Name Key

Biochemistry 5700
Fall, 2005
Exam 3

INSTRUCTIONS:
Do not begin until 10:30 AM. 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: $\Delta G = \Delta G^{\circ\prime} + RT \ln Q$ $\Delta E = \Delta E^{\circ\prime} - \frac{RT}{nF} \ln Q$ $\Delta G' = -nFE'$

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

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)*
$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$	0.816
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.771
$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$	0.421
Cytochrome *f* (Fe^{3+}) + e^- ⟶ cytochrome *f* (Fe^{2+})	0.365
$Fe(CN)_6^{3-}$ (ferricyanide) + e^- ⟶ $Fe(CN)_6^{4-}$	0.36
Cytochrome a_3 (Fe^{3+}) + e^- ⟶ cytochrome a_3 (Fe^{2+})	0.35
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.295
Cytochrome *a* (Fe^{3+}) + e^- ⟶ cytochrome *a* (Fe^{2+})	0.29
Cytochrome *c* (Fe^{3+}) + e^- ⟶ cytochrome *c* (Fe^{2+})	0.254
Cytochrome c_1 (Fe^{3+}) + e^- ⟶ cytochrome c_1 (Fe^{2+})	0.22
Cytochrome *b* (Fe^{3+}) + e^- ⟶ cytochrome *b* (Fe^{2+})	0.077
Ubiquinone + $2H^+$ + $2e^-$ ⟶ ubiquinol + H_2	0.045
Fumarate^{2-} + $2H^+$ + $2e^-$ ⟶ succinate^{2-}	0.031
$2H^+ + 2e^- \longrightarrow H_2$ (at standard conditions, pH 0)	0.000
Crotonyl-CoA + $2H^+$ + $2e^-$ ⟶ butyryl-CoA	−0.015
Oxaloacetate^{2-} + $2H^+$ + $2e^-$ ⟶ malate^{2-}	−0.166
Pyruvate$^-$ + $2H^+$ + $2e^-$ ⟶ lactate$^-$	−0.185
Acetaldehyde + $2H^+$ + $2e^-$ ⟶ ethanol	−0.197
FAD + $2H^+$ + $2e^-$ ⟶ $FADH_2$	−0.219*
Glutathione + $2H^+$ + $2e^-$ ⟶ 2 reduced glutathione	−0.23
$S + 2H^+ + 2e^- \longrightarrow H_2S$	−0.243
Lipoic acid + $2H^+$ + $2e^-$ ⟶ dihydrolipoic acid	−0.29
$NAD^+ + H^+ + 2e^-$ ⟶ NADH	−0.320
$NADP^+ + H^+ + 2e^-$ ⟶ NADPH	−0.324
Acetoacetate + $2H^+$ + $2e^-$ ⟶ β-hydroxybutyrate	−0.346
α-Ketoglutarate + CO_2 + $2H^+$ + $2e^-$ ⟶ isocitrate	−0.38
$2H^+ + 2e^- \longrightarrow H_2$ (at pH 7)	−0.414
Ferredoxin (Fe^{3+}) + e^- ⟶ ferredoxin (Fe^{2+})	−0.432

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(1) (17 points) Reduced ferredoxin (Ferredoxin Fe^{2+}) and molecular oxygen (O_2) are the products of the "light reactions" of photosynthesis (the substrates are water and oxidized ferredoxin (ferredoxin Fe^{3+}). Use information from the first page of the exam to answer the following questions. Continue on next page if needed.

(a) (3 pts) Write a complete balanced chemical equation for the oxidation of two mols water to one mol O_2 using oxidized ferredoxin as the electron acceptor.

(b) (8 pts) Calculate $\Delta G°'$ and K_{eq}' for this reaction (i.e oxid^n of 2 mol H_2O → one mol O_2)

(c) (6 pts) Under standard biochemical conditions, the oxidation of two mols of reduced ferredoxin to two mols oxidized ferredoxin with O_2 as the electron acceptor would provide sufficient free energy to synthesize how many molecules of ATP? Recall the free energy of hydrolysis of ATP is -30.5 kJ/mol. Do not round your final answer and show your work.

a) $2H_2O \rightarrow O_2 + 4H^+ + \cancel{4e^-}$ $\quad \varepsilon°' = -0.816V$

$4\,Fd\cdot Fe^{3+} + \cancel{4e^-} \rightarrow 4\,Fd\cdot Fe^{2+}$ $\quad \varepsilon°' = -0.432V$

$2H_2O + 4\,Fd\cdot Fe^{3+} \rightarrow O_2 + 4H^+ + 4\,Fd\cdot Fe^{2+}$

$\varepsilon°' = -1.248V$

b) $\Delta G°' = -nF\varepsilon°' = -(4)\left(96.5\frac{kJ}{V\cdot mol}\right)(-1.248V)$

$\Delta G°' = +481.7$ kj/mol reaction

$\Delta G°' = -RT\ln K_{eq}$; $K_{eq} = e^{-\Delta G°'/RT}$

$K_{eq} = \exp\left(-481.7\frac{kj}{mol}\right)\left(\frac{1}{8.314\frac{J}{mol\,K}}\right)\left(\frac{1}{298K}\right)\left(\frac{1000J}{kJ}\right)$

$K_{eq} = 3.65\times10^{-85}$!

c) $2\,Fd\cdot Fe^{2+} + 2H^+ + \frac{1}{2}O_2 \rightarrow H_2O + 2\,Fd\cdot Fe^{3+}$

$\Delta G°' = \frac{-481.7\,kj/mol}{2} = -240.85\,kj/mol$

$\frac{240.85\,kj}{2\,mol\,Fd} \Big/ \frac{30.5\,kj}{mol\,ATP} = \frac{7.9\,mol\,ATP}{2\,mol\,Fd\cdot Fe^{2+}}$

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(2) (12 points) Certain reactions of the citric acid cycle have counterparts in beta oxidation of fatty acids. Name each of the citric acid cycle enzymes and beta-oxidation enzymes having counterparts, and write the balanced chemical equations for each reaction (both citric acid cycle and beta oxidation reactions). You need not draw structures for this problem, just name the compounds involved. Indicate which specific enzymes are counterparts for the two pathways.

Succinate dehydrogenase: succinate + FAD ⇌ fumarate + $FADH_2$

counterpart =

acyl-CoA dehydrogenase: fatty acyl CoA + FAD ⇌ trans-Δ^2-enoyl-CoA + $FADH_2$

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fumarase: fumarate + H_2O ⇌ L-malate

counterpart =

enoyl-CoA hydratase: trans-Δ^2-enoyl-CoA + H_2O ⇌ L-β-hydroxyacyl-CoA

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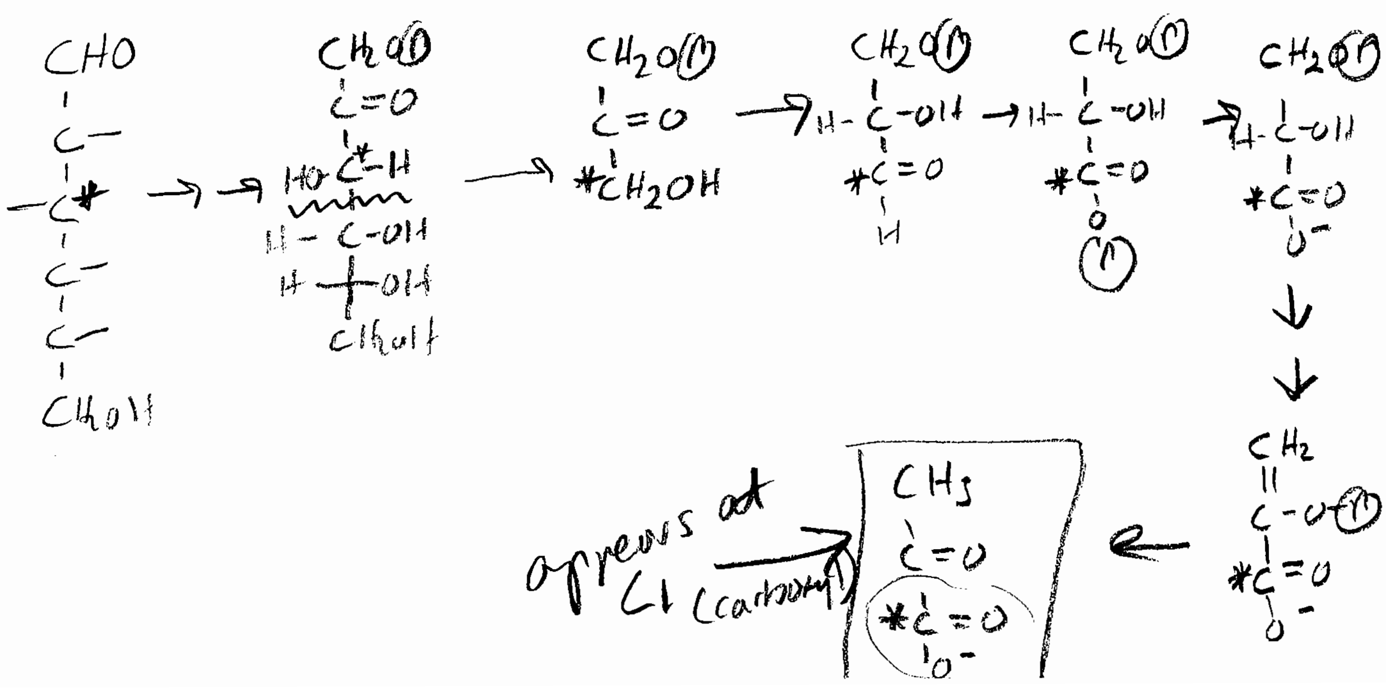
malate dehydrogenase: L-malate + NAD^+ ⇌ oxaloacetate + NADH + H^+

counterpart:

hydroxyacyl CoA dehydrogenase

L-β-hydroxyacyl-CoA + NAD^+ ⇌ β-ketoacyl-CoA + NADH + H^+

(3) (8 points) If you were to add glucose that was radiolabeled with ^{14}C at the C_3 carbon atom to a cell extract containing all the glycolytic enzymes, where would the radiolabel appear in the final product pyruvate? Show your work used to determine the answer.



appears at C1 (carboxyl)

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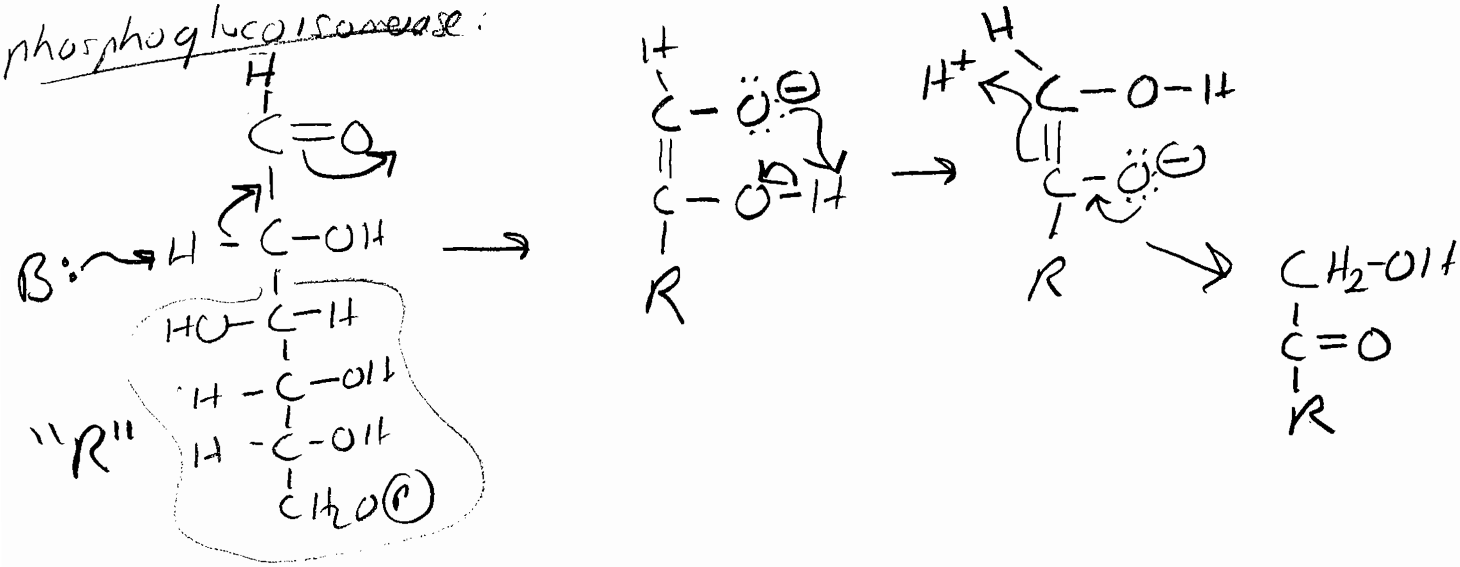
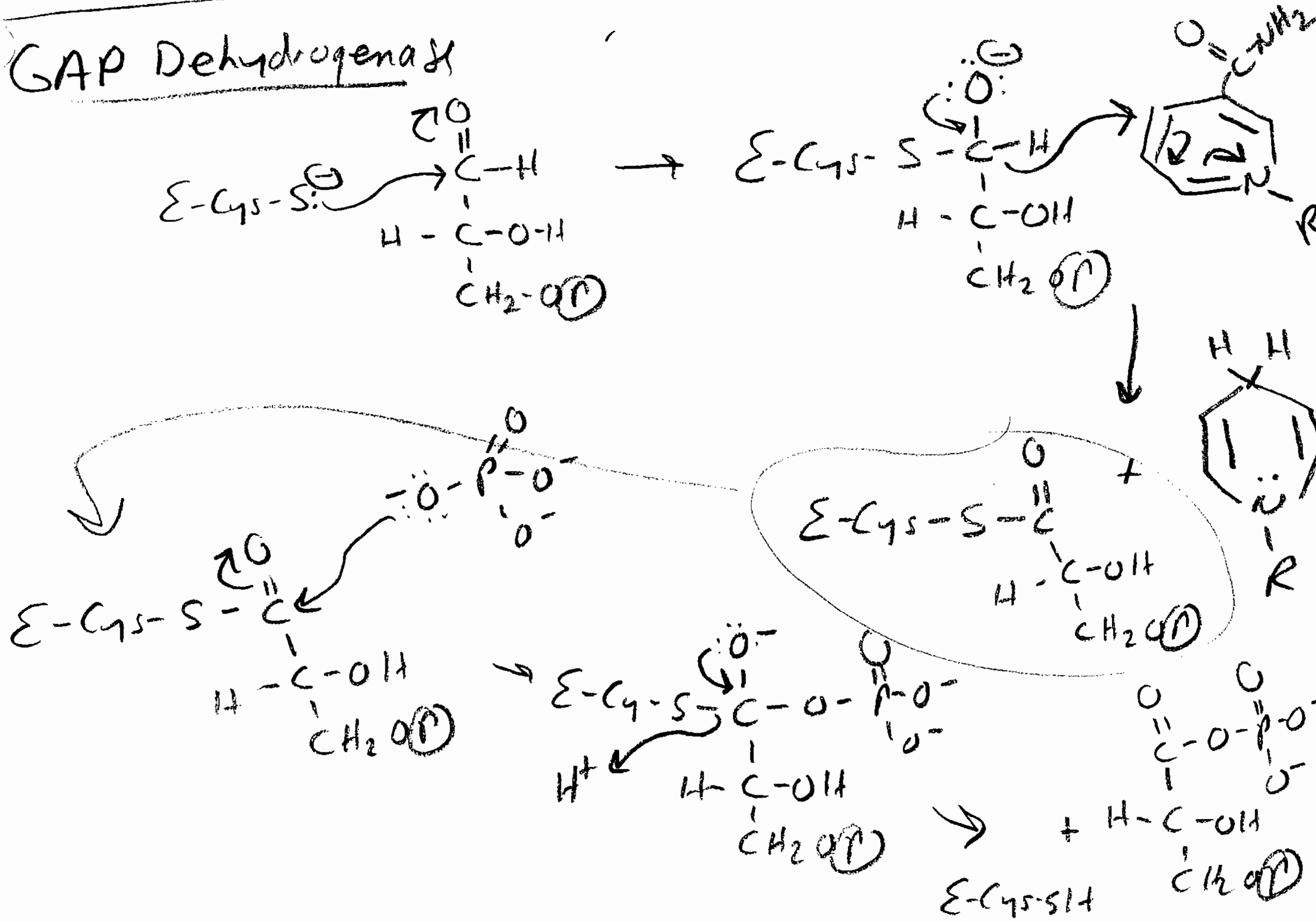
(4) (21 points) Draw complete reaction mechanisms for the reactions catalyzed by <u>any three of the four</u> enzymes listed below. Make sure to be complete in performing electron pushing, and showing all intermediates, cofactors, and general acids/bases. Continue on the top of the next page if necessary.

phosphoglucoisomerase, glyceraldehyde-3-phosphate dehydrogenase, citrate synthase, phosphoglycerate mutase

phosphoglucoisomerase:



GAP Dehydrogenase



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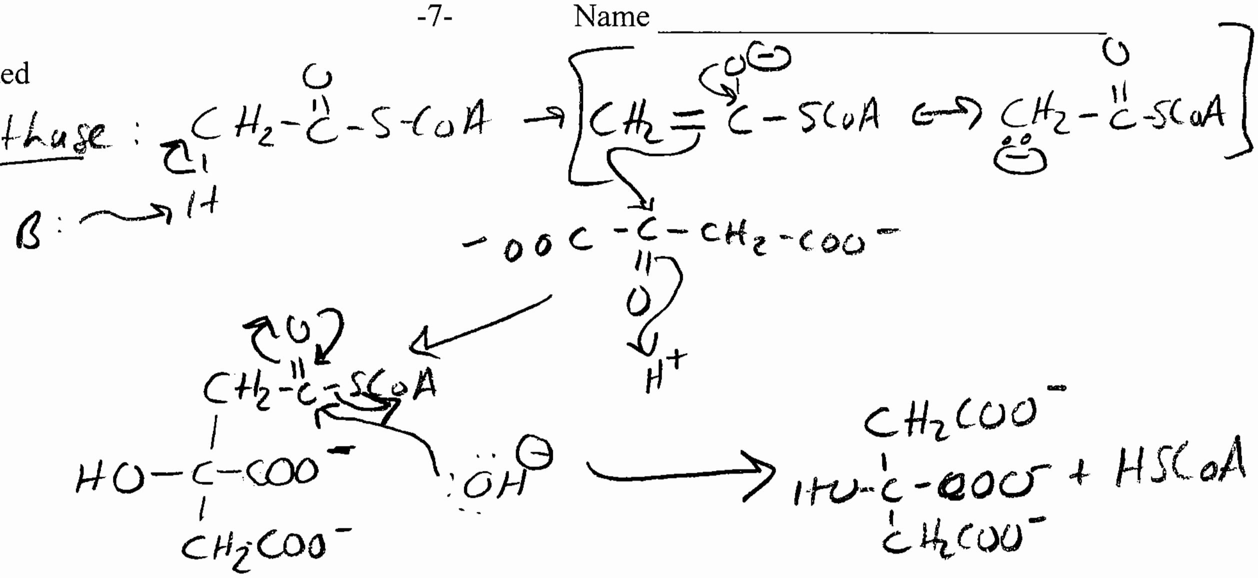
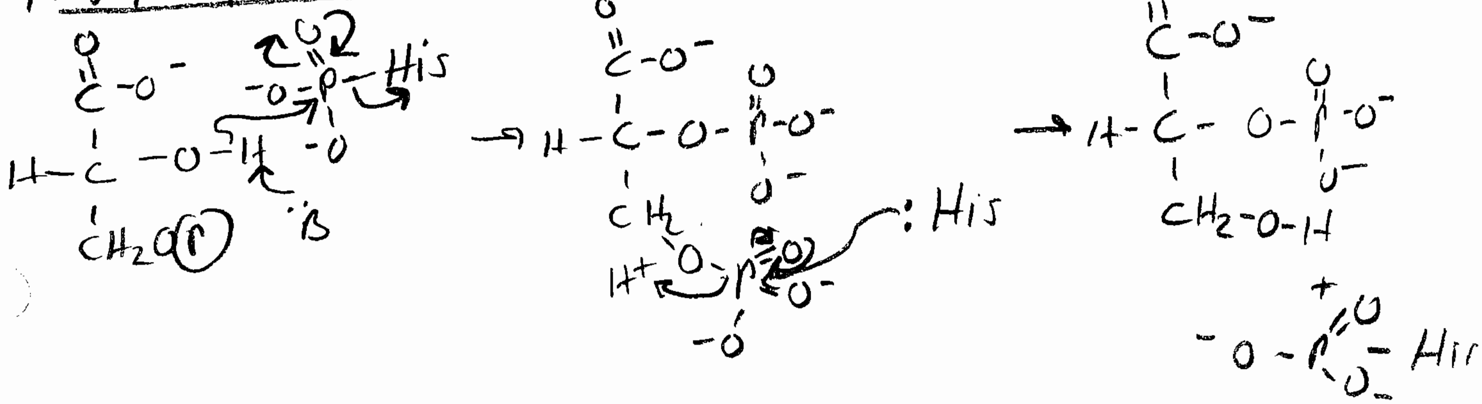
(4) continued

Citrate synthase:



phosphoglycerate mutase



(5) (10 points) Briefly explain the specific biochemical roles of the following components as they relate to the regulation of intracellular glycogen breakdown.

(a) epinephrine

the adrenaline hormone that binds to a receptor protein on the outer surface of muscle cells (myocytes), inducing a conformational change in the transmembrane receptor protein conveyed to the G protein

(b) GDP and GTP

G protein with GDP bound does not activate adenylyl cyclase (AC). The conformational change in G protein triggered by epinephrine leads to GDP dissociation & GTP binding activating G protein to bind and activate AC

(c) adenylyl cyclase

Once activated by G protein, converts ATP to 3',5'-cAMP which binds to and activates protein kinase

(d) protein kinase

Once activated by cAMP, phosphorylates phosphorylase b kinase, activating it

(e) glycogen phosphorylase

The active form of glycogen phosphorylase phosphorylyzes glycogen: $(glycogen)_n + P_i \rightarrow (glycogen)_{n-1} + Glc\text{-}1\text{-}P$

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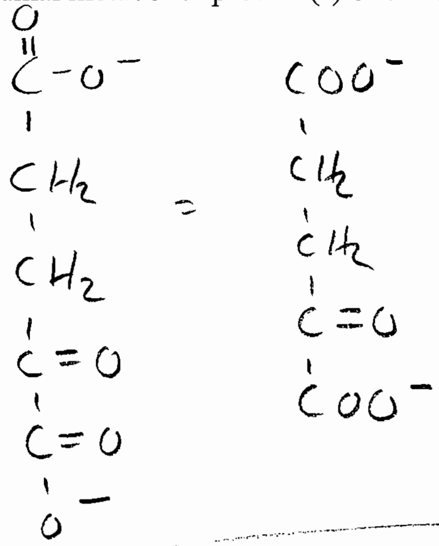
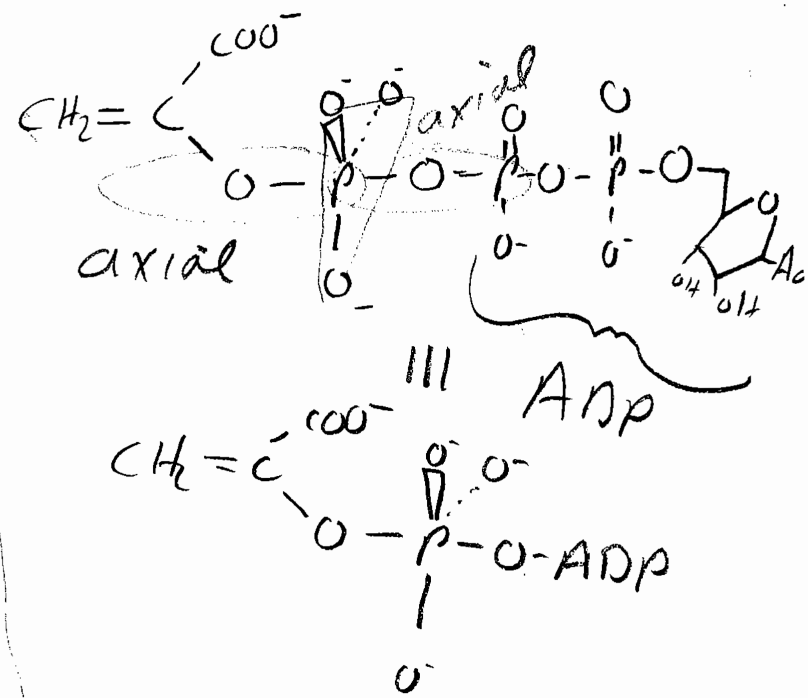
(6) (12 points) Draw chemical structures for the following
(a) the metabolite product of the reaction catalyzed by isocitrate dehydrogenase
(b) The pentavalent intermediate formed during the reaction catalyzed by pyruvate kinase
(c) The first <u>intermediate</u> formed upon reaction of hydroxyethyl-TPP carbanion with lipoamide
(d) The final metabolite product(s) of the oxidative portion of the pentose phosphate pathway

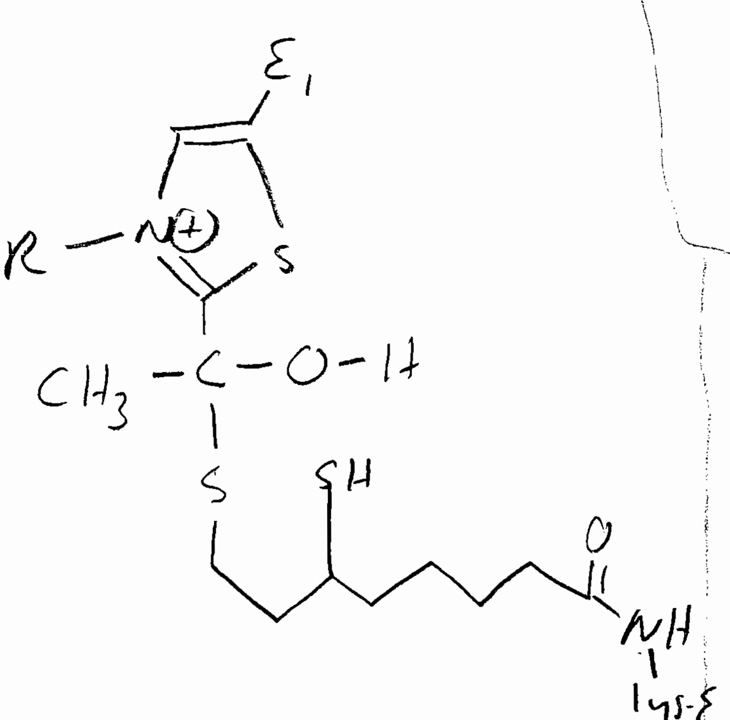
a)



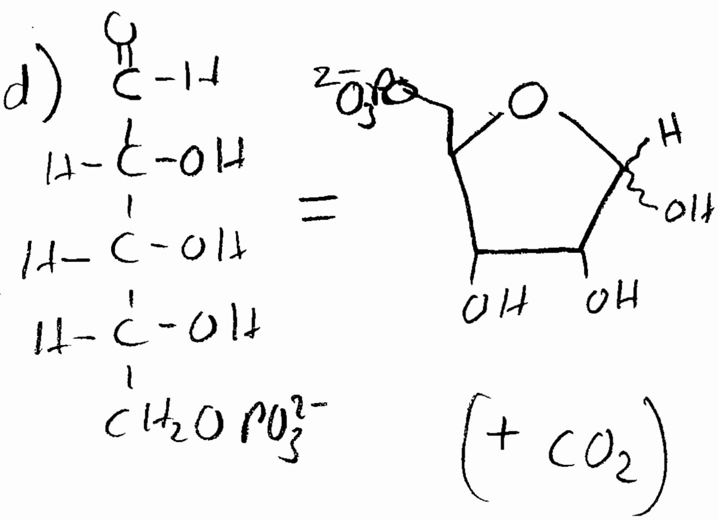
b)



c)



d)



(7) 20 points. Definitions.

An organism that grows using light as an energy source and CO_2 as a carbon source is called a:	photoautotroph
Name an enzyme from central metabolism that uses a Schiff base intermediate in catalysis	aldolase
What citric acid cycle enzyme requires thiamine pyrophosphate?	α-ketoglutarate dehydrogenase
Name a specific enzyme from central metabolism catalyzing substrate phosphorolysis	glycogen phosphorylase, others...
How many net ATP molecules are directly formed by the reactions converting glucose to pyruvate?	2
How many electrons are released from the oxidation of one acetyl-CoA to two CO_2?	8
Name the isozyme of hexokinase found in the liver	glucokinase
Name a specific enzyme from central metabolism catalyzing substrate thiolysis	thiolase
Name an enzyme that can discriminate between the two prochiral arms of its substrate	aconitase
What compound is exhaled in the breath of diabetic individuals?	acetone
Anaerobic catabolism of glucose in the muscle leads to the accumulation of what organic compound?	lactate (lactic acid)
What is the final product of beta-oxidation of an odd-chain saturated fatty acid?	propionyl-CoA
Dietary fat is transported through the bloodstream in particles called what?	chylomicrons
Fatty acids mobilized from adipocytes are transported through the bloodstream complexed to what molecule?	albumin
What molecule is used as the carrier of fatty acid units from the cytosol to the mitochondrion?	carnitine
What is the high energy intermediate formed by the enzyme fatty acyl-CoA synthetase?	fatty acyl-AMP
What enzyme catalyzes the key commited step of glycolysis?	phosphofructokinase
Name a high energy compound from central metabolism that is an acylphosphate	1,3-di(bis) phosphoglycerate
Name a high energy compound that is an enolphosphate	phosphoenolpyruvate
Name a high energy compound that is a phosphoguanidine	creatine phosphate