyzing substrate hydrolysis

What cofactor can be used both for oxidation/reduction and as an acyl group carrier?

Name an enzyme that requires/involves a phosphorylated histidine residue in catalysis

How many electrons are released from the oxidation of 1 acetyl-CoA in the citric acid cycle?

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

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

What is the high energy intermediate of fatty acyl-CoA synthetase?

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

How many net ATP are produced from the oxidation of one glucose to two pyruvate?

Name a high energy compound that is an enolphosphate

Name a high energy compound that is a thioester

(3) 20 points. Recall that acetone is formed by the spontaneous decarboxylation of acetoacetate in your blood stream.

(a) Propose a simple mechanism for nonenzymatic acetoacetate decarboxylation.

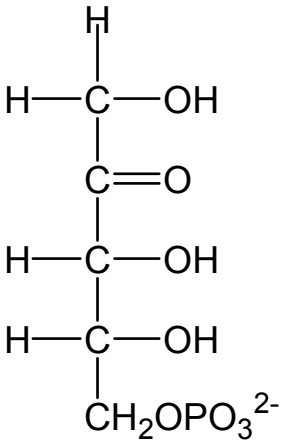
(b) The enzyme acetoacetate decarboxylase accelerates this reaction through the formation of a schiff base. Draw the mechanism for this reaction, highlighting why the Schiff base accelerates the rate. You need not show the mechanistic steps involved in Schiff base formation/hydrolysis.

(c) Do you think pyruvate will decarboxylate spontaneously like acetoacetate? Why or why not?

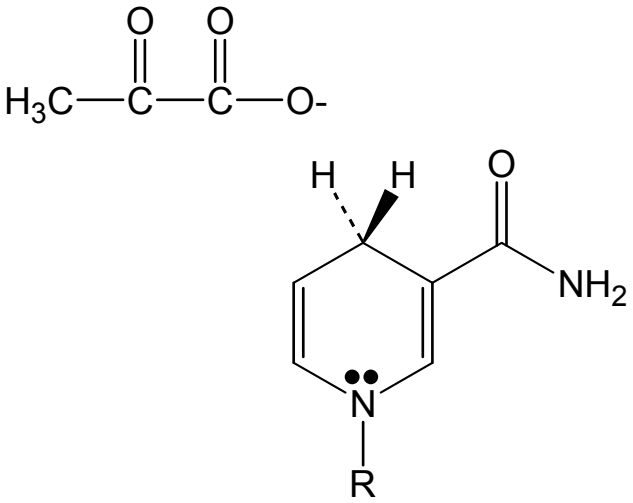
(d) What cofactor is used in the enzymatic decarboxylation of pyruvate? Draw the mechanism by which pyruvate decarboxylase converts pyruvate to acetaldehyde.

(3) continued.

(4) (a) 10 points. Ribose-5-phosphate isomerase catalyzes the interconversion of ribose-5-phosphate and ribulose-5-phosphate during photosynthetic carbon fixation. Based on your knowledge of the chemistry of aldo/keto sugar conversions, propose a mechanism for converting ribose-5-phosphate to ribulose-5-phosphate. Start with the structure drawn below:



(b) 10 points. Complete the reaction mechanism for the lactate dehydrogenase-catalyzed conversion of pyruvate to L-lactate started below:



5. (a) (10 points) Isocitrate dehydrogenase is an allosteric enzyme subject to both negative and positive regulation

i. Write a balanced chemical equation for the isocitrate dehydrogenase reaction, showing the structures of isocitrate and its oxidation product
ii. Name a molecule that would be a likely candidate for a positive regulator of isocitrate dehydrogenase, and name a molecule likely to be a negative regulator. Briefly explain the logic in your choices.

(b) 5 points. What is the difference between a feedback and product inhibitor?

(c) 5 points. Explain how ATP can be both a substrate and inhibitor of phosphofructokinase.

(6) (a) 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) Outline the series of events involved in the hormonally-controlled mobilization of glycogen for use as an energy source (i.e. describe what happens from the time of hormone production and release from the adrenal gland).