 Name _____

Biochemistry 5700
Fall, 2008
Exam 3

INSTRUCTIONS:
Do not begin until 10:30 AM. The exam must be turned in by 11:20 AM.

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

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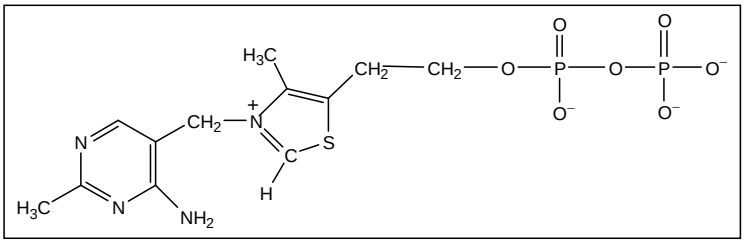
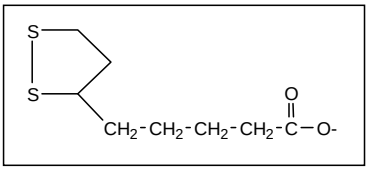
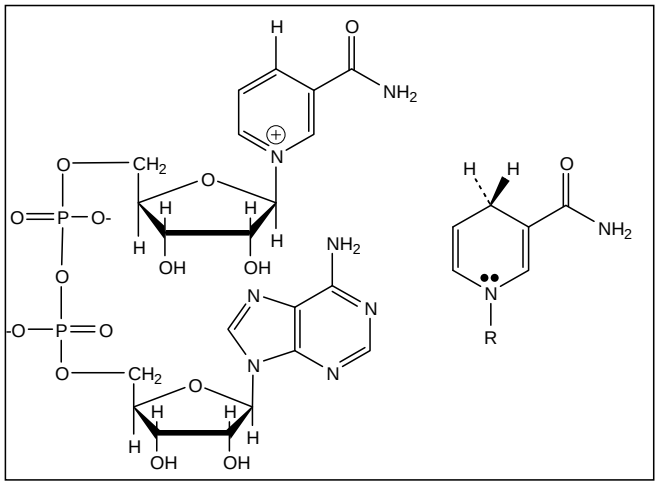
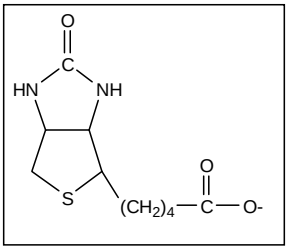
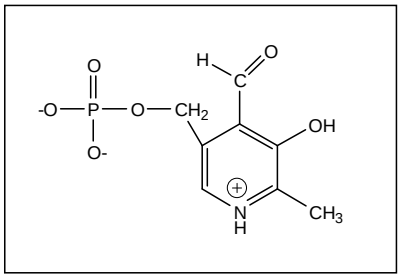
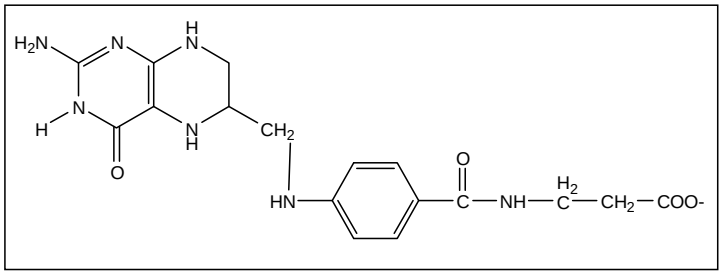


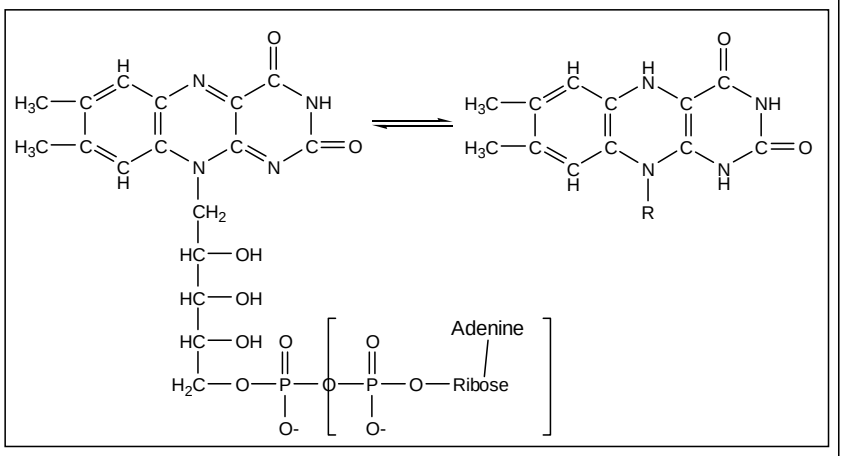


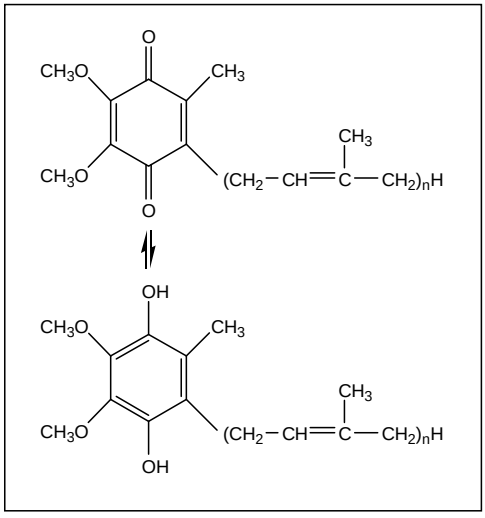












(1) Regulation of glycogen breakdown

(a) 8 pts) For each of the following proteins activated during the regulatory cascade leading to glycogen breakdown in the muscle, name the specific protein (may or may not be an enzyme), and/or small molecule ligand (effector), that directly interacts with and activates that particular protein. Note that some proteins may be regulated only by one strategy, while other(s) may use both strategies. Mark "none" in the spaces that should be blank for the proteins regulated by only one strategy.

Protein to be activated	Activating Protein (or enzyme)	Activating small molecule (effector)
Transmembrane receptor protein		
Phosphorylase kinase		
G_{α}		
Glycogen phosphorylase		
Protein kinase A		
Adenylyl kinase		

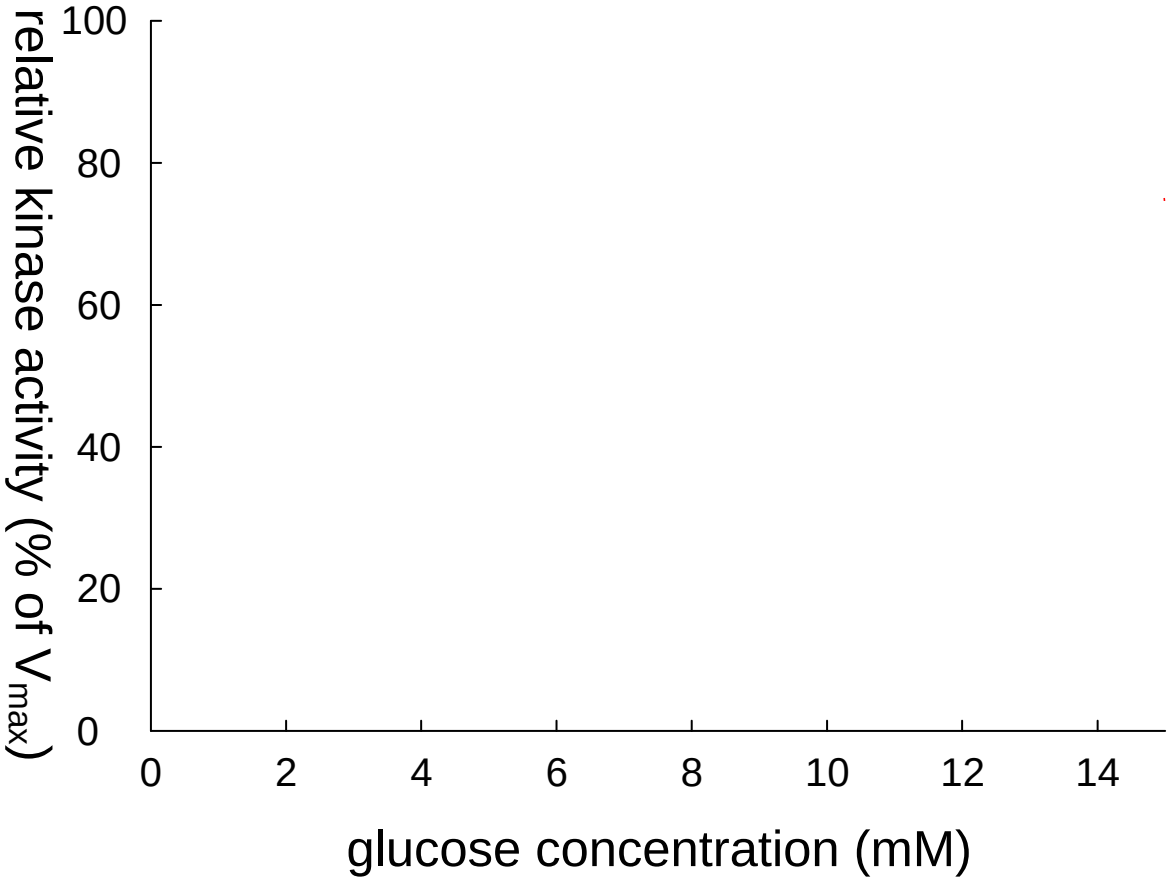
(b) (2 pts) Write the balanced chemical equation for the reaction catalyzed by active glycogen phosphorylase

(c) (2 pts) In one or two sentence, explain the mechanism by which active glycogen phosphorylase *a* in the liver undergoes deactivation when glucose levels rise

(d) (2 pts) Write the chemical reaction (full names, no structures), by which the product of glycogen breakdown is converted to a glycolytic intermediate, and name the enzyme catalyzing this transformation.

 Name _____

(2) (6 pts) Glucokinase (liver) exhibits cooperativity with respect to glucose binding (K_m = 10 mM), while hexokinase does not exhibit cooperativity (K_m = 0.1 mM). Use this information to plot the v vs. S curves for glucokinase and hexokinase over the range of glucose concentrations provided on the graph template below. Based on your plots, at approximately what percentage of V_{max} will glucokinase and hexokinase operate when the concentration of glucose is 5 mM?



(3) (4 pts) The free energy of hydrolysis of phosphocreatine is -43.0 kJ/mol. The free energy of hydrolysis of ATP is -30.5 kJ/mol. Use this information to determine the free energy change for the reaction:
Phosphocreatine + ADP → creatine + ATP

(4) (6 points) Write the balanced chemical equation for the reaction catalyzed by succinyl-CoA synthetase. What is the equilibrium constant at 298 K for this reaction given $\Delta G^{\circ\prime}$ = -2.9 kJ/mol?

Reaction: _____

K_{eq} (circle correct answer)
(a) 3.2
(b) 0.31
(c) 1.17
(d) 1.00
(e) 0.0012

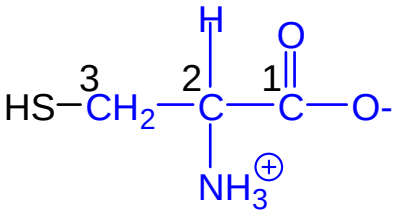
(5) (16 points) Name an enzyme from glycolysis, pyruvate oxidation, the pentose phosphate pathway, or the citric acid cycle for which the following term applies. There may be more than one correct match for each term, if so name only one.

Term	Representative enzyme
cis-ene-diolate intermediate	
thiohemiacetal intermediate	
dehydration/rehydration	
Schiff base adduct	
an acyl phosphate is the substrate for the reaction	
Phosphoenzyme intermediate in substrate level phosphorylation	
an enol phosphate is the substrate for the reaction	
A phosphoryl transfer from ATP to form an alkylphosphate	
Nonoxidative decarboxylation	
Oxidative decarboxylation involving TPP	
Oxidative decarboxylation not involving TPP	
A dehydrogenase not involving decarboxylation that produces $FADH_2$	
Dehydrogenation with production of NADPH	
Alcohol dehydrogenation	
Dehydration	
Claisen condensation	

 Name _____

(6) (5 points) Draw the structures of the keto and enol tautomers of pyruvate. Circle the tautomer that predominates.

(7) (6 points) What are the oxidation states of the indicated carbon atoms on cysteine?



(8) (4 points) Draw the structure of the pentavalent intermediate formed in the reaction catalyzed by phosphoglycerokinase. You may abbreviate ADP if you wish.

(9) (6 points) Write the balanced chemical equations for the net overall reaction of (a) glycolysis and (b) the oxidative portion of the pentose phosphate pathway

(10) (a) 6 points Name and draw the structure of the last compound formed by both pyruvate decarboxylase and pyruvate dehydrogenase before the mechanisms of the two enzymes diverge. If resonance structures for this compound are available draw both structures, You need draw only the thiazolium ring for TPP.

(b) (2 points) With regard to the compound above, what chemical species does it next react with in (i) pyruvate decarboxylase and (ii) pyruvate dehydrogenase?

(i)

(ii)

(c) 6 points. Order the following subsequent steps that occur as part of pyruvate dehydrogenation from the first to last step. Note that one or more of the steps may occur simultaneously; if so indicate that with an "=" sign (e.g.in format A>B=C>D for a reaction where A precedes B and C, which occur simultaneously, and before D).
(a) formation of NADH
(b) formation of acetyl-CoA
(c) formation of acetyl lipoamide
(d) formation of reduced lipoamide
(e) formation of $FADH_2$
(f) formation of oxidized lipoamide
(g) formation of FAD

First: _____Last

(11) (4 points) Match the name with the mode of growth.

Carbohydrate	Correct match letter
Light energy, glucose as carbon source	
Energy source = hydrogen gas, CO_2 is carbon source	
Energy and carbon source is fructose	
Light energy, CO_2 is carbon source	

Match choices:
(a) photoautotroph
(b) photoheterotroph
(c)chemoautotroph
(d) chemoheterotroph

(12) (6 points) The two molecules of CO_2 released in one turn of the citric acid cycle are derived from which carbon atoms on which of the substrate(s) that feed into the cycle? To answer this, draw the structure(s) of the compound(s) that provide the two CO_2, and label the carbon atoms that end up in the two CO_2.

(13) (3 points) What is the value of $E^{\circ\prime}$ for the reaction of succinate with ubiquinone?
(a) -0.014 V
(b) + 0.014 V
(c) -0.076 V
(d) +0.076 V

(14) (4 points) Circle all of the following compounds that are correctly referred to as "high energy compounds".

succinyl-CoA 1,3-diphosphoglycerate 2-phosphoglycerate 3-phosphoglycerate

glucose-1-phosphate phosphoenolpyruvate creatine phosphate fructose-1,6-diphosphate

(15) 2 points) Circle the correct term (e.g. either convergent or divergent) from the underlined choices to complete the sentences.
In general, catabolic pathways are **convergent/divergent** and anabolic pathways are **convergent/divergent.**