Exam I Key Spring 2013

1. (23 pts) "Enriched flour" in the US has, among other things, added niacin and thiamine.

    a. (4 points) These compounds are members of what class of molecules?

VITAMINS

    b. (5 points) Describe the general, common characteristics of molecules in this class.

MOLECULES THAT ARE ESSENTIAL FOR THE FUNCTIONING OF CRITICAL METABOLIC REACTIONS BUT CANNOT BE SYNTHESIZED BY THE ORGANISM AND THUS MUST BE INGESTED AS PART OF THE DIET

    c. (4 points) Can they be used by the body in the form they are found? Explain.

NO. THEY MUST BE CONVERTED TO THE COENZYME FORM THROUGH THE ADDITION OF A GROUP OF ATOMS SPECIFIC TO EACH VITAMIN

    d. (10 points) Why is each of these two compounds required? Explain in detail, including a discussion of what each does. Structures of only the active portion of the compounds are required. (Less than 10 atoms.)

NIACIN IS REQUIRED FOR REACTIONS INVOVING OXIDATION OF A METABOLITE, PICKING UP A HYDRIDE (SHOW C4 WITH TWO BONDS TO THE RING AND ONE BOND TO EACH OF THE H). THIAMINE IS REQUIRED IN CERTAIN C-C BOND BREAKING/MAKING REACTIONS IN ORDER TO CREATE THE ELECTRON SINK β TO THE BREAK. (SHOW THREE ACTIVE ATOMS OF TPP AND ENOUGH OF A SUBSTRATE (e.g.PYRUVATE) TO SHOW THE STABILIZED STATE.)

2. (18 points) An unusual organism is found in a meteorite. It performs glycolysis as traditionally described, and then converts the pyruvate to ethanol and CO_2. It also converts glyceraldehyde-3-phosphate to glycerol phosphate. It is found that the standard free energy of that reaction AS PERFORMED BY THAT ORGANISM is negative.
    a. What type of reaction is the conversion of glyceraldehyde-3-phosphate to glycerol phosphate. Explain.

THIS IS AN OXIDATION/REDUCTION WITH GLYCERALDEHYDE BEING REDUCED

    b. Investigators purify the enzyme that catalyzes this reaction. When they add it to a reaction vessel containing glyceraldehyde-3-phosphate in a buffer suitable for enzyme catalyzed reactions, they find that there is no significant production of glycerol phosphate. Suggest an explanation, based on an important biochemical principle other than kinetics: activation energy, presence of enzyme etc.

ANOTHER MOLECULE IS REQUIRED TO DONATE PROTONS AND ELECTRONS FOR THE REDUCTION OF GLYCERALDEHYDE

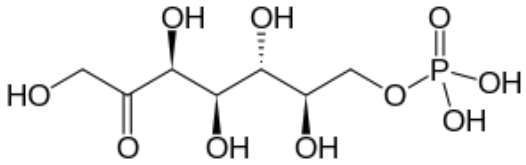
c. The required molecule is identified and studied. It is determined that the standard free energy of this reaction as it occurs in this organism is negative. What important property other than solubility, ability to be bound by the enzyme etc. is required of this molecule?

THE MOLECULE MUST BE A STRONGER REDUCING AGENT THAN GLYCERALDEHYDE (MORE NEGATIVE REDUCTION POTENTIAL).

3. (12 points) Westheimer, in studying the stereospecificity of the enzyme alchohol dehydrogenase, ran three experiments with the enzyme, as we discussed. One involved starting with ethanol and NAD^+, from which he produced acetaldehyde and NADH, and another started with acetaldehyde and NADH, producing ethanol and NAD. How could he have done this given that these two reactions have equal standard free energies but with opposite signs? Explain in detail what he did to achieve this and why it worked.

STANDARD FREE ENERGY IS A MEASURE OF THE EQUILIBRIUM CONSTANT OF A REACTION. SINCE THESE REACTIONS ARE STUDIED IN ISOLATION, THEY WILL GO TO EQUILIBRIUM, IN WHICH CASE THERE WILL BE MEASURABLE AMOUNTS OF ALL PRODUCTS AND REACTANTS, EVEN THOUGH THERE WILL BE MORE OF THOSE AT A LOWER FREE ENERGY.

4. (13 points) In a pathway we will discuss in several weeks, sedoheptulose 7-phosphate (below) is cleaved between the 3rd and 4th carbons and the resulting three carbon unit transferred to glyceraldehyde 3-phosphate. Draw the simplest mechanism you can for this reaction, taking it ONLY from sedoheptulose 7-phosphate to the intermediate in which the bond has been broken and the two pieces stabilized. Explain clearly the role of any amino acids, coenzymes or metals that are involved.



BREAKING BETWEEN CARBONS THREE AND FOUR WILL PUT A NEGATIVE CHARGE ON CARBON THREE. THIS INTERMEDIATE WILL BE STABILIZED BY CREATING A STRUCTURE WITH A DOUBLE BOND BETWEEN CARBONS TWO AND THREE, AND A NEGATIVE CHARGE ON THE OXYGEN, WHICH CAN BE STABILIZED BY THE PRESENCE OF POSITIVE METAL ION. ANSWER DISCUSSING PRODUCTION OF THE SCHIFF BASE IS ALSO ACCEPTABLE.

5. (18 pts) A previously unobserved organism is isolated from the ocean depths. It is able to carry out the reactions of glycolysis but it appears to excrete pyruvate, not lactate, ethanol or any other molecule derived from pyruvate. It is studied under conditions, similar to those employed by Harden and Young in their work studying yeast glycolysis and it is found that all the carbon ingested is excreted as pyruvate.

a. How many ATP are produced for each pyruvate excreted? Explain

ONE ATP PER PYRUVATE; Two ATP per glucose, two pyruvate per glucose

b. What reaction not included in yeast or muscle glycolysis as we studied it must this organism carry out in order to survive? Explain.

SOMEHOW, THE NADH PRODUCED IN THE OXIDATION OF GLYCERALDEHYDE TO GLYCERIC ACID MUST BE REOXIDIZED TO NAD, GIVEN THAT ITS REOXIDATION IN THE REDUCTION OF PYRUVATE TO ETHANOL OR LACTATE DOES NOT OCCUR.

6. (16 pts) An undergraduate, working in a genetic engineering laboratory, identifies the gene for a very fast, very active enzyme that is able to hydrolyze 1,3,bis phosphoglyceric acid. He inserts the gene into yeast that can normally convert glucose to ethanol and carbon dioxide and finds that the enzyme is produced in active form. In the tradition of Harden and Young, he then measures carbon dioxide, ethanol, ATP, ADP and NAD so he can write the balanced equation for glycolysis in this organism. He writes it correctly? What does he write? Explain fully.

Glucose ---> 2 CO_2 + 2 Ethanol
In sequence:

GLU + 2 ATP + 2 P_i ----->2 1,3 BPG + 2 ADP

2 1,3BPG ---->2 P_i + 2 3PGA

2 3PGA + 2 ADP ---->2 pyruvate + 2 ATP----->2 ethanol + 2 CO_2 + 2ATP

IN TOTAL: Glucose ---> 2 CO_2 + 2 Ethanol