Chemistry 135, Third Exam

November 9, 2015

This exam will be worth 15% of your overall grade. Please read all instructions/questions carefully and provide answers to the questions in the space provided. There should be **8** total pages containing **7** questions spread out over **6** pages. The first page is this coversheet, and the last page is left intentionally blank. *Please put you name and SID on the pages of the exam you wish receive credit for. We separate the pages and scan them to be graded.* You may use this last page as scratch paper, but *be sure to transfer* any answer you wish to receive credit for to the space provided. No calculators, phones, electronic devices, etc. may be used during this exam. Good luck!

(1)	___________	(21 points)
(2)	___________	(15 points)
(3)	___________	(20 points)
(4)	___________	(23 points)
(5)	___________	(12 points)
(6)	___________	(12 points)
Total	___________	(103 points)

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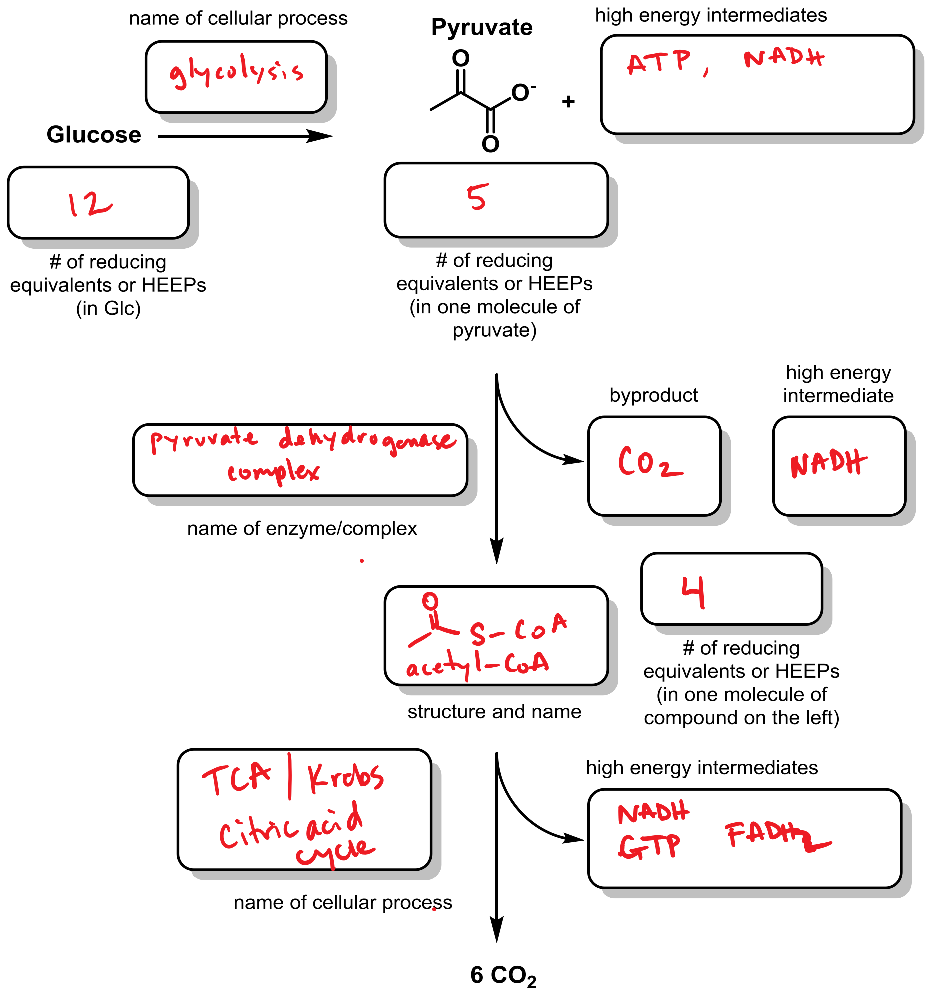
1. The chart below represents many of the cellular metabolic processes we have encountered in the last section. Fill in the missing components of the flow chart. You do not need to provide structures for the various high energy intermediates/molecules that are formed from the catabolic pathways unless specifically instructed to do so.



Commented [EWM1]: +2 for glycolysis
+2 for 12 HEEPs
+2 for 5 HEEPs
+1 for ATP
+1 for NADH

+2 for pyruvate dehydrogenase / pyruvate dehydrogenase complex
+1 for CO2
+1 for NADH
+1 for structure of Ac-CoA
+1 for name of Ac-CoA
+2 for 4 Heeps

+2 for TCA or Krebs or Citric acid cycle
+1 for NADH
+1 for FADH2
+1 for GTP

21 pts total

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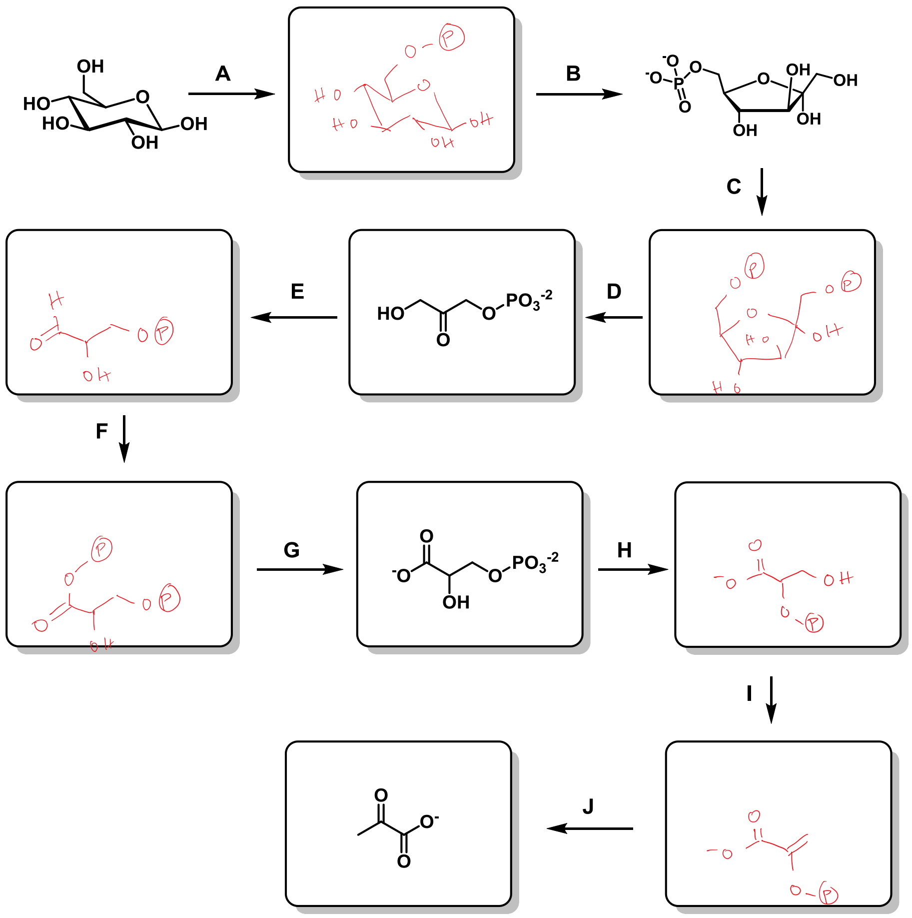
2a. Fill in the missing structures for glycolysis.

Commented [EWM2]: Question 3 part a
+1 for each structure

5 total



Several steps in glycolysis consume or produce high energy intermediates. Indicate which steps (A-J) do the following:

Commented [E3]: +1 for each correct

5 points total

b. Produce NADH: F

c. Consume ATP: A and C

d. Produce ATP: G and J

e. A sample of Glc is synthesized so that carbon 1 (C-1) is isotopically labeled with radioactive ^{14}C. This radioactive Glc* is fed into the glycolysis pathway. Where does the ^{14}C end up in the end-product of glycolysis? Provide a structure and indicate the labelled carbon.

Commented [E4]: +5 for correct carbon

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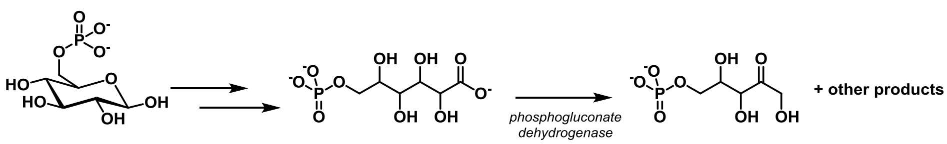
3. The first step in glycolysis is the phosphorylation of glucose to generate glucose 6-phosphate (G6P). G6P can be funneled into glycolysis, or alternatively can be shunted into other pathways to be used in anabolic reactions. One such example of this is the pentose phosphate shunt, which captures glucose for use in synthesis of nucleic acids (ribose). After oxidation of G6P to 6-phosphogluconate, the enzyme 6-phosphogluconate dehydrogenase converts the gluconate to ribulose 5-phosphate, using mechanisms similar to others we have discussed in class.



glucose 6-phosphate **6-phosphogluconate** **ribulose 5-phosphate**

a. For the conversion of 6-phosphogluconate to ribulose 5-phosphate, what cofactors, if any, are required?

NAD+

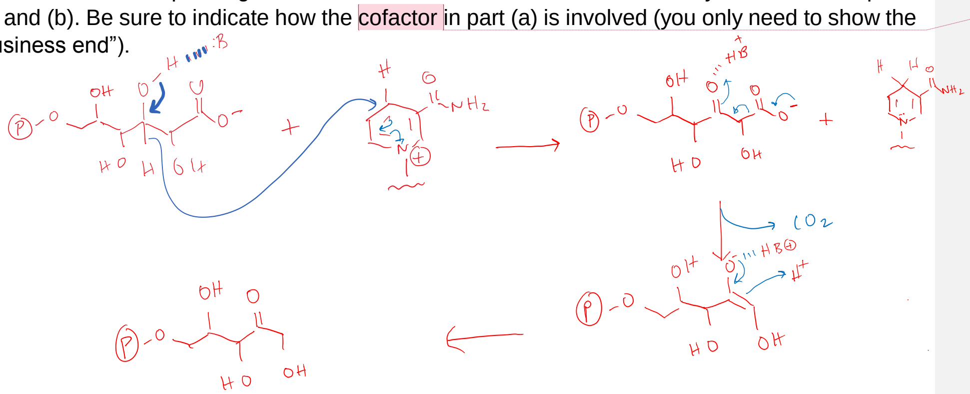
Commented [E5]: +3 for nad+

b. What are the “other product(s)” generated as a result of the action of 6-phosphogluconate dehydrogenase on 6-phosphogluconate?

CO_2

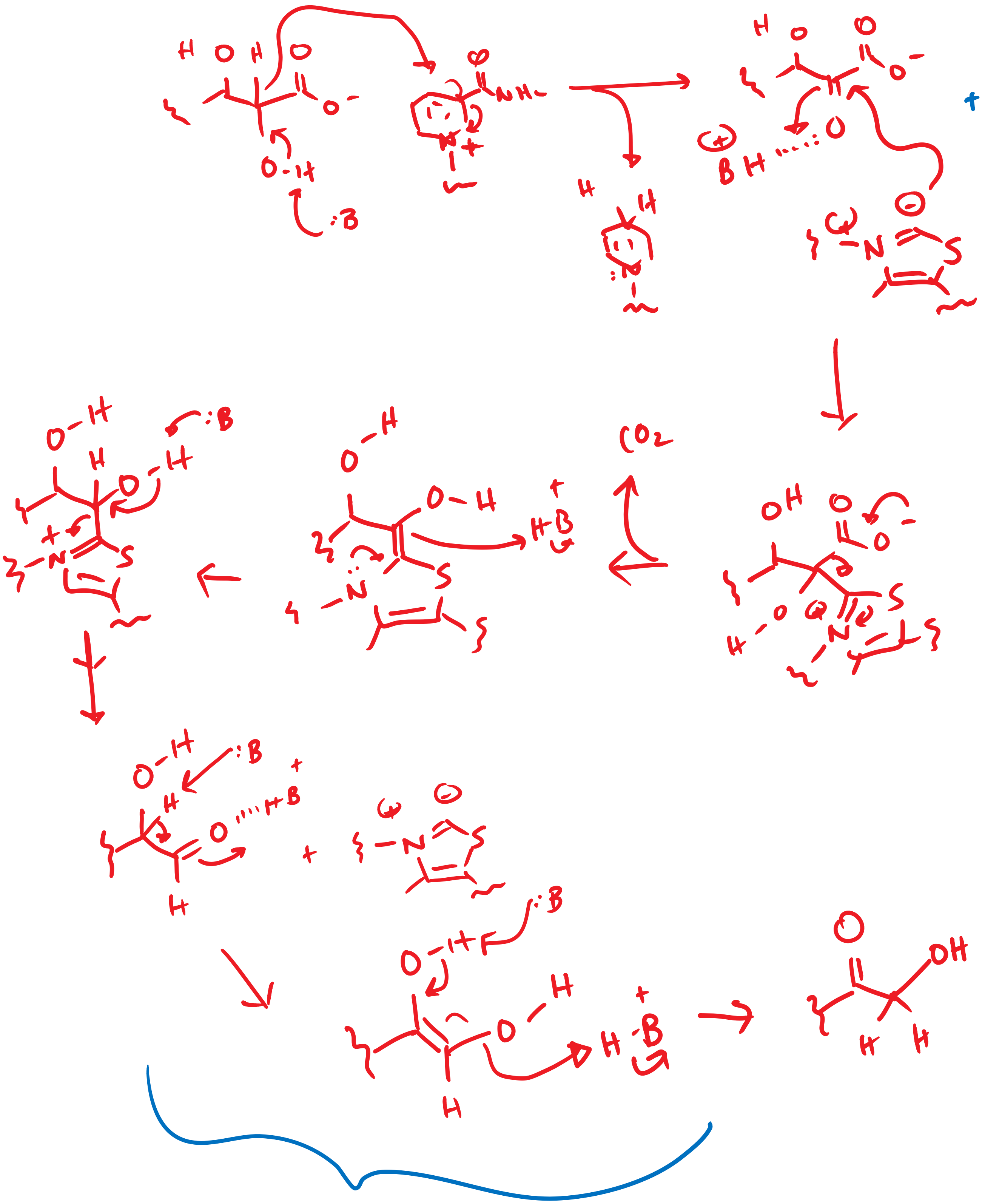
Commented [E6]: +3 for CO2

c. Provide an arrow-pushing mechanism for this reaction that accounts for your answers in parts (a) and (b). Be sure to indicate how the cofactor in part (a) is involved (you only need to show the “business end”).



Commented [E7]: 14 points total
+1 base removes proton from hydroxyl
+3 hydride transfer to NAD+
+2 formation of NADH
+2 decarboxylation arrows show electrons pushing from carboxylate into the enolate pi system
+2 for activation of the carbonyl with H+/BH+/metal ion
+2 loss of CO2
+2 tautomerization of enol to product

+2 decarboxylation facilitated by TPP



+2 isomerization

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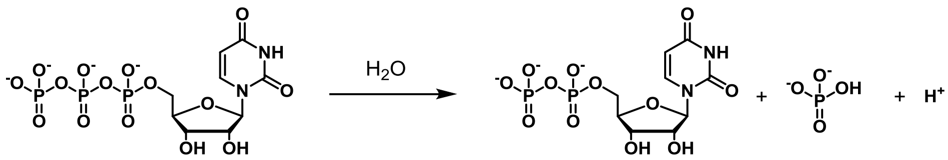


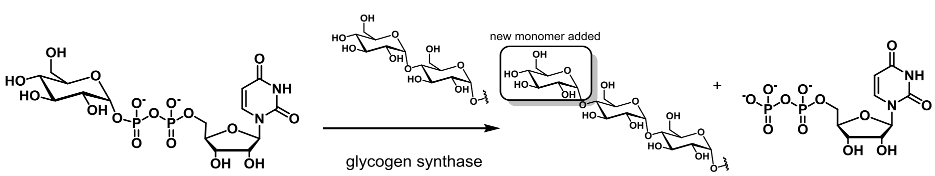
UTP UDP

4a. Shown above is the conversion of UTP to UDP. Estimate the standard free energy change for this reaction. Briefly explain your answer (1-2 sentences).

The standard free energy should be ~ -7.3 kcal/mole, similar to ATP→ADP, because the energy of ATP hydrolysis comes primarily from the phosphate ester, not the nucleotide identity.

Commented [E8]: +2 FOR -7.3 kcal/mol
+4 for comparision to ATP

Glycogen is the main sugar polymer used as energy storage in animals. The enzyme glycogen synthase uses UDP-glucose as a monomer to add glucose residues to the non-reducing end of a growing glycogen polymer, as shown below.



UDP-Glucose glycogen polymer UDP

In addition to extending the length of the glycogen chain, this reaction also generates UDP as a byproduct. In the cell, UDP can be regenerated according to the following reaction.

$$UDP + ATP \rightleftharpoons UTP + ADP$$

b. Estimate the ΔG′° for this reaction and provide a brief explanation (1-2 sentences).

Approximately 0. Standard free energy is close to 0 because the standard free energy for each ½ reaction is the same (see part a).

Commented [E9]: +2 0
+5 because forward and reverse reactions are the same
+7 total

c. In cells, the equilibrium position for this reaction lies far to the right. Provide a possible explanation for this observation. (1-2 sentences).

$\Delta G = \Delta G'^{\circ} + RT \ln (Q)$.

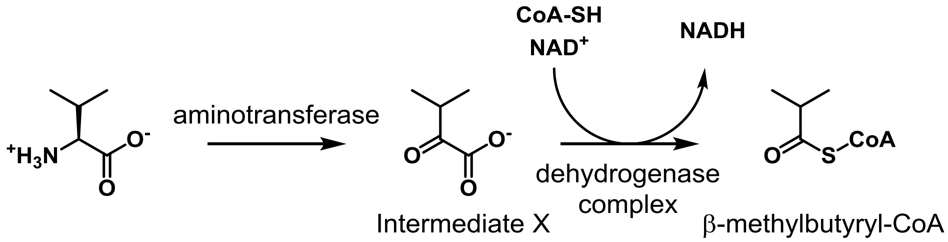
Commented [E10]: 10 points possible

+3 Possible explanation: high ratio of reactants to products (high ATP:ADP ratio,

+3 low UTP:UDP ratio)

+4 ACTUAL FREE ENERGY is negative (not standard free energy)

5. The metabolism of branched amino acids like leucine involve two enzymes, an amino transferase, which converts leucine into intermediate X (shown below) and a dehydrogenase that produces β-methylbutyryl-CoA. This dehydrogenase complex requires several cofactors, including NAD^+, Coenzyme A, lipoate, and FAD.



a. Based on our discussions in class, what might be another co-factor that is required for the function of this branched chain dehydrogenase complex? Provide the name and structure (business end is fine).

thiamine pyrophosphate (TPP).

Commented [E11]: +3 for TPP

b. What other byproducts are produced as a result of the action of the dehydrogenase complex on Intermediate X.

Commented [E12]: +3 for CO2

CO_2

c. This branched chain dehydrogenase complex is evolutionarily related to several enzymes/biochemical processes we have discussed in class. Provide the name of one of the other enzyme complexes (either enzyme complex name or the chemical transformation it performs). What part of metabolism is this enzyme/biochemical step associated with?

Commented [E13]: +3 for one of the complexes (or reactions)

+3 for part of metabolism

pyruvate dehydrogenase complex, prepping Ac-CoA from pyruvate for the TCA

alpha-ketoglutarte dehydrogenase, TCA

6. True or False. If the statement is false, provide corrections so that the statement reads true. If true, mark as true.

Commented [E14]: +1 each for False

+3 for True

+2 for explanation

a. Glycolysis, the metabolic pathway by which a cell breaks down glucose into pyruvate, is the ~~primary~~ source of ATP and reducing equivalents extracted from glucose.

False.

Glycolysis, the metabolic pathway by which a cell breaks down glucose into pyruvate, is not the primary source of ATP and reducing equivalents extracted from glucose

b. Ethanolic and lactic acid fermentation are two pathways that enable the glycolysis to occur in the absence of oxygen through the regeneration of ~~NADH~~.

False.

Ethanolic and lactic acid fermentation are two pathways that enable the glycolysis to occur in the absence of oxygen through the regeneration of NAD^+.

c. Although the standard free energy change (ΔG'°) for the hydrolysis of phosphoenolpyruvate (PEP) is highly exergonic, at approximately -14.8 kcal/mol, adenosine triphosphate (ATP), is the preferred "high energy phosphate intermediate" because it possesses negative ΔG'° for hydrolysis, in addition to kinetic stability and "pizazz," or the presence of multiple sites that enable weak, non-covalent interactions with enzymes.

True.

d. Several steps in the citric acid cycle and/or glycolysis generate high energy phosphate compounds. The production of ATP and/or GTP in this fashion is known as ~~oxidative~~ phosphorylation.

False.

Several steps in the citric acid cycle and/or glycolysis generate high energy phosphate compounds. The production of ATP and/or GTP in this fashion is known as substrate-level phosphorylation.

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